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Removal of heavy metals from binary and multicomponent adsorption systems using various adsorbents – a systematic review

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The ecosystem and human health are both significantly affected by the occurrence of potentially harmful heavy metals in the aquatic environment. In general, wastewater comprises an array of heavy metals, and the existence of other competing heavy metal ions might affect the adsorptive elimination of one heavy metal ion. Therefore, to fully comprehend the adsorbent's efficiency and practical applications, the abatement of heavy metals in multicomponent systems is important. In the current study, the multicomponent adsorption of heavy metals from different complex mixtures, such as binary, ternary, quaternary, and quinary solutions, utilizing various adsorbents are reviewed in detail. According to the systematic review, the adsorbents made from locally and naturally occurring materials, such as biomass, feedstocks, and industrial and agricultural waste, are effective and promising in removing heavy metals from complex water systems. The systematic study further discovered that numerous studies evaluate the adsorption characteristics of an adsorbent in a multicomponent system using various important independent adsorption parameters. These independent adsorption parameters include reaction time, solution pH, agitation speed, adsorbent dosage, initial metal ion concentration, ionic strength as well as reaction temperature, which were found to significantly affect the multicomponent sorption of heavy metals. Furthermore, through the application of the multicomponent adsorption isotherms, the competitive heavy metals sorption mechanisms were identified and characterized by three primary kinds

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of interactive effects including synergism, antagonism, and non-interaction. Despite the enormous amount of research and extensive data on the capability of different adsorbents, several significant drawbacks hinder adsorbents from being used practically and economically to remove heavy metal ions from multicomponent systems. As a result, the current systematic review provides insights and perspectives for further studies through the thorough and reliable analysis of the relevant literature on heavy metals removal from multicomponent systems.

1. Introduction

Among the most critical challenges the globe has been dealing with for decades is water contamination. Water bodies all across the world have recently seen significantly higher levels of contamination due to unrestrained industrial, mining, and agricultural operations, as well as human ignorance regarding unplanned waste disposal.¹ According to the UN, 80% of all industrial and urban wastewater is discharged untreated into the environment, especially in developing nations.² However, wastewater is utilized for irrigated agriculture in developing nations due to water scarcity, posing serious health issues to both farmers and consumers while also providing nutrients for cultivated plants.^{3,4}

Annually, several heavy metals are released into water sources and the environment due to anthropogenic and natural activities, which is a worldwide concern.⁵ Fig. 1 shows the detailed main sources of heavy metal pollution in the ecosystem, which include natural and anthropogenic sources. The most prevalent heavy metals discovered in wastewater that must be confiscated using the right technologies before water is recycled or used again are as follows: As(III), Cd(II), Cr(VI), Hg(II), Ni(II), Pb(II), and Cu(II) ions.⁶ These heavy metals are bio-accumulative, non-biodegradable, and detrimental to plants, animals, human beings, and other living things.⁷ For instance, they are particularly toxic to the tissues of all living organisms and human organs including the liver, kidney, lungs, and intestines.⁸ Due to the persistent, non-decaying, toxic,

mutagenic, and cancerous nature of heavy metals in humans as shown in Fig. 2, it is crucial to appropriately treat them before releasing them into the environment.⁹

Numerous traditional treatment methods presented in Fig. 3 have been used, including biological treatment, coagulation, membrane separation procedures, chemical precipitation, ion exchange, enhanced oxidation, and adsorption utilizing commercial activated carbon, to lessen the risks posed by heavy metals and limit their build-up in wastewater.^{12,13} Due to the high cost involved in the production and regeneration of exhausted commercial activated carbons, the adsorption of heavy metals using commercial activated carbons is not economical for use in wastewater treatment in underdeveloped countries.¹⁴

Nevertheless, adsorption, using locally and naturally available adsorbents from different biomass or feedstocks as shown in Fig. 4 is a cheaper and expedient technique for the decontamination of different heavy metals from water and wastewater.^{16,17} In several studies, inexpensive adsorbents synthesized from industrial and agricultural residues as well as from other sources were employed to achieve maximum heavy metals removal from water systems.^{18–26} Notwithstanding, most of these studies focused greater attention on the practical application of low-cost adsorbents derived from natural materials for the decontamination of heavy metals from synthetic wastewater typically containing a single component or pollutant. However, real wastewater comprises a mixture of several cations, anions, and compounds instead of a single ion.



Prof. Mika Sillanpää is a distinguished scholar working in the areas of environmental engineering, green chemistry, chemical engineering, water treatment, and environmental analysis. More specifically, he has worked extensively with adsorption, photocatalysis, electrochemical treatment, membrane biological processes and advanced oxidation processes as well as ion mobility

spectrometry, chromatographic methods, electrochemical sensor development and real-time monitoring. His recent research focus has been on resource recovery from waste streams. He is a well-known global achiever with extraordinary qualities as a visionary researcher and was recognized in 2018 by Clarivate Analytics as a Highly Cited Researcher.



Prof. Kelvin Mtei is an associate professor of Agro-environment and has a PhD in agricultural sciences with vast experience in research and academia of about eighteen years. He has been delivering lectures in various universities both at undergraduate and postgraduate levels. His research endeavours emphasize the application of science and technology in a social-ecological context with a focus on sustainable farming systems; remediation of degraded land; agricultural water management and re-use. He has received several research grants through which he has produced more than 70 publications in peer review journals, conference proceedings and books.

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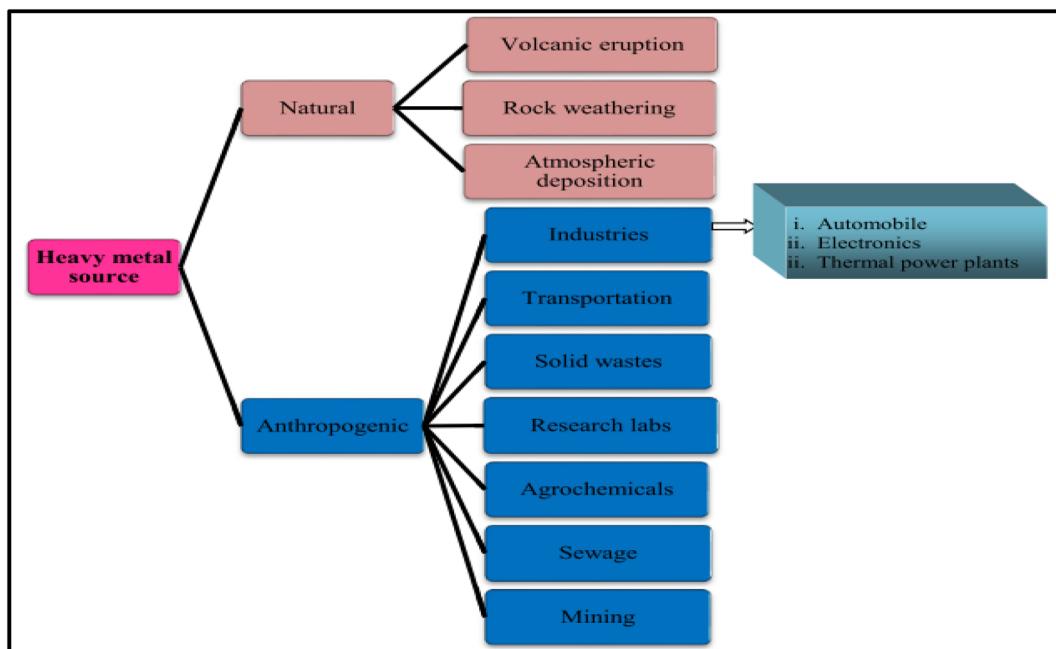


Fig. 1 Various sources of heavy metals pollution in the ecosystem (this figure has been reproduced from Kanwar *et al.*¹⁰ with permission from Springer, copyright 2020).

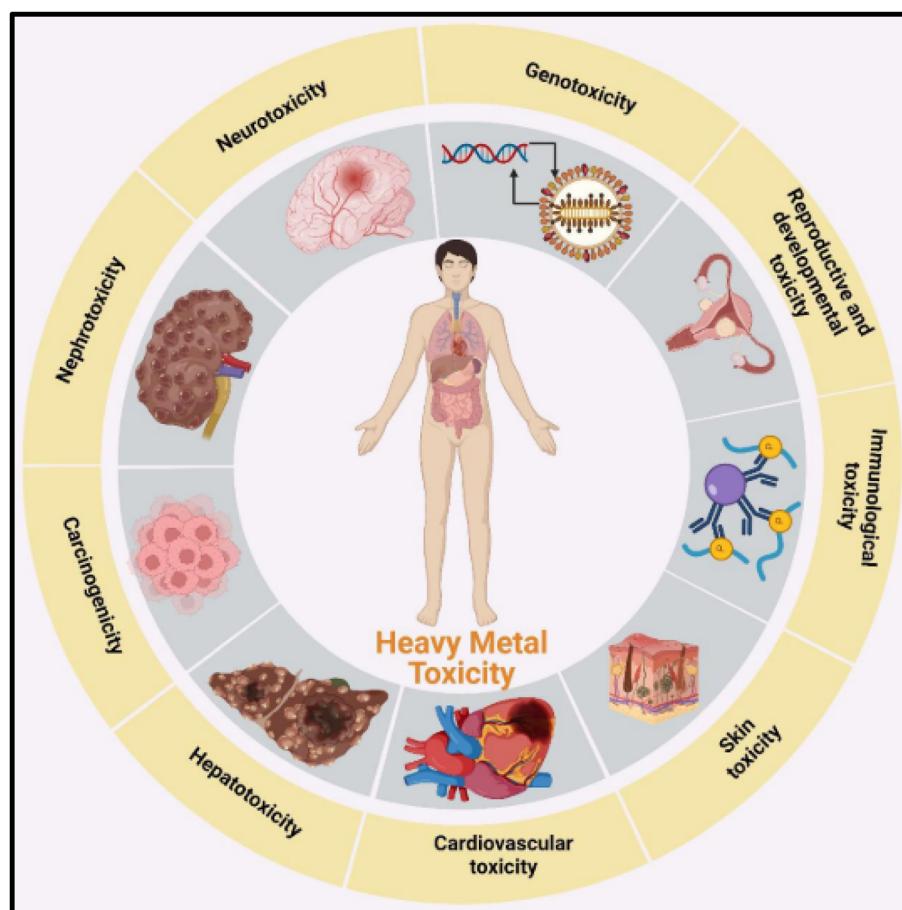


Fig. 2 A schematic diagram showing heavy metals toxicity in human organs (this figure has been reproduced from Singh *et al.*¹¹ with permission from MDPI, copyright 2023).

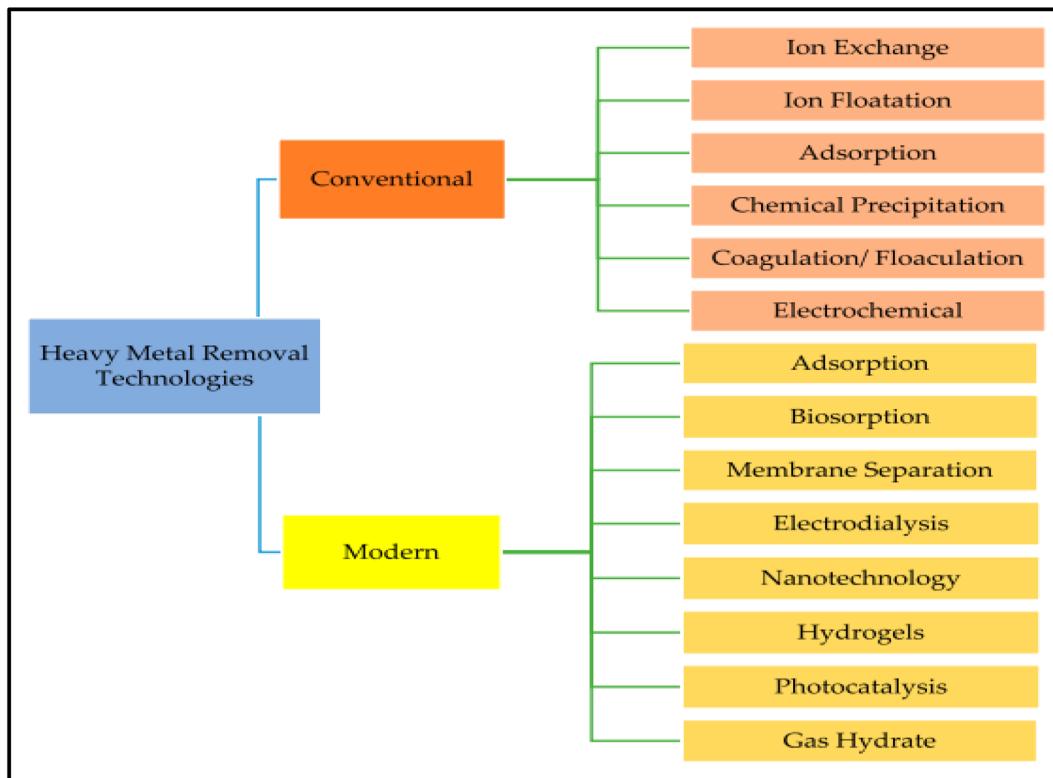


Fig. 3 Conventional and non-conventional technologies for heavy metals removal from aquatic environments (this figure has been reproduced from Nallakukkala *et al.*¹⁵ with permission from MDPI, copyright 2022).

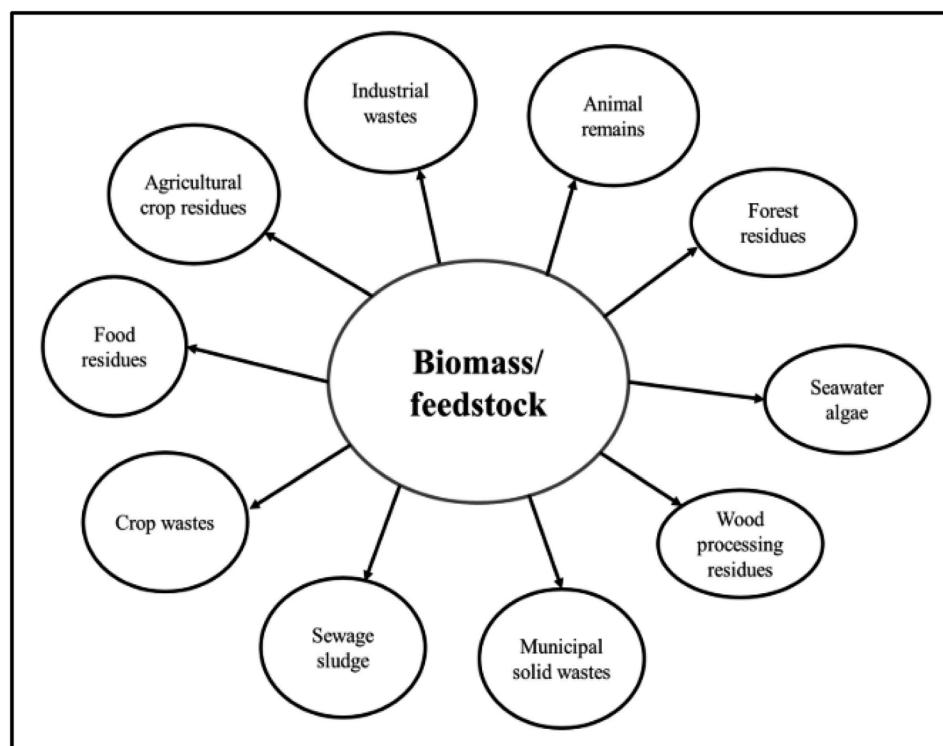


Fig. 4 Different biomass or feedstocks used for the production of various adsorbents for heavy metals remediation in water systems (this figure has been reproduced from Wani *et al.*²⁷ with permission from Springer, copyright 2022).

In recent times, studies on real wastewater treatment are gradually increasing to improve the knowledge of multicomponent adsorption of different pollutants using various adsorbents. For instance, heavy metals usually occur as multicomponent mixtures in the aquatic environment.²⁸ Hence, it is vital to comprehend the interaction of other heavy metals that coexist in a composite solution through the sorption processes in a multicomponent system.²⁹ In multicomponent adsorption, the interaction among the adsorbate molecules and their competition in the solution toward the adsorbent surface is complicated.³⁰ Hence, it is important to elucidate the mechanisms of the multicomponent sorption of adsorbate molecules from the industrial point of view.

Previously, several review articles have been published and most of these studies are based on the removal of heavy metals from single component adsorption systems by using various adsorbents as well as applying conventional isotherm and kinetic models to explain their mechanisms of adsorption.^{2,31-35} Only a very few reviews focus on heavy metals removal in multicomponent systems and the application of multicomponent adsorption isotherm models in describing sorption mechanisms.³⁶⁻³⁸ Undoubtedly, broad reviews are useful in comprehending the adsorption of different water pollutants such as heavy metals, dyes, phenols, and pharmaceuticals in multicomponent systems.

To the best of our knowledge, so far, there is no any systematic review article on the removal of heavy metals from binary- and multicomponent adsorption systems using different kinds of adsorbents including both natural and engineered adsorbents. Therefore, this systematic review is focused on assessing the potential applications of different kinds of adsorbents in water purification with an emphasis on the adsorption of toxic heavy metals in multicomponent systems. The experimental operating factors as well as the possible interaction mechanisms among the heavy metals and the adsorbents including synergistic, antagonistic, and non-interaction were also discussed using several multicomponent adsorption isotherm models. Finally, future prospectives and roadmaps are provided with suggestions for future research.

2. Methodology

2.1 Database searching and search strategy

This systematic review was carried out following the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines. The existing research findings on the removal of heavy metals from binary and multicomponent systems are contextualized and given a detailed overview in this systematic review. A computerized literature search was performed to find articles from the last 10 years regarding heavy metals removal from binary and multicomponent systems in batch adsorption processes. In this review, Web of Science, Scopus, PubMed, ScienceDirect, SpringerLink, and Google Scholar were the primary databases utilized. Each database search was carried out independently, and the selected articles were pooled together later.

To search the literary works, several pertinent keywords associated with the review focus were employed including;

adsorption, biosorption, binary component, bicomponent, bisolute, bi-metal, multi-component, multi-solute, multi-metal, equilibrium, isotherm, kinetics, thermodynamics, simultaneous, concurrent, competitive, removal, decontamination, depollution, heavy metals elimination, reduction, abatement, sequestration, adsorption factors/variables/parameters, modeling, optimization, wastewater, aqueous solution, and sorbent materials including natural or unmodified adsorbents, biochar, biosorbents, activated carbon, zeolite-based adsorbents, nano-particles and nano-based adsorbents, composites-based adsorbents, and graphene-based adsorbents. Two or more of the listed keywords were combined with "heavy metals", which is the most prevalent keyword using Boolean operators ("AND" and "OR") for searching the relevant literature.

A total of 975 articles were selected and grouped within 5 years intervals with 48% ($n = 468$) from 2019–2023, 35% ($n = 341$) from 2014–2018, 12% ($n = 117$) from 2009–2013, and 5% ($n = 49$) from 2004–2008. All the articles that were published from 2014–2023 were of interest, however, other articles below the year 2014 and based on historical discoveries and theories formulations were also included to provide complementary information. Mendeley Desktop software was then applied in the management of the gathered articles and citing all the references. Almost all of the selected articles were related to heavy metals adsorption from binary and multicomponent systems using batch experimental approaches. The selected articles were grouped by adsorbent types such as natural or unmodified adsorbents, biochar, biosorbents, activated carbon, zeolite-based adsorbents, nano-particles and nano-based adsorbents, composites-based adsorbents, and graphene-based adsorbents.

2.2 Articles inclusion criteria

The inclusion criteria were applied to judge which article should be included in the review while evaluating the titles and abstracts. Articles that demonstrated a strong relationship between heavy metals removal from binary- and multicomponent adsorption systems using different kinds of sorbent materials including natural or unmodified adsorbents, biochar, biosorbents, activated carbon, zeolite-based adsorbents, nano-particles and nano-based adsorbents, composites-based adsorbents, and graphene-based adsorbents were included. Additionally, studies on equilibrium, isotherm, kinetics, thermodynamics, modeling, and optimization of independent factors influencing heavy metals removal from multicomponent systems were also included. Therefore, after the initial reading of the titles and abstracts as well as the deletion of duplicated papers and noting down the most important information that the review wanted to highlight, a total of 402 articles written in the English Language were selected and exported into the Mendeley Desktop for this systematic review.

2.3 Articles quality study and exclusion criteria

During the drafting of the paper, which required careful reading of the contents of all the selected articles, 205 irrelevant papers were further deleted for not meeting the inclusion criteria. Specifically, 19 articles were deleted as they were non-peer-



reviewed articles; 10 articles were excluded because of inaccurate descriptions of the research methods; 61 articles were removed because they did focus on the concurrent removal of heavy metals from wastewater or aqueous solutions; 100 articles were omitted as they are very old publications above 10 years but historical works were not excluded. To ascertain the suitability and quality of this review, 15 records including books, letters or short communications to the editors, and pre-print were excluded. According to the PRISMA flowchart shown in Fig. 5, the searching, screening, and filtering produced 197 suitable full-text articles that were ultimately included in this systematic review.

3. Results and discussion

Among the 197 eligible full-text articles selected for this systematic review, 97 of these selected full-text articles based on

different types of adsorbents employed for the adsorptive removal of heavy metals from binary and multicomponent sorption systems are presented in Fig. 6. Subsequently, the selected full-text articles were comprehensively reviewed systematically and discussed according to the adsorbent type such as pristine adsorbents [raw or natural or unmodified] (Section 4.1), biochar (Section 4.2), biosorbents (Section 4.3), activated carbon (Section 4.4), zeolite-based adsorbents (Section 4.5), nano-particles and nano-based adsorbents (Section 4.6), composites-based adsorbents (Section 4.7), and graphene-based adsorbents (Section 4.8).

3.1 Competitive adsorption of heavy metals from multicomponent systems

The majority of studies in the adsorption field usually deal with the sequestration of heavy metals from single solute systems

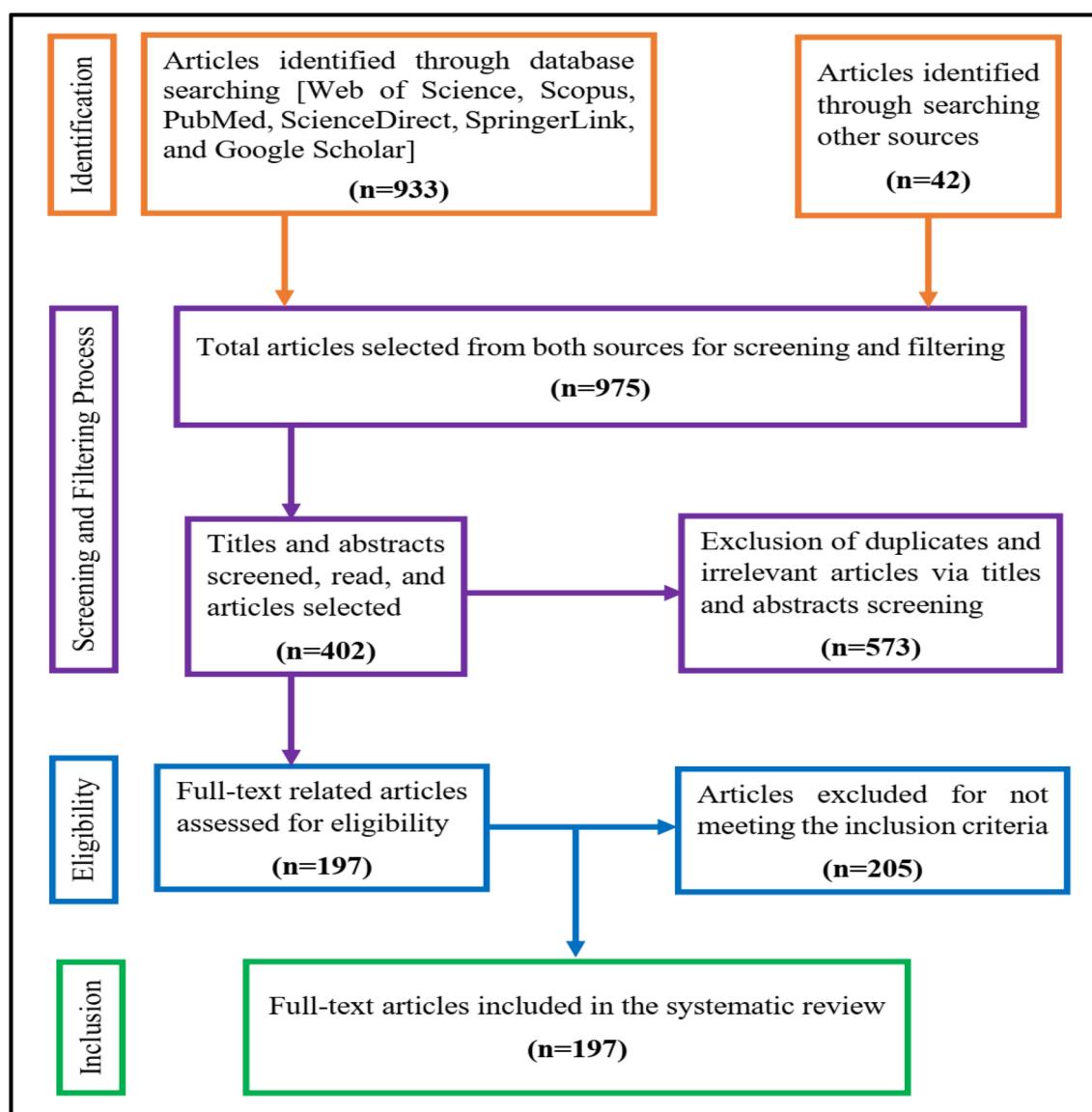


Fig. 5 PRISMA flowchart showing a standard four-step protocol for searching, screening, assessing eligibility, and inclusion of full-text articles for the systematic review.



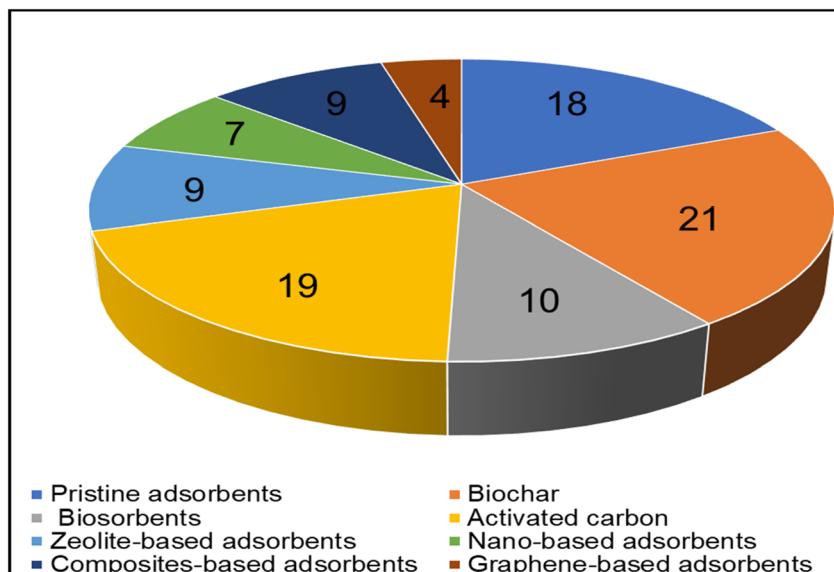


Fig. 6 Pie chart showing the number of selected full-text articles based on the different types of adsorbents cited in this article.

but real wastewater contains more than one component. Therefore, multicomponent adsorption must be studied to understand the competitive effect of the various inorganic and organic pollutants and the interactions between different pollutants. This is because competitive adsorption reveals the actual interactive behavior of the heavy metals in the multicomponent sorption system. Fig. 7 shows the schematic diagram of the competitive adsorption of adsorbate molecules from aqueous systems onto a sorbent material.

During the competitive sorption processes, several independent parameters significantly affect heavy metals uptake capacity by the promising adsorbents/biosorbents. The effectiveness of these adsorbents/biosorbents is greatly inhibited by the physicochemical properties of the aqueous solution including pH, initial metal ion concentration, temperature, ionic strength, adsorbent/biosorbent particle size, reaction time, and adsorbent/biosorbent dosage. Fig. 8 shows the schematic diagram of the different independent adsorption factors as a function of two dependent variables namely; removal efficiency and adsorption capacity. The impact of the independent adsorption parameters on the decontamination of various heavy metals from single and multi-metal systems are summarized in Table 1.

More so, in the optimization of the competitive and concurrent removal of more than one heavy metal ion in the coexistence of other cations and anions in multi-solute systems, it is essential to identify the types of interactive effects among the heavy metals. In multicomponent systems, competitive sorption typically takes place, and three primary kinds of effects are possible including synergism, antagonism, and non-interaction.⁴⁶ The effect of the ionic interactions on the multicomponent sorption system is determined by the ratio of the maximum uptake capacity for one heavy metal ion in the multicomponent system (q_{mix}), to the uptake capacity for the same heavy metal ion present in the single system (q_0).⁴⁷

Mathematically, the interaction factor (R_{qe}) is expressed in eqn (1).

$$R_{\text{qe}} = \frac{q_{\text{mix}}}{q_0} \quad (1)$$

where q_{mix} is the multicomponent adsorption capacity of the pollutant in the binary or multi-solute system and q_0 is the uptake rate of the same pollutant in the single component system at the same operating conditions as the binary or multicomponent system. Under the same operating conditions, the factor R_{qe} enables comparison of the multiphase adsorbent efficiency with that of single solute systems.⁴⁸ Table 2 shows the types of interactive effects among heavy metal ions in a multicomponent sorption system.

3.2 Multicomponent adsorption system isotherm models

Globally, multicomponent adsorption of water pollutants including heavy metals using various adsorbents has been recognized to be essential and effective. The adsorptive removal of one pollutant may be influenced by the coexistence of other pollutants in the multicomponent system due to adsorbent properties including surface charge, structure, size, porosity, number of active sites, and functional groups present on the sorbent surface.⁵¹ In a multicomponent system, the amount of the pollutant removed by the sorbent material may upsurge, reduce or remain unchanged in the existence of the other pollutants.⁵²

Adsorbent efficiency and pollutant uptake ability could be quantitatively compared using adsorption isotherm modeling to estimate the adsorption parameters.⁵³ Hence, equilibrium adsorption isotherm data are required in designing adsorption systems.⁵⁴ Several adsorption isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Redlich–Peterson, and Sips as well as kinetic models including pseudo-first-order, pseudo-second-order, Elovich, and Webber–Morris



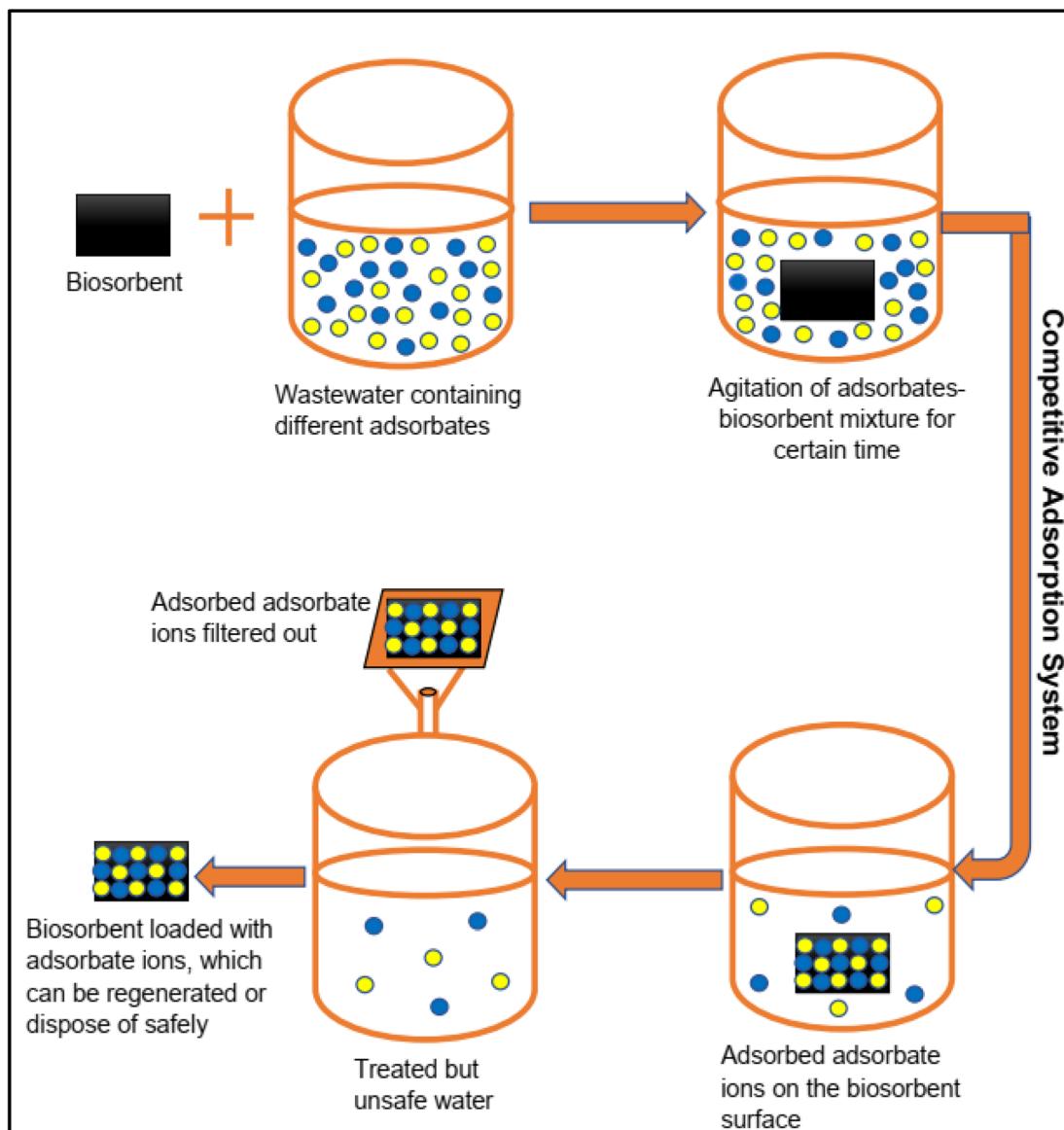


Fig. 7 Schematic diagram showing competitive adsorption of adsorbate molecules from aqueous systems onto a sorbent material.

intra-particle diffusion have been employed to explain the interactive effect between pollutants and adsorbents in single component systems.^{7,21,55-57} However, real wastewater contains a variety of contaminants that cause competition and interaction among the contaminants. The single component isotherm models are usually modified and applied to multicomponent systems since the models used in the single component systems do not apply to multicomponent systems. This is due to the sophisticated mechanism involved in multicomponent adsorption and more in-depth complex models must be utilized.⁵¹

These multicomponent adsorption isotherm models are important to establish the relationships between the uptake capacity of one pollutant by the adsorbent and the equilibrium concentration of the other coexisting pollutants in the wastewater. The competitive adsorption isotherm models could determine the type of interactions (as summarized in Table 2)

among the various adsorbates and adsorbents in the multicomponent systems at equilibrium.

3.2.1 Non-modified competitive Langmuir isotherm model. The fundamental Langmuir isotherm model, in which the sorption occurs at specified homogeneous sites within the adsorbent has been expanded to form the non-modified competitive Langmuir model.^{58,59} This non-modified competitive Langmuir isotherm model is expressed in eqn (2) and is used to analyze the competitive adsorption of a single component (*i*) in a multicomponent solution (*N*). As a result, when one component is coexisting with other components, its adsorption capacity can be computed.^{51,57}

$$q_e, i = \frac{q_{\max, i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^N (K_{L,j} C_{e,j})} \quad (2)$$

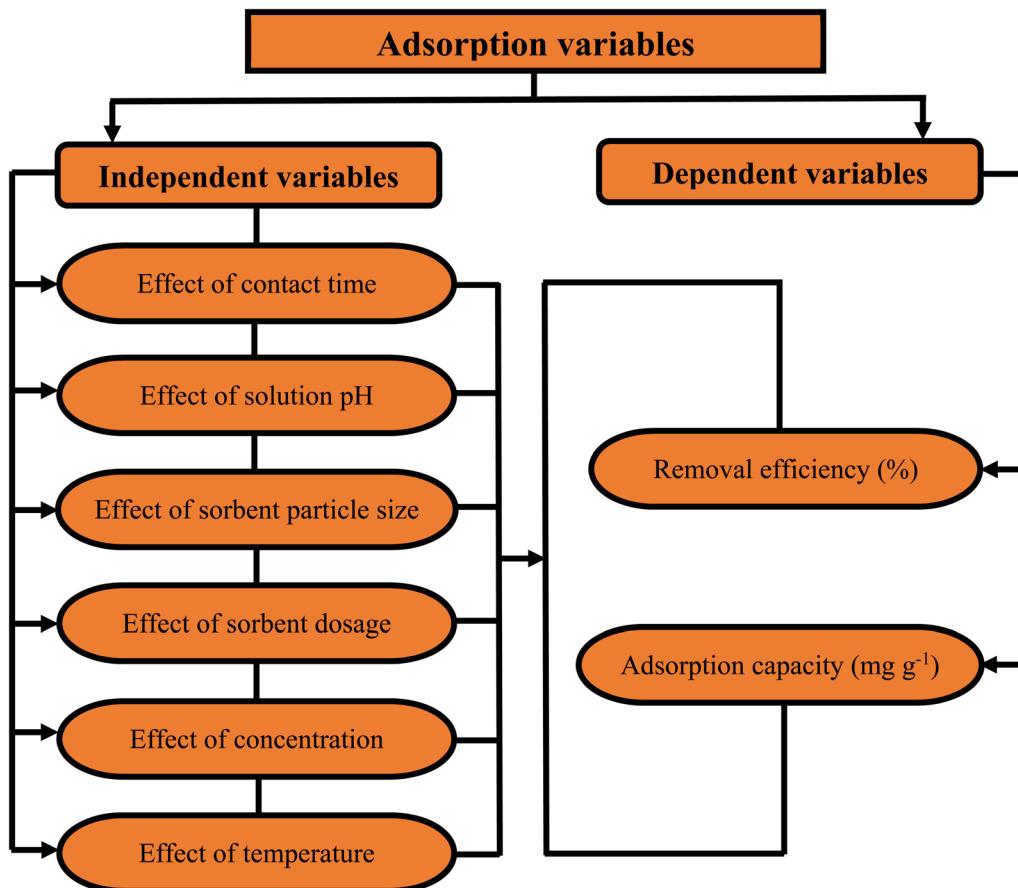


Fig. 8 Adsorption influencing independent variables as a function of two dependent variables.

where $C_{e,i}$ and $q_{e,i}$ are the equilibrium concentration and the adsorbed amount of the i component per unit gram of adsorbents, respectively. $C_{e,j}$ is the equilibrium concentration of j component in the composite solution. $q_{\max,i}$ is monolayer adsorption capacity for component i (mg g^{-1}) and $K_{L,i}$ and $K_{L,j}$ are the Langmuir constants obtained from the single component Langmuir isotherm model.

3.2.2 Modified competitive Langmuir isotherm model. The competitiveness of pollutants and their interaction in a multicomponent system is described by modifying the single component Langmuir isotherm model. Similarly, this model assumes that all of the adsorbate molecules in the solution strive for the same binding sites and that the sorbent surface sites are homogeneous.^{59,60} Adsorption equilibrium in multicomponent systems can be predicted using the modified Langmuir model for competitive adsorption as given in eqn (3).⁶¹

The parameters derived from the single component adsorption isotherm model do not describe how the interactions between the different components and the adsorbent in the solution occur. To explain the nature of the sorption process, an interaction term is typically used. This interaction factor reveals the competitive effect between the individual components and adsorbent in the multicomponent system. It is

a component's distinctive parameter that is influenced by the concentration of other constituents in the multicomponent system.³⁸

$$q_{e,i} = \frac{q_{\max,i} K_{L,i} (C_{e,i} / \eta_{L,i})}{1 + \sum_{j=1}^N K_{L,j} (C_{e,j} / \eta_{L,j})} \quad (3)$$

where $\eta_{L,i}$ and $\eta_{L,j}$ are the interaction terms of i and j components, respectively.

3.2.3 Extended Langmuir isotherm model. The extended Langmuir isotherm model presented in eqn (4) was formulated to explain multicomponent adsorption systems by expanding the monocomponent Langmuir adsorption isotherm model.⁶² This model is built entirely on the hypothesis that all of the sorbent active sites are uniform in nature and equally accessible to each of the adsorbates. Hence, all the adsorbate molecules in the multicomponent system are adsorbed on the same adsorbent active surface sites and there is no interaction between the molecules adsorbed.^{63,64} The model further presupposes that the adsorption energy at the adsorbent active sites is uniform.⁶⁵

$$q_{e,i} = \frac{q_{\max} K_i C_{e,i}}{1 + \sum_{j=1}^N K_j C_{e,j}} \quad (4)$$



Table 1 Independent adsorption parameters influencing heavy metals removal

Adsorption parameter	Description	Reference
Reaction time	The rate of heavy metals removal is greatly affected by reaction time and it is significant during the designing and development of water treatment systems. To achieve maximum heavy metals uptake capacity and to know the kinetics of the adsorption process, an equilibrium reaction time is required	39
Agitation speed	The adsorptive removal of heavy metals could be augmented or declined through agitation. However, a quicker agitation speed, might not sometimes result in higher heavy metals uptake by the sorbent material	12
Solution pH	The solution pH is an essential parameter in heavy metals sequestration and it influences the adsorbent surface charge. At pH values smaller than that of the pH point of zero charge (pH_{PZC}), the adsorbent surface becomes positively charged, which inhibits and reduces the uptake capacity of heavy metals. At pH values greater than that of pH_{PZC} , the adsorbent surface is negatively charged which enhances heavy metal ions' decontamination from water systems	40
Adsorbent particle size	The capacity of heavy metals to bind to an adsorbent surface decreases with increasing particle size while increasing with decreasing particle size. To decontaminate heavy metals effectively from aqueous systems through adsorption, the adsorbent surface area upsurges as the particle size reduces. A bigger surface area signifies the availability of many sorption sites on the adsorbent surface for the efficient uptake of heavy metal ions	41
Adsorbent dosage	The dosage of the sorbent material defines its suitability for a certain amount of heavy metal ions to be adsorbed. Higher amounts of heavy metals are decontaminated from the aqueous systems when more active surface sites are created by upping the adsorbent load. However, one alternative to minimize the adsorbent load required for removing heavy metal ions from single or multicomponent systems is to increase the adsorbent surface area	42
Initial metal ion concentration	The starting concentration shows dependence on the non-competitive and competitive decontamination of any heavy metal from individual and multi-solute systems. The initial concentration plays a key role in overcoming the resistance to mass transfer between the toxic metal ions and the adsorbent in the solution	43
Reaction temperature	The uptake ability of heavy metals from aquatic systems strongly depends on the reaction temperature. Therefore, increasing the reaction temperature between the metal ions and the sorbent material in the solution leads to endothermal exothermic adsorption, respectively	44
Ionic strength	The ionic strength is a very crucial parameter in the decontamination of various heavy metals from aquatic systems because wastewater contains other metal ions or electrolytes. Hence, the coexistence of other cations and anions in wastewater could inhibit the single removal of these heavy metal ions due to electro-statistic interactions between heavy metals and sorbent surfaces	45

Table 2 Impact of the ionic interactions on the sorption process

Relation	Meaning	Reference
$\frac{q_{\text{mix}}}{q_0} > 1$	The adsorptive elimination of one heavy metal is promoted by the coexistence of other heavy metal ions in a multicomponent system suggesting synergism	49
$\frac{q_{\text{mix}}}{q_0} = 1$	The existence of other cations and anions in the multicomponent system does not influence the individual decontamination of the various heavy metal ions indicating non-interaction	50
$\frac{q_{\text{mix}}}{q_0} < 1$	The coexistence of other ions significantly inhibited the adsorptive elimination of the individual heavy metal ions from the multicomponent system, which points to antagonism	37

3.2.4 Extended Freundlich isotherm model. The extended Freundlich model is an extension of the monocomponent Freundlich model, which describes the sorption characteristics of adsorbate molecules in multicomponent systems. The model is applied to heterogeneous adsorption where molecules that have been adsorbed on the adsorbent surface sites interact.⁶⁶ The extended Freundlich isotherm models for two components in a binary system are given by eqn (5) and (6), respectively.⁶⁷

$$q_{e,i} = \frac{K_{F,i} C_{e,i}^{(1/n_i)+x_i}}{C_{e,i}^{x_i} + y_i C_{e,j}^{z_i}} \quad (5)$$

$$q_{e,j} = \frac{K_{F,j} C_{e,j}^{(1/n_j)+x_j}}{C_{e,i}^{x_i} + y_i C_{e,j}^{z_i}} \quad (6)$$

where $q_{e,i}$ and $q_{e,j}$ are the uptake capacity of components i and j (mg g^{-1}) at equilibrium, $C_{e,i}$ and $C_{e,j}$ are the equilibrium



concentration of components i and j (mg L^{-1}). $K_{\text{F},i}$ and $K_{\text{F},j}$ are the Freundlich constants and n_i and n_j are the adsorption intensities obtained from the experimental data of the single component Freundlich isotherm models. The six parameters x_1, y_1, z_1 and x_2, y_2, z_2 is the multicomponent Freundlich model constants of two components.^{51,66,68}

3.2.5 Non-modified Redlich–Peterson isotherm. By integrating the Langmuir and Freundlich models, the Redlich–Peterson model was developed, and it can be used to analyze single component equilibrium data for a wide range of adsorbate concentrations. This model assumes that the concentrations in the numerator and denominator terms are both linear and exponential, respectively.⁶⁹ When applied to multicomponent systems, the Redlich–Peterson model can be transformed into non-modified and modified Redlich–Peterson isotherm models.⁵¹ The non-modified competitive Redlich–Peterson isotherm is expressed in eqn (7).

$$q_{\text{e},i} = \frac{K_{\text{RP},i} C_{\text{e},i}}{1 + \sum_{j=1}^N \alpha_{\text{RP},j} C_{\text{e},j}^{\beta_j}} \quad (7)$$

where $K_{\text{RP},i}$ (L mg^{-1}), β and $\alpha_{\text{RP},j}$ (L mg^{-1}) are the model constants obtained from the experimental data of individual Redlich–Peterson isotherm models. Then for a set of $C_{\text{e},i}$ values the corresponding values of $q_{\text{e},i}$ can be evaluated.⁷⁰

3.2.6 Modified competitive Redlich–Peterson isotherm model. To illustrate the type of interaction among the individual adsorbates in a multicomponent solution, the interaction term is introduced to this model. The modified Redlich–Peterson isotherm model is expressed in eqn (8).⁷¹

$$q_{\text{e},i} = \frac{K_{\text{RP},i} (C_{\text{e},i} / \eta_{\text{RP},i})}{1 + \sum_{j=1}^N \left(\alpha_{\text{RP},j} (C_{\text{e},j} / \eta_{\text{RP},j})^{\beta_j} \right)} \quad (8)$$

where $K_{\text{RP},i}$ (L mg^{-1}), β and $\alpha_{\text{RP},j}$ (L mg^{-1}) are the model constants evaluated from the experimental values of individual Redlich–Peterson isotherm models. The interaction parameter $\eta_{\text{RP},i}$ for various components can be calculated from the experimental values of $q_{\text{e},i}$ and $C_{\text{e},i}$ by minimizing the error in non-linear regression analysis.⁷²

3.2.7 Sheindorf–Rebuhn–Sheintuch (SRS) isotherm model. Following the assumptions of the monocOMPONENT Freundlich isotherm model, which assumes that the distribution of adsorption energy occurs exponentially for each solute, the Sheindorf–Rebuhn–Sheintuch (SRS) isotherm model was developed for multicomponent systems.^{70,73} To demonstrate how component j suppresses component i 's adsorption, the competition parameter (α_{ij}) is added. The values of the competition indices for α_{ii} and α_{jj} are both equal to one.⁷⁴ The SRS isotherm model is given as in eqn (9).⁷⁵

$$q_{\text{e},i} = K_{\text{F},i} C_{\text{e},i} \left(\sum_{j=1}^N (\alpha_{ij} C_{\text{e},j}) \right)^{\left(\frac{1}{n_i} \right) - 1} \quad (9)$$

where $K_{\text{F},i}$ is the constant of the Freundlich model and n_i is the intensity of sorption calculated from the experimental data of

the conventional Freundlich model. The competition factors α_{ij} in the SRS isotherm model represent the inhibitory effect of component i on the adsorptive removal of component j and may be calculated from the experimental sorption data of binary component systems.⁷⁶

3.2.8 Non-modified Sips isotherm model. The non-modified Sips model is an expanded form of the Sips isotherm model for single component adsorption system and has variable parameters (a_{si} , b_{si} , and n_{si}) for each adsorbate in a competitive component system. This isotherm model is given in eqn (10) and assumes energetic heterogeneity on the surface of the adsorbent.⁷⁷

$$q_{\text{e},i} = \frac{a_{\text{si}} C_{\text{e},i}^{1/n_{\text{si}}}}{1 + \sum_{j=1}^N b_{\text{si}} C_{\text{e},j}^{1/n_{\text{si}}}} \quad (10)$$

3.2.9 Extended Sips isotherm model. The Sips adsorption model, which is applied to heterogeneous systems, combines the Freundlich and Langmuir models.⁵¹ This model can be expanded to explain the sorption in systems with several components. The improved Sips isotherm model for multicomponent systems is presented in eqn (11).

$$q_{\text{e},i} = \frac{q_{\text{max},i} K_{\text{SP},i} C_{\text{e},i}^m}{1 + \sum_{j=1}^n K_{\text{SP},j} C_{\text{e},j}^m} \quad (11)$$

where $q_{\text{max},i}$ is the monolayer adsorption capacity for component i (mg g^{-1}), $K_{\text{SP},i}$ is the Sips isotherm constant (L mg^{-1}), m is the Sips model exponent. The isotherm data of individual components are used to calculate the extended Sips isotherm constants. For a m value of 0, the model approaches the Freundlich isotherm at decreasing pollutant concentrations. The model can be changed to a Langmuir isotherm for larger adsorbate concentrations for m values close to 1.⁷⁸

3.2.10 The P-factor. A correlative method called the *P*-factor was formulated by McKay and Al Duri.⁷⁹ This model, which makes use of a Langmuir isotherm, can be explained using eqn (12) below.⁸⁰

$$q_{\text{e},i, \text{multi}} = \frac{1}{P_i} \left(\frac{K_{\text{L},i} C_{\text{e},i, \text{multi}}}{1 + a_{\text{L},i, \text{multi}}} \right) \quad (12)$$

where P_i is a “lumped” capacity factor and can be defined as follows in eqn (13).

$$P_i = \left(\frac{K_{\text{L},i} / a_{\text{L},i}}{K_{\text{L},i} / a_{\text{L},i, \text{multi}}} \right) \frac{\text{mono}}{\text{multi}} = \frac{Q_{\text{max}, \text{mono}}}{Q_{\text{max}, \text{multi}}} \quad (13)$$

where $(K_{\text{L},i} / a_{\text{L},i})$ mono and $(K_{\text{L},i} / a_{\text{L},i})$ multi are the maximum adsorption capacities for component i in monocOMPONENT and multicomponent systems, respectively.

4. Competitive decontamination of heavy metals from sorption systems

The possibility of various adsorbents derived from natural, agricultural, and industrial waste materials as well as



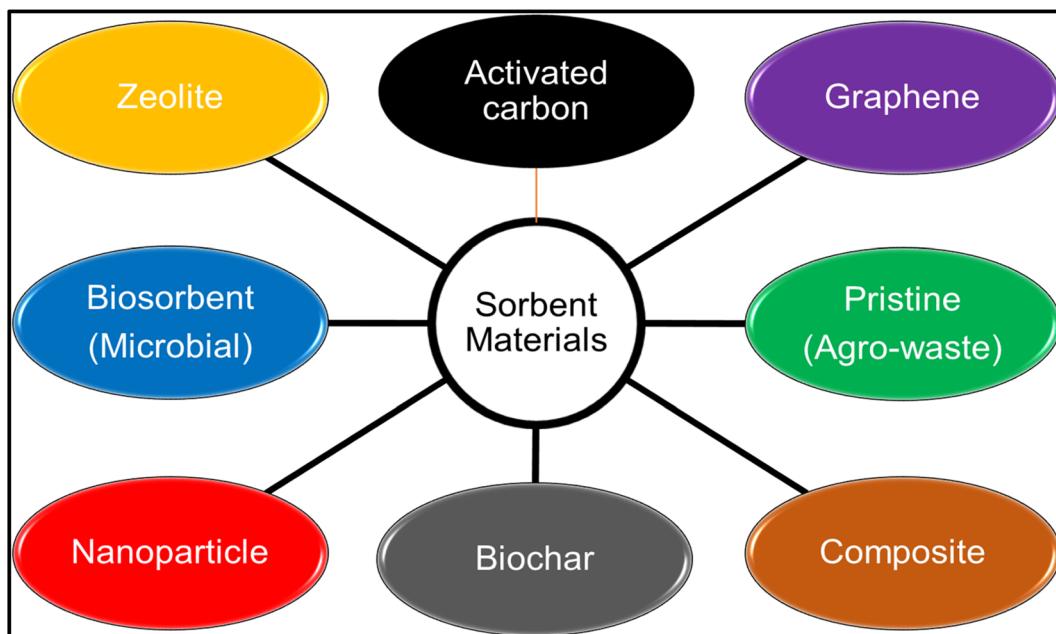


Fig. 9 A schematic diagram showing different sorbent materials for the determination of heavy metals from aquatic environments.

biosorbents synthesized from microorganisms including algae and bacteria have been reported in several studies. In the present study, the simultaneous adsorptive elimination of heavy metals from multicomponent systems using various sorbent materials as shown in Fig. 9 has been systematically reviewed. This systematic review has categorized the sequestration of various heavy metal ions in the multicomponent systems by these sorbent materials into eight (8) types including natural or unmodified adsorbents, biochar, biosorbents, activated carbon, zeolite, nano-, composite-, and graphene-based adsorbents. In most of the studies, the uptake capacities of the different heavy metals in the binary and multicomponent adsorption systems achieved by these sorbent materials have been reported and discussed in this review to

establish the interactive mechanisms among the heavy metals involved.

4.1 Natural or unmodified (pristine) adsorbents

The application of natural materials as adsorbents have shown that they are versatile and promising for the removal of both inorganic and organic contaminants from aquatic environments. A schematic diagram showing the preparation of unmodified or pristine adsorbents from agro-waste or biomass is displayed in Fig. 10. The simultaneous removal of several heavy metals from multicomponent adsorption systems using natural, raw, unmodified, and pristine adsorbents has been reported and discussed.

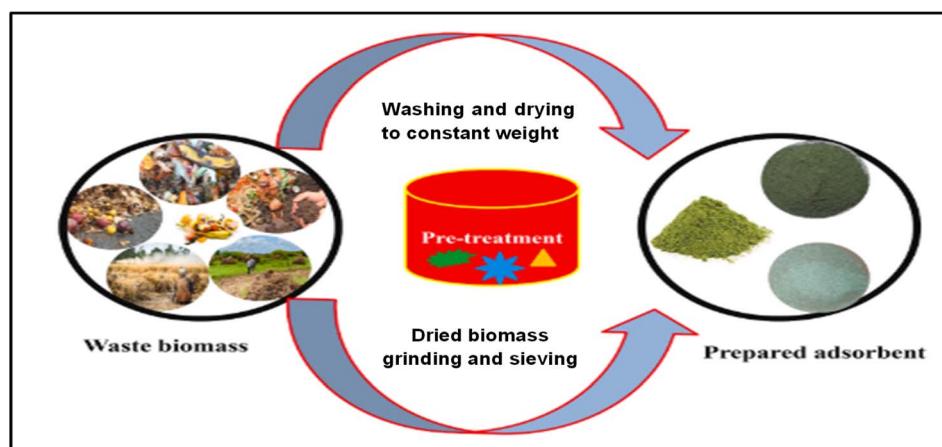


Fig. 10 Schematic illustration of the preparation of unmodified or pristine adsorbents from agro-waste or biomass (this figure has been adapted from Bilal *et al.*³² with permission from Elsevier, copyright 2022).

Natural banana peels were used for Pb(II) and Cu(II) ions removal from a binary solute system by varying operating variables such as initial concentration, adsorbent dose, pH, and adsorbent particle size in a batch mode through the application of central composite design (CCD).¹⁹ The analysis of variance indicates a good fit with the coefficient of determination of 0.998 and 0.988 for Cu(II) and Pb(II), respectively. The removal efficiency of Cu(II) and Pb(II) augmented with increasing adsorbent dose with the sorption rate of Pb(II) being the highest. The optimized operating conditions gave 99.79 and 88.94% removal efficiency for Cu(II) and Pb(II), respectively with 100.00 mg L⁻¹ concentration, pH 5.00, 1.00 g adsorbent load, particle size of 75.00 µm, and desirability of 0.959. The good correlation between the actual and predicted values indicates the validity of the second-order polynomial equation for Cu(II) and Pb(II) ions removal using the banana peels.

More so, the potential of tea pulp in the decontamination of Pb(II) and Cu(II) from single and binary systems was investigated.¹³ The impact of pH, adsorbent dosage, agitation time, and initial single- and binary-metal concentrations on Pb(II) and Cu(II) removal was conducted using batch technique. At a pH of 5.00–8.00 and pH of 4.00–8.00, Cu(II) and Pb(II) ions optimum uptake capacities were achieved by the adsorbent, respectively. For the single system, the optimum uptake capacities of Pb(II) and Cu(II) attained by the tea pulp were 48.54 and 37.17 mg g⁻¹, respectively, and 43.47 and 28.41 mg g⁻¹ for Pb(II) and Cu(II), correspondingly in the competitive system. The isothermal and kinetic data achieved by tea pulp were well explained by the pseudo-second-order kinetic and Langmuir isotherm models. The study found the tea pulp to be a less-cost bio-adsorbent that could decontaminate Pb(II) and Cu(II) ions effectively from single and bicomponent systems.

Also, the confiscation of Pb(II) and Cu(II) by an adsorbent derived from chili seed in single and multicomponent systems was studied by Forgionny *et al.*⁵ In single component systems, it was observed that the uptake capacity of 48.00 mg g⁻¹ for Pb(II) was greater than the Cu(II) uptake capacity of 4.10 mg g⁻¹ as achieved by the chili seed. This suggests that the chili seed has greater selectivity for Pb(II) ions than for Cu(II) ions in the single sorption systems. For multicomponent systems, it was observed that the elimination of Pb(II) and Cu(II) ions by the adsorbent was due to antagonistic interactive effects between Pb(II) and Cu(II) ions. The study revealed that under equal initial concentrations of Pb(II) and Cu(II) and at higher amounts of Pb(II), about 50.00 and 56.00% decline in Pb(II) and Cu(II) removal were observed, correspondingly.

The potentiality of vetiver roots as an adsorbent in removing Ni(II), Cd(II), and Pb(II) from synthetic ternary aqueous systems was carried out.⁸¹ Single and ternary metal solutions were prepared and used to perform the batch experiments using optimum operating conditions. Out of five isotherm models tested, the Langmuir isotherm was best fitted to the equilibrium sorption data of Ni(II), Cd(II), and Pb(II) with uptake capacities of 13.55, 10.99, and 17.33 mg g⁻¹, respectively. The impact of competitive sorption was predicted using the modified Langmuir competitive isotherm model. In the mono-metal systems, the highest uptake capacity of Ni(II) and Pb(II) by the biosorbent

was decreased by about 3.00 and 33.00 times, respectively in a ternary component system. However, it was later found to improve by about 1.64 times for Cd(II). Based on the findings of this study, it is concluded that the adsorbent could be employed in the elimination of heavy metals.

An adsorbent derived from rice husk was utilized in removing Cu(II), Pb(II), Fe(III), and Cr(III) from multicomponent sorption media.⁸² The study indicated that at a reaction time of 2.00 h and solution pH of 5.00, the equilibrium removal rate of Cu(II), Pb(II), Fe(III), and Cr(III) was accomplished with Fe(III) ions being the most highly adsorbed. The experimental data of Pb(II), Cr(III), Fe(III), and Cu(II) achieved by the adsorbent well correlated to the pseudo-second-order kinetic model. While the sorption data of Pb(II), Cr(III), Fe(III), and Cu(II) at equilibrium were best represented by the Langmuir model. The study showed the efficacy and affordability of utilizing rice husk-derived adsorbent to simultaneously remove Pb(II), Cr(III), Fe(III), and Cu(II) from aquatic systems.

Similarly, the depollution of Zn(II), Hg(II), and Cd(II) in mono-, binary- and tertiary-metals systems by rice husk ash (RHA) has been investigated.²⁶ Batch tests were performed for both the mono- and multi-metals aqueous media with varying metal ions concentrations to investigate the non- and competitive adsorption characteristics. The study indicated that the decontamination of these metal ions exhibited this trend: Zn(II) > Cd(II) > Hg(II) in the single solute systems. In the binary and tertiary component systems, the sorption process was inhibited by the existence of other ions in the aqueous solutions. It was found that the Freundlich and Langmuir models best fitted the equilibrium data of Zn(II), Cd(II), and Hg(II) in all the sorption systems. The study recommended that there is a need to grasp the mechanisms of competitive sorption of coexisting ions onto RHA for the effective operation of the sorption processes for removing these toxic metal ions from polluted water.

The capability of an adsorbent derived from thiourea spent grated *Cocos nucifera* (TSGC) was explored for the concurrent depollution of Pb(II), Ni(II), and Cu(II) from ternary water systems.⁸³ The study found that TSGC had a greater affinity for the Cu(II) ions than that of Ni(II) and Pb(II) ions present in the ternary sorption medium. Hence, the uptake capacity of Cu(II) ions by the adsorbent was greater than Ni(II) and Pb(II). The maximum uptake capacity of Ni(II), Pb(II), and Cu(II) attained by the adsorbent was 1.38, 0.32, and 0.24 mmol g⁻¹, respectively. The sorption kinetic data of Cu(II), Ni(II), and Pb(II) best fitted the pseudo-second-order kinetic model. Also, the Langmuir model was well correlated to the sorption data of Ni(II), Pb(II), and Cu(II). The study suggested that TSGC is a promising locally available adsorbent for heavy metals remediation from contaminated water.

Unmodified pomelo peels were applied as a bio-adsorbent to decontaminate Pb(II) ions present in multi-solute systems.⁸⁴ The study found that 99.90% of the Pb(II) ions were removed using this bio-adsorbent at 210.00 min of agitation time, 20.00 mg L⁻¹ Pb(II) concentration, pH of 3.00, and 50.00 °C temperature. There was no influence of Zn, Cu(II), Mg(II), and Cd(II) on the efficiency of pomelo peels to decontaminate Pb(II) from the liquid phase. The kinetic and equilibrium isotherm data of



Pb(II) were observed to obey the Langmuir and pseudo-first-order models, correspondingly. Pomelo peels exhibited the possibility to be employed for the concurrent decontamination of harmful heavy metals coexisting in wastewater.

Likewise, the concurrent sequestration of Cd(II), Ni(II), Zn(II), and Cu(II) from competitive sorption media was examined using orange peel biomass.⁸⁵ The uptake capacity of the adsorbent was found to be reduced in the binary solute system suggesting an antagonistic effect on the heavy metals removal. There was the existence of a synergistic effect on Cu(II) ions sequestration from the multicomponent system while an antagonistic effect existed during the single decontamination of Zn(II), Cd(II), and Ni(II) ions from the multi-solute medium. The modified Langmuir isotherm model demonstrated good fitness to the equilibrium competitive data of Cd(II), Zn(II), Ni(II), and Cu(II). The results of this study showed that an orange peel-based adsorbent is employable for the multicomponent sequestration of heavy metals found in aqueous media.

An adsorbent was produced from wheat bran and used for removing Cd(II), Pb(II), and Cu(II) from multicomponent media.⁸⁶ The optimum removal capacity of the adsorbent was found as 901.00, 978.00, and 1136.00 mg g⁻¹ for Cu(II), Cd(II), and Pb(II), respectively. The adsorbent was observed to have the highest affinity towards Pb(II) and Cd(II) ions. The study revealed that there exist synergistic effects among the three heavy metals, in which the adsorptive removal of an individual metal is promoted by the occurrence of other ions. The prepared adsorbent possessed a large specific surface area of 140 m² g⁻¹ obtained from BET sorption data. Hence, this adsorbent is found to be proficient in treating heavy metals contaminated water.

Also, unmodified peanut shells, sawdust, and activated carbon were used to eliminate Cd(II), Cu(II), and Pb(II) from non- and competitive sorption systems.⁸⁷ The study found that as the contact time progressed and then approached equilibrium, Cd(II), Pb(II), and Cu(II) ions were eliminated by the activated carbon, peanut shell, and sawdust. Also, the quantity of Pb(II), Cu(II), and Cd(II) ions adsorbed augmented but the removal efficiency thereof decreased as the initial Cd(II), Pb(II), and Cu(II) concentrations increased. The activated carbon exhibited the highest uptake capacity of 5.50, 13.10, and 14.01 mg g⁻¹ for Cd(II), Cu(II), and Pb(II), respectively. While the uptake capacity of Cd(II), Pb(II), and Cu(II) attained by the unmodified peanut shell were 5.07, 9.50, and 49.10 mg g⁻¹, respectively. The untreated sawdust had the lowest sorption capacity of 3.99, 5.30, and 5.50 mg g⁻¹ for Cd(II), Cu(II), and Pb(II) ions, correspondingly. The sorption data of both single and competitive systems was best represented by the pseudo-second-order and Langmuir models. In the multicomponent sorption systems, there existed antagonistic effects among the adsorptive elimination of Pb(II), Cd(II), and Cu(II) ions from the competitive aqueous media.

More so, the elimination of Cd(II), Pb(II), and Cu(II) from unitary, binary, and ternary sorption systems by white pottery clay was conducted.⁸⁸ The study revealed that the white pottery clay's maximum uptake capacities of Pb(II), Cu(II), and Cd(II) were attained at an equilibrium reaction time of 180.00 min. The kinetic and isothermal data of Pb(II), Cu(II), and Cd(II) were

well explained by the pseudo-second-order and Langmuir isotherm models, correspondingly. The Langmuir maximal monolayer uptake capacities attained for Pb(II), Cu(II), and Cd(II) were 159.24, 38.49, and 26.99 mg g⁻¹, respectively. In the Pb(II)-Cu(II) binary sorption medium, the Cu(II) ions exhibited an antagonistic effect on Pb(II) ions elimination by the adsorbent while Cd(II) ions demonstrated very low inhibitory influence on Pb(II) ions decontamination from the Pb(II)-Cd(II) binary medium. The ability of white pottery clay to depollute Cd(II), Pb(II), and Cu(II) ions is significantly reduced as a result of the competitive effect superimposing in the ternary system [Pb(II)-Cu(II)-Cd(II)]. In comparison, the sorption capacity of Pb(II) reduced with rising Cu(II) and Cd(II) initial concentrations. However, the adsorptive elimination of Cu(II) and Cd(II) ions is insignificantly inhibited by Pb(II) initial concentration in the aqueous solution.

Secondary composts (SC) derived from solid wastes of a municipal and wood (W-SC) were synthesized and utilized in removing Cd(II), Ni(II), Zn(II), and Cu(II) from mono- and multi-solutes sorption media.⁸⁹ It was found that in the mono-metal system, the W-SC had a higher affinity towards the heavy metals than SC with maximum sorption capacity of 42.70, 38.60, 34.90, and 28.70 mg g⁻¹ for Cd(II), Cu(II), Zn(II), and Ni(II), correspondingly. In multi-solute media, the Ni(II) ions uptake rate by both adsorbents was greatly inhibited than that of Cu(II), Zn(II), and Cd(II). The equilibrium sorption data of Cu(II), Cd(II), Ni(II), and Zn(II) was best described by Freundlich and Langmuir models. The study demonstrated that W-SC is very useful for decontaminating several heavy metals from water systems.

In another study, cork stopper particles were utilized as a bio-adsorbent to decontaminate Zn(II) and Cd(II) from monocomponent and bicomponent simulated wastewater.⁹⁰ The study found that in a single sorption medium, the optimum percentage decontamination of Cd(II) and Zn(II) ions was 82.62 and 90.96%, respectively at 150.00–180.00 min contact time, pH of 5.50–6.00, a biosorbent dosage of 0.85–1.00 g, with 50 mg L⁻¹ initial metal ion concentration. For Zn(II) and Cd(II) ions decontamination from the binary component system, an optimum solution of pH 6.00 was used. In both mono- and bi-solutes sorption systems, the heavy metal ions elimination occurred in this order, Zn(II) > Cd(II). However, in the bi-solute medium, the percentage removal of both heavy metals was observed to be reduced. The kinetic sorption data of Zn(II) and Cd(II) achieved by the cork stopper particles was well explained by the pseudo-first-order kinetic model. Also, the isothermal data of Cd(II) and Zn(II) was best correlated to extended Freundlich and Langmuir models for the non-complex and complex component systems, correspondingly.

The simultaneous depollution of Fe(II) and Cu(II) from binary component sorption media was examined by microcrystalline cellulose (MCC) as an adsorbent.⁹¹ The result of the adsorption experiment revealed that MCC could remove more than 70.00% of Fe(II) and Cu(II) indicating that there were sturdy electrostatic attractions among the adsorbent surface and cationic heavy metal ions. Also, the sorption data of Fe(II) and Cu(II) attained by MCC were best represented by the pseudo-second-order kinetic model, demonstrating chemisorption between the polymeric



MCC adsorbent and heavy metal molecules. The study concluded that the MCC is a reliable and low-cost sorbent in treating water polluted by $\text{Fe}^{(\text{II})}$ and $\text{Cu}^{(\text{II})}$ and other water pollutants.

Also, Tekin and Unsal⁹² conducted a study to investigate the individual and competitive uptake of $\text{Ni}^{(\text{II})}$ and $\text{Cu}^{(\text{II})}$ onto sepiolite. For the monocomponent systems, the initial mono-metal concentration, mixing speed, and temperature were studied as a function of time to determine the operating conditions where the adsorbents showed a great deal of affinity towards the $\text{Ni}^{(\text{II})}$ and $\text{Cu}^{(\text{II})}$ ions in the solutions. Among the applied isotherm models, the one-component sorption data did fit the Langmuir isotherm best. The simultaneous and competitive uptake of $\text{Cu}^{(\text{II})}$ and $\text{Ni}^{(\text{II})}$ was assessed using the extended Langmuir and Freundlich adsorption isotherm models. It was revealed that both isotherm models described the two-component sorption data perfectly with uptake capacities of 222.22 and 256.41 mg g^{-1} attained by the sepiolite for $\text{Ni}^{(\text{II})}$ and $\text{Cu}^{(\text{II})}$, correspondingly. Therefore, the single- and binary-sorption results unclosed that the effect of sepiolite on $\text{Cu}^{(\text{II})}$ is greater than that of sepiolite on $\text{Ni}^{(\text{II})}$.

Bassam *et al.*⁹³ carried out a study to establish the ease of removing $\text{Cd}^{(\text{II})}$, $\text{As}^{(\text{III})}$, and $\text{Cr}^{(\text{VI})}$ ions competitively from aqueous media using raw rock. The impact of adsorbent dose, agitation time, reaction temperature, pH, and initial concentration on $\text{Cd}^{(\text{II})}$, $\text{Cr}^{(\text{VI})}$, and $\text{As}^{(\text{III})}$ ions removal in the batch mode was undertaken. The kinetic and isothermal data attained by the adsorbent conformed to the pseudo-second-order and Langmuir models, respectively. The optimum monolayer adsorption capacities of the Langmuir isotherm model were found to be 16.36, 17.54, and 15.23 mg g^{-1} for $\text{As}^{(\text{III})}$, $\text{Cr}^{(\text{VI})}$, and $\text{Cd}^{(\text{II})}$, respectively. The thermodynamic variables suggested that the adsorptive removal of all the investigated heavy metals was exothermic, feasible, and spontaneous. The heavy metal

ions desorption showed that this raw rock had excellent recycling capacity. Based on the results, these untreated rocks can be used as inexpensive and environmentally friendly adsorbents to treat water contaminated by heavy metals.

Granular gravel was explored as an adsorbent to decontaminate $\text{Cu}^{(\text{II})}$, $\text{Zn}^{(\text{II})}$, $\text{Ni}^{(\text{II})}$, and $\text{Fe}^{(\text{II})}$ ions from single- and multi-solutes.⁹⁴ It was revealed that the removal rate of $\text{Cu}^{(\text{II})}$, $\text{Fe}^{(\text{II})}$, $\text{Zn}^{(\text{II})}$, and $\text{Ni}^{(\text{II})}$ from the single metal system was 98.00, 87.50, 76.05, and 36.38%, respectively. While the removal rate of 7.32, 48.00, 83.00, and 98.30% for $\text{Ni}^{(\text{II})}$, $\text{Zn}^{(\text{II})}$, $\text{Fe}^{(\text{II})}$, and $\text{Cu}^{(\text{II})}$, respectively, were attained in the multi-solute medium at a pH of 7.00. The sorption rates of these metal ions using this adsorbent ranged from 0.91–42.86 mg g^{-1} as well as 0.04–1.63 mg g^{-1} in the single and mixed metal systems, respectively. The kinetic and isothermal data conformed to the pseudo-second-order and Freundlich models, correspondingly.

4.2 Biochar

In the absence of oxygen and at low temperatures, feedstock or any biomass is pyrolyzed to produce biochar, a solid by-product rich in carbon. Due to electrostatic interactions between heavy metal ions and the negatively charged surface of the biochar as well as ion exchange among the surface electrons and metallic cations, biochar can adsorb heavy metals. A schematic diagram showing the conversion of agro-waste into biochar for the adsorptive removal of heavy metals from aqueous systems is presented in Fig. 11.

Ferrihydrite-modified biochar (Fh@BC) was utilized for the simultaneous decontamination of $\text{As}^{(\text{III})}$ and $\text{Cd}^{(\text{II})}$ ions from binary-metal aqueous systems as well as determine the mechanism of the sorption process.⁹⁵ The Langmuir model best correlated with equilibrium sorption data with optimum sorption rates of 18.38 and 18.18 mg g^{-1} for $\text{As}^{(\text{III})}$ and $\text{Cd}^{(\text{II})}$,



Fig. 11 Schematic diagram showing the conversion of agro-waste into biochar for heavy metals removal from aqueous systems carbon (this figure has been adapted from Wang *et al.*³¹ with permission from RSC, copyright 2023).



respectively. The mechanisms of the simultaneous elimination of As(III) and Cd(II) by Fh@BC were due to cation exchange, complexation, and oxidation. The study showed that Fh@BC is a promising bio-adsorbent for the concurrent decontamination of As(III) and Cd(II) ions present in wastewater.

Likewise, the simultaneous elimination of Cd(II) and As(III) from water systems was achieved by a unique α -FeOOH-treated wheat straw biochar (α -FeOOH@BC).⁹⁶ The highest removal capacity of α -FeOOH@BC for Cd(II) and As(III) was 78.30 and 62.90 mg g⁻¹, correspondingly, in the single component system. While the maximum adsorption capability of α -FeOOH@BC decreased to 39.30 and 67.20 mg g⁻¹ for Cd(II) and As(III), respectively, in the binary component system. The Langmuir adsorption isotherm and pseudo-second-order models provided good fits for the experimental data of As(III) and Cd(II). Ion exchange and co-precipitation were the two main sorption mechanisms, and the removal of As(III) and Cd(II) ions on α -FeOOH@BC exhibited a competitive effect. The study demonstrated that α -FeOOH@BC can be a useful remediation bio-adsorbent for the simultaneous As(III) and Cd(II) from aquatic environments.

Also, wheat straw was used to produce activated biochar for decontaminating Pb(II) and Cd(II) competitively from aquatic systems.⁶ At an equilibrium reaction time of 2.00 h, pH of 8.00, and 30.00 mg L⁻¹ metal ion concentration, optimum sorption capacity of 8.85 and 9.03 mg g⁻¹ for Pb(II) and Cd(II) ions, correspondingly, were attained. The Langmuir isotherm and pseudo-second-order models best described the isothermal and kinetic data of Pb(II) and Cd(II), respectively. The optimum monolayer adsorption rates of Pb(II) and Cd(II) ions attained by the biochar at 298 K were 0.60 and 9.30 mg g⁻¹, correspondingly.

Additionally, biochar obtained from anaerobic sludge was utilized to decontaminate Cd(II) and Pb(II) from non- and competitive aqueous systems.⁹⁷ In a single sorption system, the biochar exhibited a greater removal rate for Pb(II) ions than Cd(II) ions. For the single component system, the optimum removal capacities of 0.55 and 0.75 mmol g⁻¹ were achieved by the biochar for Cd(II) and Pb(II), correspondingly. In the binary-metal systems, the Cd(II) ions decontamination by the biochar was highly inhibited, while Pb(II) ions uptake by the biochar was not significantly interfered with. The sorption data of Pb(II) and Cd(II) at equilibrium was best explained using both Dubinin-Radushkevich and Langmuir models for the single metal system, while the competitive Langmuir adsorption isotherm model well represented Pb(II) and Cd(II) equilibrium data obtained from the bi-solute systems.

Similarly, a corn stalk biochar-supported nanoscale zero-valent iron (nZVI-BC) with diverse ratios of nZVI and BC was used for the concurrent elimination of As(III) and Cd(II) from aquatic media.⁹⁸ The batch tests results revealed that nZVI-BC (1 : 1) had the greatest uptake capacity for Cd(II) and As(III) ions and optimum Cd(II) and As(III) sorption capacity was 33.81 and 148.50 mg g⁻¹ achieved at 2.00 and 1.00 h, respectively. More so, the study found that the synergistic effects between As(III) and Cd(II) ions in a competitive system improved the nZVI-BC (1 : 1) sorption capacity. In the competitive system, the uptake rate of

As(III) and Cd(II) was increased to 158.50 and 179.90 mg g⁻¹, respectively. The experimental data attained for the concurrent abatement of As(III) and Cd(II) from the solution was well correlated to the pseudo-second-order kinetic and Redlich-Peterson isotherm models, respectively. Therefore, nZVI-BC (1 : 1) is a good choice for the treatment of Cd(II) and As(III) ions in polluted water bodies.

The simultaneous detoxification of Cd(II) and As(V) ions from water systems were studied using ultrasonic and nanoscale TiO₂ (TD) biochar.⁹⁹ The experimental data were well explained by the pseudo-second-order model whereas the equilibrium data fitted well to the Langmuir isotherm model. The maximum uptake capacities of 118.06 and 72.62 mg g⁻¹ were achieved by the adsorbent for As(V) and Cd(II), correspondingly. The removal efficiency of 70.00% accomplished for both Cd(II) and As(V) occurred at optimum pH of 5.00. The presence of both As(V) and Cd(II) ions in the bicomponent system revealed a competitive effect at 100.00 mg L⁻¹ concentration. The study offered a practical technique for the development of the adsorbent, which is a safe adsorbent to simultaneously decontaminate water pollutants, particularly heavy metals.

The chitosan-EDTA treated magnetic biochar (E-CMBC) was employed to remove Cd(II), Ni(II), and Cu(II) in mono-metal and binary-metal sorption media.¹⁰⁰ It was observed that the kinetic and equilibrium data of Cd(II), Ni(II), and Cu(II) on E-CMBC were best explained by the Avrami fractional order and the Langmuir models. The optimum uptake capacities were 40.38, 48.73, and 61.95 mg g⁻¹ for Ni(II), Cu(II), and Cd(II), correspondingly. In a binary-metal system, coexisting ions have obvious competitive adsorption behavior on E-CMBC. The maximum sorption capacities of these metal ions were found to be lesser than that in single component systems. The order of the competitive decontamination was: Cu(II) > Ni(II) > Cd(II). Therefore, the study recommended that E-CMBC had the potential to depollute a variety of pollutants from water systems.

The decontamination of Zn(II) and Pb(II) from mono- and bi-solutes sorption media was examined by animal-derived biochar (ADB) was studied.¹⁰¹ The optimum uptake capacity of Zn(II) and Pb(II) onto ADB in the mono-solute system was 2.74 and 3.23 mmol g⁻¹, respectively. While in the bi-solute medium, the uptake capacity of Zn(II) and Pb(II) by the ADB was observed to be 2.31 and 2.7 mmol g⁻¹, respectively. The removal efficiency of Zn(II) and Pb(II) in the mono-solute system was 99.90 and 78.00–80.60%, respectively. In the binary sorption system, the existence of Pb(II) ions altered the removal mechanism of Zn(II) by ADB. The study found that ADB is proficient biochar for the competitive decontamination of Zn(II) and Pb(II) from their aqueous media.

Also, biochar obtained from chicken manure (CM), rice straw (RS), and sewage sludge (SS) was employed to remove Pb(II) and Zn(II) from mono-solute and binary-solute systems.¹⁰² The RS biochar was observed to have the highest uptake capacity for Pb(II) and Zn(II) ions from both mono-solute and binary-solute systems. This is because the RS was found to be a highly negatively charged surface, possess enormous aromatic functional groups, and is physically stable. The sorption data obtained from both single- and binary-metal systems were best



correlated to both the Freundlich and Langmuir models, respectively. Therefore, this study provided crucial information for using biochar derived from locally available resources for wastewater purification.

More so, the individual and simultaneous sequestration of $\text{Pb}(\text{II})$ and $\text{Cr}(\text{VI})$ by engineered biochar synthesized from pine-wood sawdust were investigated.¹⁰³ The study revealed that the uptake capacity of $\text{Pb}(\text{II})$ and $\text{Cr}(\text{VI})$ from the binary sorption medium was found to be greater than that obtained from the single systems at a temperature of 298 K. However, the detoxification of $\text{Pb}(\text{II})$ ions from both individual and binary component systems was higher than that of $\text{Cr}(\text{VI})$ attained by the biochar. The uptake capacity of $\text{Cr}(\text{VI})$ and $\text{Pb}(\text{II})$ at the equilibrium was found to be 346.00 and 606.00 mg g^{-1} in monocomponent systems and 488.00 and 1420.00 mg g^{-1} , correspondingly in the binary system. The study revealed that biochar could be fruitfully employed for the individual detoxification of $\text{Pb}(\text{II})$ and $\text{Cr}(\text{VI})$ ions from wastewater and in multicomponent systems.

Wu *et al.*²³ produced biochar (BC) and magnetic biochar (MBC) from pomelo peel at different temperatures for the adsorptive elimination of $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Zn}(\text{II})$ from single-, binary-, and ternary-metals systems. It was observed that the pyrolysis temperature and magnetization could influence the uptake rate of biochar. The study found that the competitive sorption order of the metals in the ternary-solute system was $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Zn}(\text{II})$. The kinetic and isothermal data best agreed with the pseudo-second-order and Langmuir models. The study showed that pomelo peel biochar is effective in the adsorptive elimination of heavy metals from wastewater where the major contaminant is $\text{Pb}(\text{II})$ and maximum uptake capacity could reach about 48.74 mmol g^{-1} . The study also proposed technical support for the effective utilization of the pomelo peels as well as the engineering application of its biochar.

Similarly, biochar derived from raw tea waste (RTW) was produced under different pyrolysis conditions for the elimination of $\text{Cd}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Pb}(\text{II})$ from single and ternary solute systems.²⁰ However, the biochar produced by pyrolysis of RTW at 900.00 °C (BC 900) demonstrated the highest uptake capacity. The affinity of these metals in the ternary solutions towards the BC 900 followed the pattern: $\text{Pb}(\text{II}) > \text{Cd}(\text{II}) > \text{Cu}(\text{II})$. While the single metal ions' affinity towards the BC 900 was in the order of $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Cd}(\text{II})$. It was observed that the uptake of $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$ ions from the single and ternary solute systems was best explained using the pseudo-second-order model suggesting chemisorption. The results of the investigation provided new insight into the employability of RTW in water purification.

Also, an alkali-modified biochar prepared from ginkgo leaves was produced by simply one-step pyrolysis and was employed for the concurrent elimination of $\text{Cd}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Pb}(\text{II})$ from competitive aqueous systems.²² The study found that after the ginkgo leaves were modified with alkali, the biochar exhibited abundant surface functional groups and large porosity, resulting in high adsorption capacities for 589.32, 563.55, and 81.70 mg g^{-1} for $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$, correspondingly. The isothermal and kinetic data best fitted the Freundlich and pseudo-second-order kinetic model, correspondingly. The

alkali-modified biochar could act as a functioning sorbent for heavy metals elimination in actual wastewater because of its superior performance over a wider pH range and its high uptake capacity.

A raw cassava root husk-derived biochar (CRHB) and modified CRHB using ZnO nanoparticles (CRHB-ZnO₃) was applied for the simultaneous removal of $\text{Cr}(\text{VI})$, $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{As}(\text{III})$ ions from competitive aqueous solutions by batch mode.¹⁰⁴ It was found that at pH 6.00–7.00, 60.00 min contact time, and concentration of 80.00 mg L^{-1} , maximum removal of these heavy metals was achieved. The uptake capacities of these heavy metals by CRHB-ZnO₃ were observed to be in this trend: $\text{Pb}(\text{II}) > \text{Cd}(\text{II}) > \text{As}(\text{III}) > \text{Cr}(\text{VI})$. The overall maximum uptake capacity achieved by the CRHB and CRHB-ZnO₃ during the removal of these four metal ions was observed to be 115.11 and 154.21 mg g^{-1} , correspondingly. The individual uptake capacity by the CRHB-ZnO₃ was determined as 44.27, 42.05, 39.52, and 28.37 mg g^{-1} for $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, $\text{As}(\text{III})$, and $\text{Cr}(\text{VI})$, correspondingly. The optimum uptake capacity of $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, $\text{As}(\text{III})$, and $\text{Cr}(\text{VI})$ ions attained by CRHB was found to be 34.47, 32.33, 26.42, and 21.89 mg g^{-1} , respectively. The study also revealed that the pseudo-first-order and pseudo-second-order models best described the kinetic data of the bio-adsorbent. While the sorption data were well correlated to the Langmuir model. The study found that the cassava root husk can be applied as an alternative, inexpensive, non-toxic, and highly suitable adsorbent in removing various toxic cations from aquatic systems.

Peanut shell-derived biochar (PBC) was utilized in removing $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Zn}(\text{II})$ ions from single and competitive wastewater.¹⁰⁵ The study found that the biochar demonstrated efficient decontamination of these metals from the single component system. Besides, the competitive sorption revealed that the selectivity of the biochar for the heavy metal ions declined according to the following manner $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Cd}(\text{II}) > \text{Ni}(\text{II}) > \text{Zn}(\text{II})$, which was found lower than that in the single sorption system. The kinetic and isothermal data of both single and competitive sorption systems were best explained by the Langmuir isotherm and pseudo-second-order models, correspondingly. Therefore, the study indicated that peanut shells-derived biochar is a profitable green adsorbent for water contaminants cleanup.

The single and ternary detoxification of $\text{Hg}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Zn}(\text{II})$ from wastewater onto a flamboyant char was studied by Sellaoui *et al.*¹⁰⁶ It was found that the flamboyant char is more proficient and suitable for the decontamination of $\text{Hg}(\text{II})$ in both mono- and ternary component medium than that of $\text{Pb}(\text{II})$ and $\text{Zn}(\text{II})$ ions. However, the adsorptive removal of $\text{Zn}(\text{II})$ and $\text{Pb}(\text{II})$ was observed to be varied based on the existence of the other competitive ions in the ternary system. The existence of other competing heavy metal ions in the ternary component system resulted in the recognition of high antagonistic effects on the sequestration of $\text{Zn}(\text{II})$ from the multi-metal sorption system.

In batch and column adsorption tests, the competitive decontamination of $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Ni}(\text{II})$ from aquatic systems using date seed biochar was explored.¹⁰⁷ The study revealed that the decontamination of $\text{Ni}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Cu}(\text{II})$ by date seed biochar in the multi-solute systems demonstrates



a competitive effect. In all column and batch modes, the uptake capacity of each heavy metal ion was decreased by 48.00–75.00% when compared to single metal systems. Subsequently, $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Ni}(\text{II})$ was the order in which the uptake and affinity towards the adsorbent occurred. The sorption system was well explained by the modified Langmuir model. The date seed biochar in this study demonstrated high potential in removing $\text{Pb}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$ competitively from the aqueous media.

Groundnut shells biochar (GB) obtained from different pyrolysis temperatures including GB350 and GB700 was explored in the decontamination of $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Pb}(\text{II})$ from single and competitive aqueous media.¹⁰⁸ It was revealed that $\text{Cd}(\text{II})$ percentage removal by groundnut shell biochar was 99.60%, which is greater than that of $\text{Pb}(\text{II})$ and $\text{Hg}(\text{II})$. The GB700 was efficient and resulted in 100.00% of $\text{Cd}(\text{II})$ removal and $\text{Pb}(\text{II})$ ions from the binary component system. Similarly, the percentage of $\text{Hg}(\text{II})$ and $\text{Pb}(\text{II})$ removal using GB350 was 100.00% except for $\text{Cd}(\text{II})$ ions having a removal efficiency of 99.05, 99.46, and 99.69% obtained from the single, binary, and ternary systems, respectively. The Langmuir adsorption isotherm model showed a good fitness to $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Hg}(\text{II})$ to the equilibrium data obtained from the mono-, binary, and ternary component systems. The study demonstrated that biochar made from groundnut shells could be employed as a practical and affordable bio-adsorbent in remediating various water contaminants.

An investigation of the competitive reduction of $\text{Zn}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, and $\text{Fe}(\text{II})$ ions in a quaternary solution by hybrid biochar developed from sugarcane bagasse (SCB) mixed with low-density polyethylene (LDPE) and pure SCB biochar was conducted.¹⁰⁹ For the two adsorbents utilized, more than 99.00% removal efficiency was recorded, which implied they can remove heavy metals from the simulated wastewater. The Langmuir isotherm fitted best in each domain and based on the correlation coefficient; the kinetic sorption data best fitted the pseudo-first-order model well.

More so, the simultaneous removal of $\text{Zn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Pb}(\text{II})$ from the quaternary system by biochar derived from oil palm (*Elaeis guineensis*) fibers was conducted.¹⁰⁹ The uptake capacity of 16.54, 16.59, 16.65, and 16.67 mg g^{-1} for $\text{Zn}(\text{II})$,

$\text{Cu}(\text{II})$, $\text{Fe}(\text{II})$, and $\text{Pb}(\text{II})$ was achieved by the biomass biochar while the hybrid biochar uptake capacity of $\text{Pb}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Fe}(\text{II})$ and $\text{Cu}(\text{II})$ was 16.66, 16.54, 16.65 and 16.57 mg g^{-1} , correspondingly. The sorption kinetic and isothermal data conformed to the pseudo-second-order and Elovich isotherm models, respectively.

Also, a study explored the adsorptive removal of $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Ni}(\text{II})$ from mono- and multi-solute media by soil amended with plant residue biochar including corn straw, wheat straw, rice husk, and licorice root pulp each at 3.00% w/w.¹¹⁰ For the single component system, the uptake capacities of the metal ions were in the sequence of $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Ni}(\text{II})$, and the Freundlich isotherm fitted well to the sorption data of $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Pb}(\text{II})$ at equilibrium. In the competitive system, the coexistence of different metal ions reduced the uptake capacity for each metal ion and the selectivity followed this trend: $\text{Ni}(\text{II}) > \text{Pb}(\text{II}) > \text{Cu}(\text{II})$. The corn straw biochar (CSB) was found to have the greatest uptake capacity of 0.23, 1.41, and 2.73 mg g^{-1} for $\text{Ni}(\text{II}) > \text{Pb}(\text{II}) > \text{Cu}(\text{II})$, correspondingly.

4.3 Biosorbents

The decontamination of various heavy metals from water systems using biosorbents produced from microbial biomasses, agricultural waste, industrial by-products, or natural materials is efficient, cost-effective, and economical due to the possibility of regenerating the biosorbent. Fig. 12 demonstrates the step-by-step procedure for biosorbent preparation from microbial biomass or agro-based waste.

The capability of dry biomass derived from two species of macrophytes was used to decontaminate $\text{Pb}(\text{II})$ and $\text{Cu}(\text{II})$ from a binary sorption medium.¹¹¹ The study revealed that maximum removal efficiency was achieved by *Pontederia rotundifolia* and *Salvinia biloba* at an agitation time of 120.00 and 240 min, respectively. The biosorbent, *Salvinia biloba* was suitable in decontaminating $\text{Cu}(\text{II})$ from the aquatic media while both the biosorbents could be effective for $\text{Pb}(\text{II})$ ions removal. The data of $\text{Cu}(\text{II})$ and $\text{Pb}(\text{II})$ at equilibrium showed good fitness to the Langmuir isotherm model. The high removal rate, high uptake

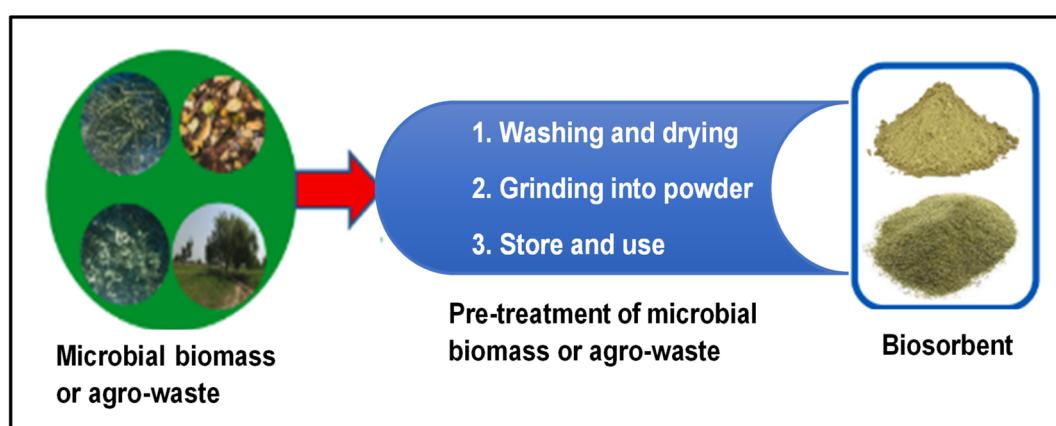


Fig. 12 A schematic diagram showing the step-by-step procedure for the preparation of the biosorbent from microbial biomass or agro-based waste (this figure has been adapted from Bilal *et al.*³² with permission from Elsevier, copyright 2022).



capacity, and low cost of *P. rotundifolia* and *S. biloba* biomass make them suitable for use in biosorption systems to treat wastewater.

Similarly, microalgae waste was modified and applied as an environmentally friendly biosorbent for eradicating Cd(II) and Pb(II) ions from mono- and bicomponent synthetic wastewater.¹¹² The study showed that the kinetic data of Pb(II) and Cd(II) obtained by the biosorbent for both the mono- and bicomponents media agreed well with the pseudo-second-order model. The isothermal data of Pb(II) and Cd(II) also showed good fitness to the Langmuir and Freundlich models, respectively. The Langmuir optimum uptake capacities achieved by the biosorbent were 337.00 and 232.00 mg g⁻¹ for Pb(II) and Cd(II), correspondingly. The results of the binary sorption system indicated that Cd(II) and Pb(II) exhibited antagonistic effects, in which the decontamination of Pb(II) and Cd(II) individually reduces the coexistence of each other. The study showed that the biosorbent has great capability in treating wastewater polluted by heavy metal ions.

Sodium chloride-treated *Cystoseira indica* as a biosorbent was employed to decontaminate Ni(II) and Co(II) ions simultaneously from polluted water.¹¹³ The CCD was employed to elucidate the interactive behavior of the biosorption parameters and optimum operating conditions were observed at 5.90 pH, 0.06 g biosorbent dose, 91.94 mg L⁻¹ Ni(II) concentration, 89.36 mg L⁻¹ Co(II) concentration. The sorption data were best explained by the intra-particle diffusion model at an equilibrium sorption time of 80.00 min. While the extended Freundlich isotherm model showed good representation with the equilibrium data of Ni(II) and Co(II) from the binary component system with an optimum biosorption capacity of 69.99 and 75.21 mg g⁻¹ for Co(II) and Ni(II), correspondingly.

Similarly, a magnetic composite obtained from green macroalgae (*Enteromorpha prolifera*) as a biosorbent was utilized for Co(II) and Ni(II) depolluting from mono- and binary component systems.¹¹⁴ The study found that the biosorbent had a strong selectivity for both Ni(II) and Co(II) ions with the optimum sorption capacities of 135.00 and 137.00 mg g⁻¹, respectively. The coexistence of alkali and alkali earth metal ions including Na⁺, K⁺, Mg(II), and Ca(II) inhibited the decontamination of Ni(II) and Co(II). In comparison with the single sorption system, the sorption capacity of Ni(II) and Co(II) from the binary system was reduced due to the presence of the other ions. The study disclosed that the biosorbent is resourceful in the removal of heavy metals in addition to alkali and alkali earth cations in wastewater simultaneously.

The competitive detoxification of Ni(II) and Cd(II) from aquatic systems was explored using brown algae (*Cystoseira indica*) as a biosorbent.¹¹⁵ The study revealed that optimum operating conditions for maximum Ni(II) and Cd(II) removal were a biosorbent dosage of 1.00 g L⁻¹, initial concentration of 100.00 mg L⁻¹, and solution pH of 6.00. The kinetic data of Cd(II) and Ni(II) was best fitted to the intra-particle-diffusion kinetic model. While the equilibrium isothermal data of Ni(II) and Cd(II) was better fitted to the extended-Freundlich model with optimum biosorption efficiencies of 55.34 and 18.17 mg g⁻¹ for Ni(II) and Cd(II), correspondingly.

Similarly, the concurrent sorption of Ni(II) and Cd(II) ions in wastewater onto *Streptomyces rimosus* biomass was conducted.¹¹⁶ The study found that Ni(II) and Cd(II) biosorption from the bi-solute medium attained equilibrium at a shaking time of 3.00 h and the maximum biosorption capacities achieved by the biosorbent were 9.86 and 22.80 mg g⁻¹ for Cd(II) and Ni(II), correspondingly. The sorption data of Cd(II) and Ni(II) showed good representation with the pseudo-second-order and Langmuir models, respectively. The *Streptomyces rimosus* biomass has been demonstrated to have a high biosorption ability and would be an effective biosorbent for Cd(II) and Ni(II) ions elimination from water systems.

The adsorptive elimination of Cr(III) and Ni(II) from mono- and binary component systems was conducted by using *Durvillaea antarctica* as a biosorbent.¹¹⁷ The study observed that optimum sorption capacity of 32.85 and 102.72 mg g⁻¹ for Ni(II) and Cr(III) occurred at a pH of 5.00, and a reaction time of 240.00 and 420.00 min, respectively. It was observed that the increasing Ni(II) initial concentration increases its uptake capacity but reduces the uptake capacity of Cr(III) ions. The binary component equilibrium data of Ni(II) and Cr(III) showed the best fit to the Sips model. The competitive biosorption indicated that Cr(III) and Ni(II) ions present in wastewater compete strongly for the same active biosorbent sites.

Also, a study was conducted to decontaminate Cd(II), Cu(II), and Zn(II) from both mono- and ternary aqueous media using phosphogypsum as a biosorbent.¹¹⁸ The uptake capacity of Cu(II), Zn(II), and Cd(II) ions onto the biosorbent upsurged with the pH and the optimum decontamination was attained at pH of 8.00, 9.00, and 9.50, respectively. The sorption rate of Cd(II) attained by the biosorbent was greater than Cu(II) and Zn(II) in both mono- and multi-solute sorption media. Also, in a ternary sorption system, the biosorbent retained its overall uptake capacity with an increment in the uptake of Cu(II) while the uptake capacity of Zn(II) and Cd(II) ions decreased. The experimental data of Cu(II), Zn(II), and Cd(II) were well described by the pseudo-second-order kinetic and Freundlich isotherm models. The study demonstrated that phosphogypsum may be used as a cheap biosorbent for the sequestration of various water contaminants.

The uptake ability of Pb(II), Co(II), Cd(II), Zn(II), Cu(II), and Ni(II) ions from non- and competitive sorption systems by *Leucodon sciuroides* (LS) mosses as a biosorbent was carried out.¹¹⁹ It was revealed that the optimum uptake efficiency of these heavy metal ions occurred at 30.00 min of agitation time and a pH of 6.00 with Pb(II) and Cu(II) being the most adsorbed by the LS. The equilibrium sorption data of Ni(II), Co(II), and Cu(II) well-fitted to the Langmuir model whereas Pb(II), Zn(II), and Cd(II) equilibrium data conformed to the Freundlich model. Also, the experimental data attained by LS for all six heavy metals correlated well with the pseudo-second-order model. The competitive biosorption showed that the biosorbent can concurrently remove Cu(II) and Pb(II) from complex water systems including the other four heavy metals.

The detoxification of Cd(II), Cu(II), and Ni(II) from mono- and multicomponents sorption medium was conducted by using biogenic vaterite induced by *Bacillus subtilis* as a biosorbent.¹²⁰



The study revealed that the sorption data agreed well with the Langmuir in comparison to the Freundlich isotherm model. While the experimental results were best represented using the pseudo-second-order kinetic model. The Langmuir maximum biosorption capacity of Cd(II), Cu(II), and Ni(II) obtained from the single component medium was 270.27, 172.41, and 178.57 mg g⁻¹, respectively. However, in the multi-solute medium, the maximum uptake capacities of 94.34, 30.30, and 175.44 mg g⁻¹ were attained by the adsorbent for Ni(II), Cu(II), and Cd(II), correspondingly. The study observed that in the multi-metal sorption systems, competitive effects occurred amongst the heavy metal ions and with Cu(II) ions uptake by the adsorbent being the least affected by the existence of the other two competing for heavy metal ions.

4.4 Activated carbon

Due to its great adsorption capacity, activated carbon can be used in a variety of applications. It has numerous uses, such as the treatment of industrial effluent, medicine, the discoloration of sugar, and a lot more. The porous nature of activated carbon, which results in a high surface area makes it an effective adsorbent. Fig. 13 is a schematic illustration of the production of activated carbon from biomass. Several studies have employed activated carbon in the remediation of heavy metals from complex water systems as discussed in this section.

The elimination of As(III) from binary systems onto hybrid granular activated carbon has been investigated using the batch technique.⁷ The removal of As(III) was found to show dependence on the adsorption factors studied. The equilibrium isothermal and kinetic data attained from both mono- and binary solutes sorption media were best correlated with the Langmuir and pseudo-second-order models, suggesting the mechanism of As(III) removal was due to chemical adsorption. The Langmuir monolayer adsorption capacities of the activated carbon were 205.76 for the mono-solute and 153.09 mg g⁻¹ for

binary solute sorption systems, correspondingly. This implies that there existed an antagonistic effect on the removal of As(III) due to the presence of Hg(II) ions in binary sorption media. The thermodynamic variables indicated that the elimination of As(III) ions from both sorption media were endothermic and spontaneous with an increase in randomness at the adsorbate-sorbent interface. The successive regeneration studies showed that the spent activated carbon uptake capacity is renewable after multi-cycles of adsorption-desorption. This suggested that activated carbon has economic prospects and practical industrial applications for As(III) remediation in wastewater.

A response surface methodology (RSM) was utilized to investigate the parameters that influence the competitive uptake capacity of Ni(II) and Cu(II) from binary component systems by activated carbon derived from sewage sludge.¹²² The uptake efficiencies of Ni(II) and Cu(II) were optimized by the application of CCD under RSM. It was found that the model-predicted data correlated well with the experimental results. While the ANOVA results indicated that the process was mainly influenced by the Ni(II) concentration and adsorbent dose, whereas the remaining factors exhibited very low effects. The best-operating conditions were Ni(II) and Cu(II) concentration, agitation time, adsorbent dosage, and reaction temperature were 40.00 mg L⁻¹, 100.00 min, 4.00 g L⁻¹, and 30.00 °C. Under these optimal settings, the maximum uptake capacities of 4.04 and 7.48 mg g⁻¹, respectively were attained for Cu(II) and Ni(II). From the results of the study, the activated carbon derived from sewage sludge could be utilized beneficially for removing Cu(II) and Ni(II) from aquatic environments.

Similarly, the depollution of Cu(II) and Ni(II) in mono- and bicomponent systems was performed by using activated carbon derived from corn cob.¹²³ The impact of sorption parameters was considered and equilibrium was attained at 240.00 and 100.00 min with uptake capacity of 0.39 and 0.28 mmol g⁻¹ for Cu(II) and Ni(II), correspondingly. It was observed that at higher

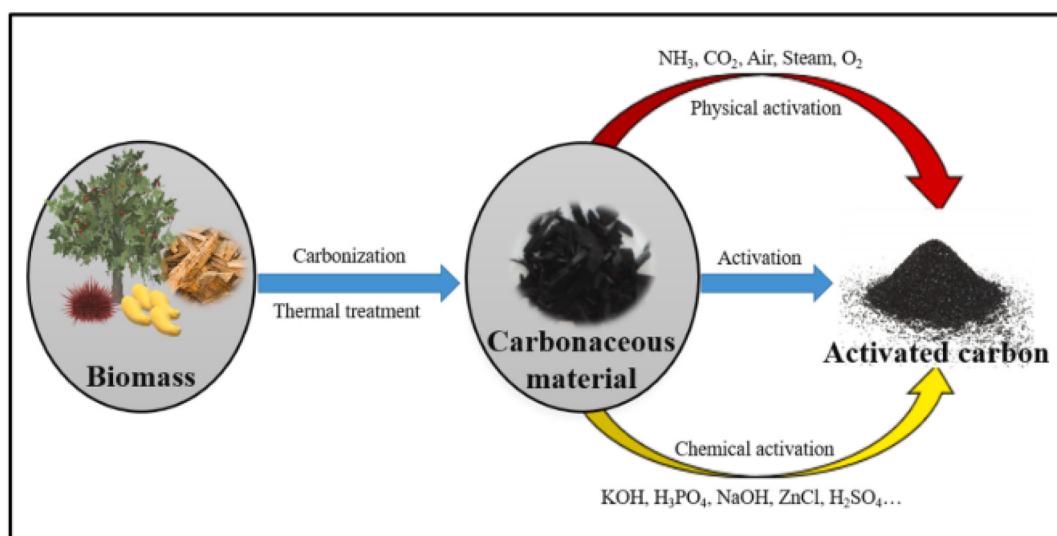


Fig. 13 Schematic illustration of the classical fabrication and activation techniques of activated carbon (this figure has been reproduced from Mariana et al.¹²¹ with permission from Elsevier, copyright 2021).



pH and initial concentration, the sorption process was enhanced and Cu(II) uptake by the adsorbent was not influenced by the coexistence of Ni(II) in the solution. The influence of temperature on Cu(II) and Ni(II) elimination from the monocomponent system was statistically insignificant and statistically significant only during Cu(II) removal from the bicomponent system. The sorption data of the monocomponent system was best explained by Sips and pseudo-second-order models and that of the bicomponent system was best conformed to the extended Langmuir model. The study showed that corn cob-activated carbon is efficient in heavy metals remediation from water systems.

The adsorptive decontamination of Cu(II) and Zn(II) from binary solute systems onto carbonaceous materials obtained by chemical activation and ammoniation of polish brown coal was investigated.¹²⁴ The influence of agitation time, temperature, solution pH, and initial concentration as well as the existence of competing ions on the uptake ability of activated carbons, were studied. It was revealed that the sorption capacity upsurges with increasing concentration and the agitation time and optimum removal were found at pH of 8.00 and 6.00 for Cu(II) and Zn(II), correspondingly. The carbonaceous adsorbent derived from ammoniation was more proficient in the decontamination of Zn(II) and Cu(II) from binary component systems. However, the uptake capacities of Cu(II) and Zn(II) by the carbonaceous adsorbent relative to that of unmodified adsorbent were much smaller. The isothermal and kinetic data obtained from both systems were well represented by the Langmuir and pseudo-second-order models.

More so, the adsorptive decontamination of Cd(II) and Pb(II) ions from mono- and binary component systems with commercial granular activated carbon was conducted in batch mode.¹²⁵ It was observed that the maximum agitation time was 120.00 min for both heavy metal ions and the optimum pH ranged from 5.50–6.00 and 7.00–8.00 for Pb(II) and Cd(II), correspondingly. The study revealed that the uptake capacity of 9.30 mg g⁻¹ for Pb(II) attained by the activated carbon was higher than Cd(II), which is 9.26 mg g⁻¹. The kinetic data of Pb(II) and Cd(II) showed good fitness to the pseudo-second-order model while both the extended Freundlich and Langmuir models best correlated to the binary component system adsorption data. The optimization results using RSM revealed that initial pH of 6.30, a temperature of 56.80 °C, and a shaking speed of 308.00 rpm as optimum operating conditions.

The depollution of Co(II) and Pb(II) ions from a bicomponent aqueous medium was performed by thiolated sawdust.²⁸ According to the study, the saw dust-activated carbon appeared to be a proficient adsorbent for the concurrent sorption of Co(II) and Pb(II). The Langmuir multicomponent isotherm demonstrated that the existence of Co(II) in the solution reduced the affinity of Pb(II) towards the bio-adsorbent, and so, the effect of the mixtures appeared to be antagonistic. Therefore, the current study emphasized the possibility of sawdust in eliminating heavy metals from mono-solute and multi-solute systems, particularly for small-scale companies.

The elimination of Hg(II) and Zn(II) from the binary system was examined by activated carbon produced from *Theobroma*

cacao pod husk.¹²⁶ The batch experiment disclosed that the elimination of Hg(II) and Zn(II) simultaneously attained equilibrium rapidly at an agitation time of 90.00 min. The Temkin and Langmuir models well-fitted the equilibrium sorption data of Hg(II) and Zn(II). The sorption kinetic data were best described by four models notably among which are the pseudo-first-order, Elovich, pseudo-second-order, and intraparticle diffusion models. The study indicated that the *Theobroma cacao* pod husk could be proficient in decontaminating of Hg(II) and Zn(II) from aquatic systems.

Besides, a modified pine bark (as activated carbon) efficiency was tested for the single and simultaneous reduction of Cr(III) and Ni(II) ions from aquatic systems.¹²⁷ The sorption kinetic data of Cr(III) and Ni(II) obtained by the adsorbent in the single- and binary solute systems was best explained using the pseudo-second-order kinetic model. Also, the isothermal data of Cr(III) and Ni(II) at equilibrium are well correlated with the Langmuir isotherm with monolayer maximum sorption efficiencies of 31.40 and 23.70 mg g⁻¹, correspondingly. In the binary solute system, Ni(II) ions coexistence showed little influence on Cr(III) ions removal but the occurrence of Cr(III) ions decreased Ni(II) ions uptake rate by the adsorbent. In the binary solute medium, the modified Langmuir model well described the sorption data of Cr(III) and Ni(II) achieved by the activated carbon at equilibrium.

The possibility of removing Ni(II), Pb(II), and Zn(II) concurrently from two binary-metal sorption media including Ni(II)–Pb(II) and Ni(II)–Zn(II) onto oxidized activated carbon fiber (ACF-Ox) was conducted.⁷⁴ The simultaneous sequestration of Pb(II) and Ni(II) ions from the bi-solute sorption medium [Ni(II)–Pb(II)] by the ACF-Ox suggested that the affinity of Pb(II) ions towards ACF-Ox was much greater than that of the Ni(II). However, the concurrent sequestration of Ni(II) and Zn(II) by the ACF-Ox in the bi-solute system [Ni(II)–Zn(II)] indicated that the Ni(II) ions uptake capacity was 1.12 times higher than Zn(II) ions. The competitive sorption data attained by ACF-Ox for Ni(II), Pb(II), and Zn(II) in the binary sorption systems were best fitted to the extended Freundlich isotherm.

A commercial wood-based granular activated carbon (GAC) was acquired and its ability to adsorb Cu(II), Pb(II), and Zn(II) ions in mono- and bicomponents systems was explored.¹²⁸ The study discovered that the maximum abatement of Cu(II), Zn(II), and Pb(II) from both sorption systems was accomplished at solution pH of 5.50, 4.50, and 6.00, respectively. It was found that the selectivity of these metals towards the GAC was in this trend Pb(II) > Cu(II) > Zn for all the pH ranges studied. The Sips and Langmuir models conformed to the equilibrium data Cu(II), Zn(II), and Pb(II) obtained from the mono-solute system at a pH of 5.00. The Langmuir optimum sorption capacities of Cu(II), Pb(II), and Zn(II) achieved by the activated carbon were 0.094, 0.142, and 0.058 mmol g⁻¹, respectively. The uptake capacities of Zn(II), Cu(II), and Pb(II) at a concentration of 0.01 mmol L⁻¹ were 0.040, 0.085, and 0.130 mmol g⁻¹, respectively. The IAS-Sips and Ideal Adsorbed Solution (IAS)-Langmuir models best represented the bi- and ternary solutes sorption data, respectively. The study added to the body of knowledge on the



modeling of binary and ternary sorption systems on GAC, a flexible adsorbent widely utilized in wastewater treatment.

Multicomponent competitive elimination of phenol, Pb(II), Cd(II), and Cr(III) was performed with KOH-activated carbon obtained from mangrove charcoal.¹²⁹ The study discovered that the optimum removal rates of phenol, Pb(II), Cd(II), and Cr(III) from the multicomponent system were found to be 76.00, 92.00, 47.00, and 31.00%, respectively obtained at optimum pH 5.00, 2.50 g L⁻¹ adsorbent dosage, 120.00 min of reaction time, and 50.00 mg L⁻¹ concentration for phenol and 30.00 mg L⁻¹ of each heavy metal. The optimum uptake rates of phenol, Pb(II), Cr(III), and Cd(II) were 46.00, 32.00, 11.00, and 3.80 mg g⁻¹, respectively. The study observed that the concurrent elimination of phenol, Pb(II), Cr(III), and Cd(II) from the multi-solutes system was fierce due to the comparable sorption mechanisms. The equilibrium data of Pb(II) and Cr(III) showed good fitness to the Langmuir model whereas the sorption data of Cd(II) at equilibrium agreed with the Redlich-Peterson model. Besides, the Freundlich model best explained the phenol sorption data. However, the pseudo-second-order best fitted the kinetic data of phenol, Pb(II), Cd(II), and Cr(III) obtained from the multicomponent system suggesting chemisorption as the adsorption mechanism. The adsorption and desorption for the multicomponent system indicated that HCl could recover the heavy metal ions while NaOH solution was the best eluent for phenol desorption.

The decontamination of Pb(II), Cu(II), Cd(II), Zn(II), and Cr(VI) from both single and multicomponent systems onto wooden commercial activated carbon was conducted.¹³⁰ The study found that at a pH of 3.00, optimum Cr(VI) removal was accomplished, while a pH of 7.00 resulted in maximum decontamination of Pb(II), Cd(II), Cu(II), and Zn(II) in the single system. The maximum uptake capacities of the heavy metals were observed to exhibit the pattern of Pb(II) > Cr(VI) > Cd(II) > Cu(II) > Zn(II) at a temperature of 25.00 °C in the mono-metal system. For the single component system, the equilibrium sorption data obeyed the Langmuir and pseudo-first-order models. In comparison, the study showed that Cr(VI) and Cu(II) depollution was enhanced by the presence of Cd(II), Zn(II), and Pb(II), while the removal of Zn(II) and Cd(II) was influenced by the coexistence of Pb(II), Cu(II), and Cr(VI) ions in the multicomponent systems. This study offered useful recommendations for the future use of wooden commercial activated carbon in complex wastewater purification including different heavy metals.

The decontamination of Pb(II), Cu(II), Cd(II), and Zn(II) ions as well as Mg(II), Ca(II), and K⁺ as alkali and alkali earth metal ions in mono- and multi-metals sorption media onto bagasse activated carbon were performed.¹³¹ The study revealed that at 60.00 min agitation time, optimum removal of Pb(II), Cd(II), Cu(II), Zn(II), Mg(II), K⁺, and Ca(II) ions by the bagasse activated carbon was 0.77, 0.64, 0.49, 0.69, 0.47, 0.67 and 0.09 mmol g⁻¹, correspondingly, which was much higher than the untreated bagasse. The kinetic data attained from the monocomponent system obeyed the pseudo-second-order kinetic model. The multicomponent sorption showed that the bagasse-activated carbon had a greater affinity for the heavy metals than the alkali and alkali earth metal ions. At 0.015 g adsorbent load, the

optimum Pb(II), Cu(II), Zn(II) and Cd(II) ions removal rate from the wastewater was 94.53, 92.74, 70.46 and 83.30%, respectively while that of Mg(II), Ca(II) and K⁺ was only 6.64, 4.75, and 0.00%, respectively. This implied that the heavy metals have the chance of being removed selectively from wastewater by the modified bagasse.

The simultaneous removal of Zn(II) and Hg(II) in the coexistence of Mg(II) onto chemically activated bentonite using the batch technique was explored by Mudasir *et al.*¹³² At 6.00 pH and 60.00 min reaction time, maximum concurrent removal of Zn(II) and Hg(II) ions in the existence of Mg(II) was accomplished. The uptake capacity, selectivity, and affinity of modified bentonite towards Zn(II) and Hg(II) were higher than unmodified bentonite. The kinetic data achieved by the adsorbent for both Zn(II) and Hg(II) in the coexistence of Mg(II) was well correlated to the pseudo-second-order model. While the equilibrium data of Zn(II) and Hg(II) showed good representation with the Langmuir and Freundlich models. The results demonstrated that the existence of Mg(II) ions in the multicomponent system did not inhibit the uptake of Zn(II) and Hg(II) ions signifying that dithizone-immobilized bentonite had a greater affinity for heavy metals.

The peels of *Artocarpus nobilis* fruit were used to produce NaOH-activated carbon solutions to concurrently remove Cr(VI) and Cr(III) from aqueous systems.¹³³ The study observed that the best solution pH for Cr(III) and Cr(VI) ions detoxification was found to be pH of 5.00 and 2.00, respectively. At pH of 5.00 and 2.00, the maximum uptake rates of Cr(VI) and Cr(III) ions were 4.94 and 4.89 mg g⁻¹, correspondingly. The kinetic data of Cr(III) and Cr(VI) correlated well with the pseudo-first-order model.

Similarly, untreated and NaOH-modified waste cotton yarn was utilized in removing Pb(II), Cr(III), As(V), and Cd(II) from single- and multi-metal aqueous solutions.¹³⁴ The study revealed that NaOH-modified cotton yarn adsorbent insignificantly affected the uptake ability of the cations. The uptake rates of Pb(II) were observed to be the greatest in the mono- and multi-sorption media whereas As(V) ions demonstrated the least affinity to the cotton yarn surface. The equilibrium sorption data of Pb(II), Cd(II), Cr(III), and As(V) ions onto cotton yarn was well correlated to the pseudo-second-order and Freundlich models. The study concluded that cotton yarn, a waste product from the textile industry, might potentially be applied as a cheap adsorbent for depolluting various heavy metals from aqueous media.

The elimination of Ni(II) and Cr(VI) from mono- and bisolutes sorption media by modified diatomite waste as an adsorbent were performed in batch mode.¹³⁵ In the mono-solute medium, the sorption data of Cr(VI) and Ni(II) achieved by the adsorbent was accurately represented by the Langmuir and Freundlich models. At a solution pH of 3.00 and 8.00, maximum uptake efficiencies of 3.64 and 2.90 mg g⁻¹ for Ni(II) and Cr(VI) were attained. In the bicomponent medium, the coexistence of Ni(II) ions affected Cr(VI) ions removal, but Cr(VI) existence promoted the adsorptive elimination of Ni(II). The kinetic sorption data of Cr(VI) and Ni(II) attained by the adsorbent in the single and binary systems were observed to exhibit good fitness to the pseudo-second-order model. Besides, the extended



Freundlich and Langmuir extended multicomponent adsorption isotherm models were found to fit well with the competitive equilibrium data of Ni(II) and Cr(VI). This study provided insights regarding the utilization of modified diatomite wastes for heavy metals elimination from the ecosystem.

Besides, modified argillaceous limestone was used in removing Cd(II), Pb(II), and Ni(II) from the mono- and multicomponent system.¹³⁶ In the monocomponent system, the decontamination rate of Cd(II), Pb(II), and Ni(II) were much higher than that in the multi-solute media. The study showed that Pb(II) ions uptake capacity by the adsorbent in the competitive system was much higher than the other heavy metal ions. The kinetic and isothermal data of Cd(II), Pb(II), and Ni(II) obtained by the adsorbent demonstrated good fitness to the Langmuir and pseudo-second-order models, respectively. The study uncovered the efficacy of argillaceous limestone in the remediation of aquatic systems for heavy metal ions.

Similarly, raw and activated clay was employed in decontaminating of Cd(II), Zn(II), Pb(II), and Cu(II), ions both individually and simultaneously from wastewater.¹³⁷ In the single sorption system, the study found the uptake capacity of Pb(II) to be 26.78 and 45.94 mg g⁻¹ for natural and activated clay, correspondingly. For the multicomponent system, the sorption process showed dependence on the initial metal concentration with the uptake rate of 41.71 mg g⁻¹ for Pb(II) being the highest in the binary systems. In multicomponent systems, the removal efficiency of each metal was significantly reduced in the existence of other heavy metal ions. The study indicated that clay can be employed as a viable adsorbent for wastewater treatment.

4.5 Zeolite-based adsorbents

Zeolites are extensively utilized in the petroleum industries as water softeners, and catalysts for the synthesis of laundry detergents, and molecular sieves. Zeolite has a porous and intergranular microstructure with thermal and mechanical stability. Many different forms of zeolites have been employed as adsorbents for removing contaminants, particularly the removal of heavy metals in fields of water treatment, due to their strong ion exchange and adsorption capacities. Fig. 14 and 15, respectively are schematic illustrations of the general synthesis of zeolite and its adsorption characteristics. Several studies have employed zeolite-based adsorbents in the remediation of heavy metals from complex water systems as discussed in this section.

Dahake *et al.*¹³⁹ reported on the synthesis of oxime-modified zeolite-A as a promising adsorbent for uranium U(VI) ions sequestration from competitive solute solutions. The influence of several experimental variables was studied using the prepared adsorbent. Maximum U(VI) removal efficiency of 98.00% attained at a pH of 4.00–6.00. The uptake capacities of 4.92 mg g⁻¹ were observed for U(VI) in presence of other competing ions such as Cr(VI), Cd(II), Co(II), Pb(II), and Mn(II) ions. The equilibrium data was found to be best agreed with the Langmuir and pseudo-second-order models. More so, the spent adsorbent could be regenerated and reusable up to eight multicycles of adsorption and desorption with high removal efficiency for each run. It can be inferred from the results that oxime-modified zeolite-A is a capable adsorbent for the recovery of U(VI) ions due to its easy separation, high adsorption, and excellent reusability.

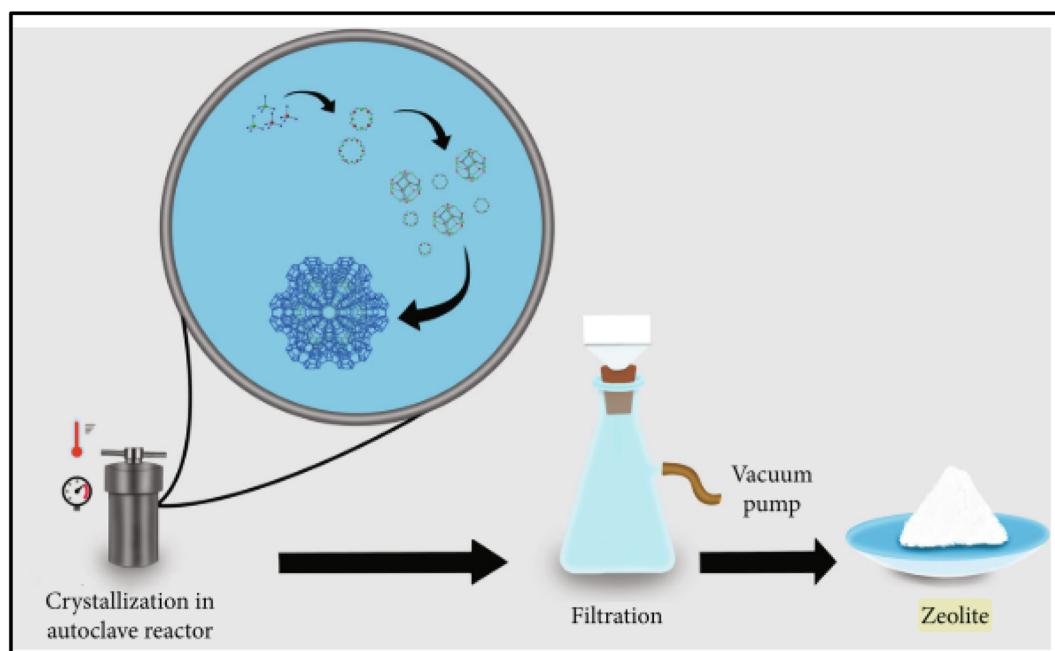


Fig. 14 A schematic diagram showing hydrothermal processes for synthesizing zeolite sorbent material for water pollutants removal (this figure has been adapted from De Magalhães *et al.*¹³⁸ with permission from Hindawi, copyright 2022).



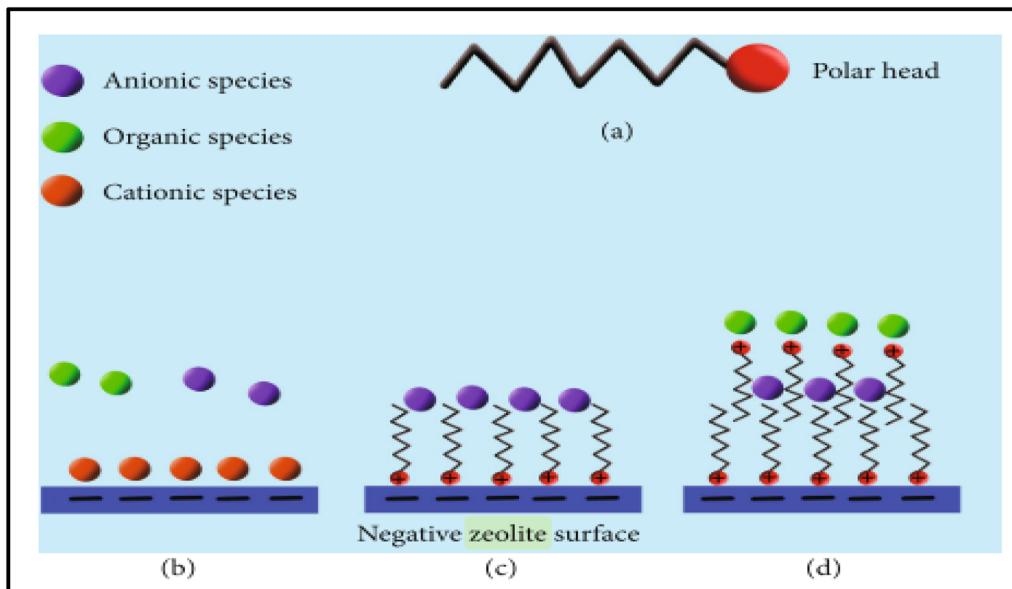


Fig. 15 A schematic diagram showing zeolite can only adsorb cationic species (b) when modified by a cationic surfactant (a), zeolite can also remove anionic (c) and organic species or both (d) (this figure has been adapted from De Magalhães *et al.*¹³⁸ with permission from Hindawi, copyright 2022).

More so, de Moraes França *et al.*⁴⁶ applied isotherm models to investigate the interactions between zeolite 4A and Cu(II), Ni(II), and Zn(II) with varying concentrations in single- and multicomponent adsorption media. The Freundlich, Langmuir, and Sips models well represented the sorption data of Cu(II) and Ni(II) at equilibrium whereas the Freundlich and Langmuir models correlated well to the isothermal data of Zn(II). The adsorption kinetics was discovered to be fast during Zn(II) and Cu(II) and slow for Ni(II). Hence, higher diffusion values were obtained during the decontamination of Cu(II) and Zn(II) from the sorption systems indicating a strong affinity of the synthesized zeolite 4A for the Zn(II) and Cu(II) in both the mono- and multi-solute sorption media.

Also, zeolite X was employed for the competitive elimination of Cu(II) and Zn(II) from the binary sorption system.¹⁴⁰ It was discovered that as Cu(II) initial concentration increased, the uptake capacity of Zn(II) significantly dropped from 175.20 to 7.10 mg g⁻¹. On the contrary, as Zn(II) concentration upsurges, Cu(II) sorption capacity went up from 142.90 to 148.30 mg g⁻¹. It was found that Cu(II) has a greater affinity for and selectivity toward zeolite X in the bicomponent sorption medium. The kinetic data of Zn(II) and Cu(II) showed a good fit for the pseudo-second-order kinetic model. Furthermore, the isothermal data exhibited good fitness to the Langmuir model. According to the study, diatomite-derived zeolite X might be a useful adsorbent for decontaminating different heavy metals from industrial aqueous systems.

The performance of clinoptilolite for removing Zn(II) and Cd(II) ions from wastewater in a batch mode was investigated.¹⁴¹ Zn(II) and Cd(II) concentrations varied between 10.00 and 20.00 mg L⁻¹, and the sorbent loading ranged between 10.00 and 60.00 g L⁻¹ in the aqueous media. The maximum removal

rate of both Zn(II) and Cd(II) was reached at 10.00 g L⁻¹ with very low metal ion concentrations. However, the uptake capacity declined when Cd(II) and Zn(II) amounts increased to 200.00 mg L⁻¹. Further experimentations were performed using the maximum concentration of 200.00 mg L⁻¹ while increasing the adsorbent loading to 40.00 and 60.00 g L⁻¹. The findings revealed that maximum percentage removal of more than 50.00%. The clinoptilolite was found to have a greater affinity for Cd(II) ions in a single system. The adsorbent exhibited a better affinity for Zn(II) due to a unique sorption mechanism in the presence of two metals in the binary system with a higher removal rate.

Similarly, clinoptilolite was treated with hexadecyltrimethylammonium bromide (HDTMA-Br) and employed as an adsorbent to decontaminate Cr(VI) and Cu(II) simultaneously from water systems.¹⁴¹ The optimum operating parameters obtained for the concurrent maximum elimination of Cr(VI) and Cu(II) ions from binary solute media were found to be 2.00 g adsorbent dosage, 56.50 mg L⁻¹ Cu(II) concentration, and 10.00 mg L⁻¹ Cr(VI) concentration. It was observed that the existence of Cu(II) in the bi-solute system enhanced the adsorbent surface charge and subsequently increased Cr(VI) ions uptake. The Langmuir model fitted well to the sorption data. While the thermodynamic studies showed that both Cr(VI) and Cu(II) ions uptake by the adsorbent was endothermic and exothermic in nature, respectively.

Furthermore, in mono- and binary solute systems, the comparative decontamination of Cd(II) and Pb(II) by amine-functionalized MCM-48 (NH₂-NH-NH-MCM-48) and amine-grafted MCM-48 was studied.¹⁴² The study utilized batch adsorption techniques in both single component and multi-component systems. The effects of the experimental factors

were examined, and the findings showed that MCM-48 with an amine attachment demonstrated greater $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ removal efficiency than MCM-48. The binary metal sorption results indicated that the elimination of the single metal ions is inhibited by the presence of the other heavy metal. The binary component sorption data agreed well with the extended Langmuir model, whilst the sorption data were best explained by the Freundlich and Langmuir models in the single system. The optimum uptake rates of $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ attained by $\text{NH}_2\text{-NH-NH-MCM-48}$ were 82.70 and 119.24 mg g^{-1} , respectively, in the single component system. It was discovered that $\text{NH}_2\text{-NH-NH-MCM-48}$ had a greater affinity for $\text{Cd}(\text{II})$ ions in both sorption systems.

On synthesized silica-based Mobil composition of matter no. 41 (MCM-41), $\text{Zn}(\text{II})$, and $\text{Cr}(\text{VI})$ ions were removed from single- and binary solute systems.¹⁴³ The $\text{Zn}(\text{II})$ and $\text{Cr}(\text{VI})$ ions were effectively removed under the optimal working conditions of pH 7.00, 0.10 g L^{-1} adsorbent load and 2.00 h of contact time. It was found that raising the initial $\text{Zn}(\text{II})$ amount caused the uptake capacity of $\text{Zn}(\text{II})$ to improve, whereas increasing the $\text{Cr}(\text{VI})$ concentration triggered the uptake capacity of $\text{Zn}(\text{II})$ to decrease. The elimination of $\text{Cr}(\text{VI})$ ions followed a similar pattern as $\text{Zn}(\text{II})$ concentration increased. The antagonistic effects on $\text{Zn}(\text{II})$ and $\text{Cr}(\text{VI})$ removal from the binary metal aqueous solutions were established. The experimental data of $\text{Zn}(\text{II})$ obtained from the binary solute system fitted best with the modified Redlich-Peterson isotherm model.

The concurrent decontamination of $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Pb}(\text{II})$ from aquatic systems by FAU-type zeolites produced from coal fly ash.¹⁴⁴ The study revealed that in the co-existence of other heavy metal ions, FAU zeolite derived from

coal fly ash could decontaminate heavy metal ions simultaneously in competitive aqueous solutions. The equilibrium sorption data of $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Co}(\text{II})$, $\text{Zn}(\text{II})$, and $\text{Cu}(\text{II})$ fitted well to the pseudo-second-order and Langmuir models, correspondingly. The heavy metal ion which was found most adsorbed was $\text{Pb}(\text{II})$ having an optimum uptake rate of 109.90 mg g^{-1} while that of $\text{Co}(\text{II})$ was the least with an uptake efficiency of 12.20 mg g^{-1} . The removal efficiency of FAU-type zeolite for the quinary-metals sequestration declined in the trend of $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Cd}(\text{II}) > \text{Zn}(\text{II}) > \text{Co}(\text{II})$.

In another study, the competitive elimination of $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$ from quaternary solute systems onto fly ash-based Linde F(K) zeolite was carried out.¹⁴⁵ It was found that $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Cd}(\text{II})$ removal from the quaternary component systems upsurged with rising pH values, and equilibrium was achieved at a pH of 6.00–7.00. The percentage elimination of these metals was observed to be high at the beginning of the sorption process and then progress slowly until equilibrium was established. The sequence of these heavy metals' uptake capacity at equilibrium was $\text{Pb}(\text{II}) > \text{Cd}(\text{II}) > \text{Cu}(\text{II}) > \text{Ni}(\text{II})$. The pseudo-second-order and internal surface diffusion were the best-fitted models, which accurately described the equilibrium sorption data of $\text{Pb}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$.

4.6 Nano-particles and nano-based adsorbents

Many contaminants in wastewater, including heavy metals, organic and inorganic solvents, dyes, biological toxins, and pathogens, have been reported to be successfully eliminated by nanomaterials. Nanomaterials are well suited for use in wastewater treatment because of their high surface-to-volume ratio,

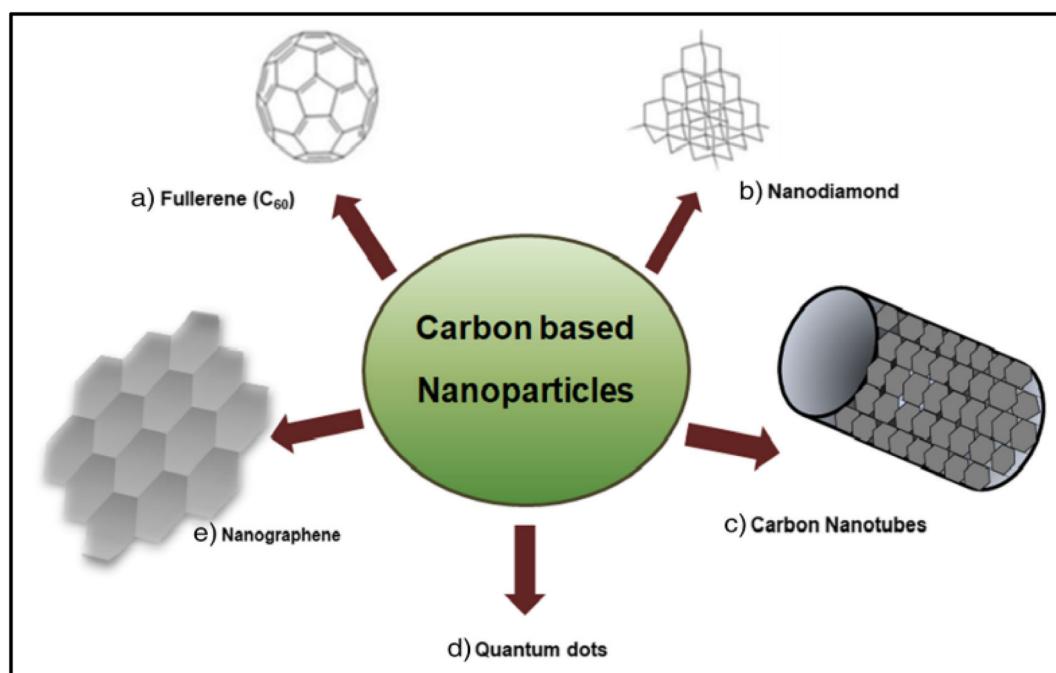


Fig. 16 Carbon-based nanoparticles: fullerene (a), nano-diamond (b), carbon nanotube (c), quantum dots (d) and nanographene (e) for wastewater treatment (this figure has been reproduced from Thakuria and Kataria¹⁴⁶ with permission from Springer, copyright 2021).



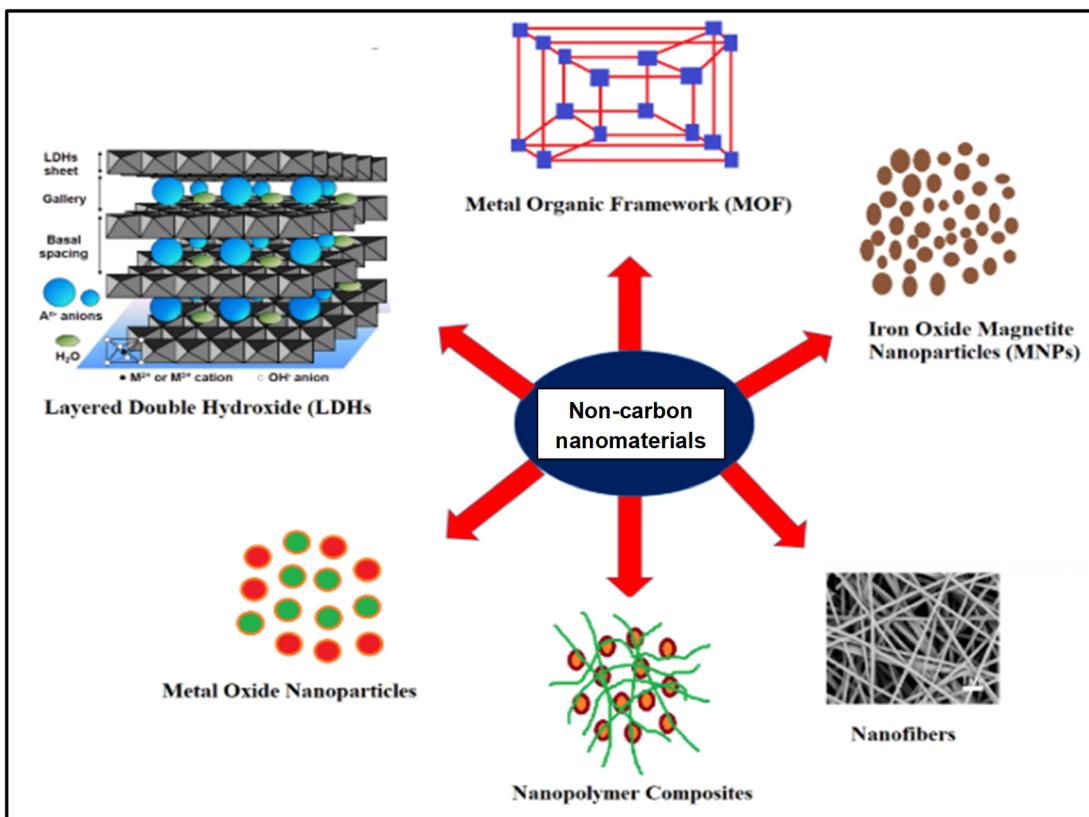


Fig. 17 Different non-carbon nanomaterials, used for the treatment of heavy metal-contaminated water (this figure has been adapted from Baby et al.¹⁴⁷ with permission from MDPI, copyright 2022).

high sensitivity and reactivity, high adsorption capacity, and simplicity of functionalization. As shown in Fig. 16 and 17, nanomaterials are divided into carbon-based nanoparticles and non-carbon nanomaterials.

In a study, a magnetic core nanoparticle coated in metallic nanometric silver and functionalized with L-cysteine was employed to remove monomethyl mercury, dimethyl mercury, ethyl mercury, and Hg(II) from aquatic systems simultaneously.¹⁴⁸ The results showed that at 30.00 s of agitation time, 400.00 μ L of nanoparticles were sufficient to achieve 100.00% sorption performance for all Hg species in the aqueous media at a solution pH of 6.20 and under room temperature. The sorption data obtained for all the Hg species at equilibrium was well explained by the Langmuir isotherm model. The efficacy of this adsorbent in treating wastewater is suggested by its capacity to simultaneously adsorb all species of mercury present in water and achieve full adsorption in just a few seconds.

Magnetic nanoparticles were employed as an adsorbent in removing Cd(II) and Cu(II) concurrently from water systems.¹⁴⁹ The study found that the maximum elimination of Cu(II) and Cd(II) ions was accomplished at a pH of 7.00 and 60.00 min shaking time. The sorption kinetic data of Cu(II) and Cd(II) was well fitted to the pseudo-second-order model while the isothermal data best fitted the Langmuir isotherm with optimum uptake efficiencies of 73.50 and 79.40 mg g^{-1} for Cd(II) and Cu(II), correspondingly. This study indicated that the

adsorbent is efficient and reliable to eliminate Cd(II) and Cu(II) from contaminated aquatic systems.

Also, individual and binary sequestration of Ni(II) and Pb(II) from wastewater using polyether sulfone (PES)/chitosan (CS)/ $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-SH}$ nanofiber was investigated by Jafarnejad *et al.*¹⁵⁰ using RSM. The RSM was employed to determine the impact of the pH of the solution, $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-SH}$, and adsorbent loads on the adsorptive elimination of Ni(II) and Pb(II) ions from wastewater. The optimum predicted uptake capacity of 91.15 and 52.27 mg g^{-1} was obtained for Ni(II) and Pb(II), respectively, using the following optimum operating settings: pH = 5.50, adsorbent dosage = 1.00 g L^{-1} , and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{-SH}$ content = 10.00 wt%. In the binary system, the uptake capacity of these heavy metals declined with the upsurge of multi-metal ion concentration and selectivity followed the order: Pb(II) > Cu(II) > Ni(II) > Co(II) > Zn(II). The kinetic sorption data of Ni(II) and Pb(II) showed good fitness to the double-exponential model. While the isothermal data agreed well with the Langmuir model with optimum uptake efficiencies of 95.30 and 282.40 mg g^{-1} for Ni(II) and Pb(II) ions, correspondingly. The regeneration capability of the nanofiber adsorbent revealed that the uptake capacity reduced slightly after the fourth adsorption–desorption cycle indicating the suitability of the adsorbent.

Besides, zero-valent iron nanoparticle was employed to remove Cd(II), Cu(II), and Pb(II) simultaneously from water systems.¹⁵¹ The study showed that the competitive

decontamination of the Cd(II), Cu(II), and Pb(II) ions was affected by reaction time, pH, concentration as well as the coexistence of other competing ions in the solution. It was revealed that Cu(II) ions were removed faster than Cd(II) and Pb(II) during the first 5.00 min until at about 120.00 min, 95.00–99.00% maximum removal of the studied heavy metals was accomplished. The kinetic and isothermal data of Pb(II), Cu(II), and Cd(II) obtained by the adsorbent from the aqueous systems was best represented using the pseudo-second-order and Langmuir models.

Additionally, magnetically modified mesoporous nanoparticles were utilized for decontaminating Cd(II), Cu(II), and Pb(II) simultaneously from wastewater.¹⁵² Through the application of the CCD, it was found that 90.00–105.00% and 90.30–107.00% optimum detoxification of Cd(II), Cu(II), and Pb(II) from real and synthetic wastewaters, respectively was attained by the adsorbent within 10.00 min. The isothermal data correlated well to the Langmuir model with maximum uptake capacities of 238.09, 208.33, and 178.57 mg g⁻¹ for Cd(II), Cu(II), and Pb(II), correspondingly.

Multicomponent adsorptive reduction of Cu(II), Co(II), and Ni(II) by nanostructured layered sodium vanado-silicate (Na-V-Si) adsorbent was carried out in a ternary system.¹⁵³ The study found that the simultaneous decontamination of Cu(II), Ni(II), and Co(II) was attained within 5.00 min and at a mono-solute concentration of 10.00 mg L⁻¹. The study revealed the sorption capacity and adsorbent affinity were observed to be in the sequence of Cu(II) > Co(II) > Ni(II). More so, the Cu(II) ions had an antagonistic effect on the decontamination of Ni(II) and Co(II) ions in the ternary system. The sorption kinetic data was best

explained by pseudo-second-order and pseudo-first-order models. The optimum sorption capacity of the nanostructured layered Na-V-Si was found to be 154.00, 70.70, and 55.40 mg g⁻¹ for Cu(II), Co(II), and Ni(II), correspondingly in the single component systems. The design, operation, and optimization of a practical sorption system for the sequestration of multiple heavy metals from water systems could benefit from the in-depth insights provided by this study.

The concurrent depollution of Cd(II), Pb(II), Cu(II), and Ni(II) from river water has been investigated by Fato *et al.*¹⁵⁴ using ultrafine mesoporous magnetite (Fe₃O₄) nanoparticles (UFMNP). The study found that the single elimination of Pb(II), Ni(II), Cu(II), and Cd(II) from the river water by the adsorbent was effective with a maximum removal rate of 98.00, 78.00, 90.00, and 87.00%, respectively. For the multicomponent system, the optimum percentage decontamination of Pb(II), Ni(II), Cu(II), and Cd(II) from the river was found to be 86.00, 54.00, 84.00, and 80.00%, respectively. The study showed that the decontamination efficiency of Pb(II), Ni(II), Cu(II), and Cd(II) from the multi-ion systems was much lower than in the single component system. This study had shown that UFMNP have a great ability in treating wastewater, particularly for such competitive elimination of several pollutants from aqueous systems.

4.7 Composite-based adsorbents

When it comes to water and wastewater treatment facilities, composites are an excellent option because they require less maintenance and upkeep. Synthetic adsorbents for the removal of hazardous metals from aquatic environments are efficient

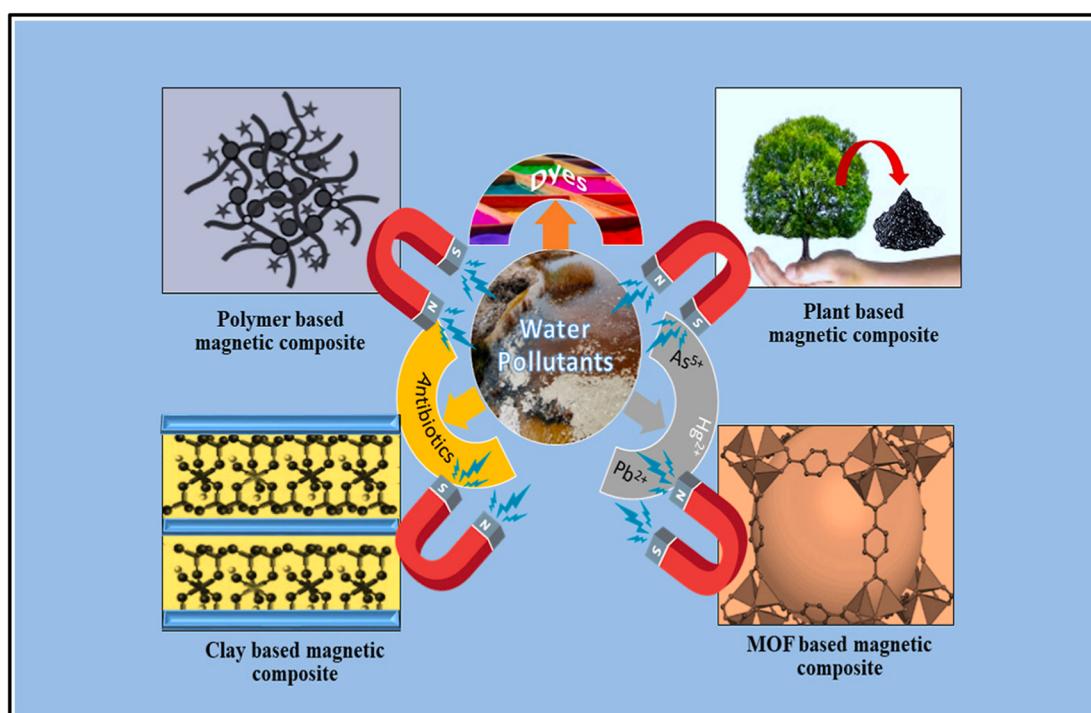


Fig. 18 A schematic diagram showing different types of composite for the treatment of various water contaminants (this figure has been adapted from Sharma *et al.*¹⁵⁵ with permission from Elsevier, copyright 2022).



due to the flexibility with which these sorbent materials can be tuned into any form of composite with desirable surface functional groups. Fig. 18 represents the schematic diagram of different types of composite materials that could be applied in the treatment of various water contaminants including heavy metals, dyes, and pharmaceuticals.

A bio-composite adsorbent synthesized from magnetic pine cone gel beads (MPCB) was employed for the individual and simultaneous decontamination of Cu(II) and Cr(VI) from binary sorption media.⁴⁹ The uptake of Cr(VI) and Cu(II) onto MPCB showed dependence on solution pH, initial Cu(II) and Cr(VI) concentration, and reaction time. The optimum uptake capacity of Cu(II) and Cr(VI) ions attained by the magnetic bio-composite was 69.77 and 132.52 mg g⁻¹, respectively. The sorption data of Cr(VI) and Cu(II) best correlated to the Langmuir pseudo-second-order models with Langmuir maximum sorption capacity of 68.64 and 212.22 mg g⁻¹ for Cu(II) and Cr(VI), respectively. For the binary components system, it was found that both antagonistic and synergistic effects existed. The Cu(II) ions exhibited an antagonism effect on Cr(VI) ions removal while the presence of Cr(VI) ions promoted Cu(II) ions decontamination from the binary solutions, pointing to a synergistic effect. The competitive equilibrium sorption data were best explained by the modified competitive Langmuir model. The study discovered that the MPCB is a promising bio-adsorbent and could be employed in the adsorptive elimination of heavy metals from aquatic environments.

The simultaneous and competitive interactive effect between As(V) and As(III) from aqueous media onto chitosan/diatomaceous earth composite (CSD) was also carried out.¹⁵⁶ At 60.00 min equilibrium, reaction time, and 0.50 g dosage, maximal uptake capacities of 106.00 and 88.00 mg g⁻¹ were achieved by the adsorbent at pH of 6.00 and 2.00 for As(V) and As(III), correspondingly. The sorption data obtained for As(V) and As(III) at equilibrium was found to be well-fitted to the Langmuir and pseudo-second-order models. The Langmuir optimum uptake rate attained by the adsorbent for As(V) and As(III) was 87.81 mg g⁻¹ and 44.07 mg g⁻¹ at a pH of 6.00, respectively. The study indicated that the synthesized adsorbent demonstrated considerable prospects for usage in the decontamination of arsenic species from aqueous media.

Besides, in a study, ZSM-5 zeolite supporting sulfide nanoscale zero-valent iron (S-nZVI@ZSM-5) composite adsorbent was produced to decontaminate Cr(VI) and As(V) in single and binary systems.¹⁵⁷ The adsorbent was found to demonstrate higher uptake capacity for Cr(VI) and As(V) in the single system, and the optimum sorption capacity of Cr(VI) and As(V) was found to be 52.16 and 161.66 mg g⁻¹ at a reaction time of 14.00 and 18.00 h, respectively. In the binary solute medium, the optimum sorption rates of As(V) and Cr(VI) achieved by the adsorbent were lowered by 13.01 and 63.08%, respectively, due to the competitive sorption process, demonstrating that S-nZVI@ZSM-5 exhibited a stronger chemical affinity towards As(V) ions than of Cr(VI). The equilibrium sorption data of As(V) and Cr(VI) attained from both single and binary systems best fitted the pseudo-second-order and Langmuir models.

Also, a jacobsite–biochar nanocomposite (MnFe₂O₄–BC) was synthesized and applied to eliminate Sb(III) and Cd(II) concurrently from wastewater.¹⁵⁸ It was observed that optimum Sb(III) elimination efficiency was greater from the bi-solute medium in comparison to the mono-solute medium. This showed that the presence of Cd(II) promoted Sb(III) ions removal from the binary component systems. The equilibrium data of Sb(III) and Cd(II) attained from the binary solute was best correlated to the Langmuir model with optimum sorption capacities of 237.53 and 181.49 mg g⁻¹, correspondingly. It was established that the produced MnFe₂O₄–BC nanocomposite could serve as a promising adsorbent for the competitive elimination of Sb(III) and Cd(II) from aqueous phases.

More so, a bentonite–alginate composite (BAC) was employed in eliminating Hg(II) and Pb(II) from both mono- and bicomponents sorption media.¹⁵⁹ The study revealed that the adsorbent was more effective for the uptake of Pb(II) ions than Hg(II) ions in the single component system. However, the sorption capacity of these heavy metals decreases in the binary component system suggesting inhibitory effects between the Pb(II) and Hg(II). The equilibrium data of Hg(II) and Pb(II) achieved by the adsorbent in the single metal and binary metal systems best fitted the Hill and competitive Hill isotherm models, respectively.

Likewise, the competitive removal of Cu(II), Zn(II), and Pb(II) by polypyrrole/TiO₂ composite was conducted in batch technique.¹⁶⁰ The study found that Zn(II) had a greater affinity towards the surface of the adsorbent with a sorption capacity of 77.81 mg g⁻¹. While Cu(II) uptake rate by the adsorbent was highly inhibited by the occurrence of the other competing ions [Zn(II) and Cu(II)] in the aqueous medium. The adsorptive decontamination of the heavy metals was in a pattern of Zn(II) > Pb(II) > Cu(II) in the multi-metal systems. The selectivity of the Zn(II) ions towards the adsorbent over that of Cu(II) and Pb(II) was not known. This study offered some helpful suggestions for developing adsorbents that are selective for particular heavy metals coexisting in wastewater.

The depollution of Cu(II), Pb(II), and Zn(II) from mono- and ternary solute systems using hydroxyapatite–biochar nanocomposite was investigated.¹⁶¹ The kinetic data of Pb(II), Zn(II), and Cu(II) attained by the adsorbent showed good fitness to the pseudo-second-order model. In both mono- and ternary solutes media, the sorption data of Pb(II) attained by the adsorbent obeyed the Langmuir isotherm model whereas the sorption data of Cu(II) and Zn(II) achieved at equilibrium conformed to the Freundlich isotherm model. The study revealed that the adsorbent can be utilized in wastewater purification, especially those polluted with heavy metals.

The detoxification of Cd(II) and Pb(II) from monocomponent and bicomponent media using chitosan functionalized EDTA-silane/MgO as an adsorbent in batch technique was studied.¹⁶² The study found that a solution pH of 5.00 and dosage of 0.30 g L⁻¹ were the maximum operating conditions for Pb(II) and Cd(II) removal from the monocomponent medium. At these optimum conditions in the single component system, the optimum uptake rates of Cd(II) and Pb(II) attained by the adsorbent were 1.05 and 2.33 mmol g⁻¹,



correspondingly. The results of the binary component system indicated that Cd(II) ions possess synergistic effects on the decontamination of Pb(II) in the competitive system. While the presence uptake by the adsorbent was observed to have an antagonistic effect at Pb(II) high initial concentration. The Pb(II) on Cd(II) experimental data showed good fitness to the pseudo-first-order model. The thermodynamic studies revealed that the decontamination of Pb(II) and Cd(II) was endothermic and spontaneous in nature.

Similarly, the competitive decontamination of Cd(II), Pb(II), Cu(II), and Ni(II) from aquatic systems was studied in the batch system using a nanosized zirconia composite.¹⁶³ The batch experiments indicated that agitation time, pH, concentration, and coexisting ions affected the concurrent elimination of Pb(II), Ni(II), Cu(II), and Cd(II). It was found that the competitive decontamination of the heavy metals was in the sequence of Pb(II) > Cu(II) > Ni(II) > Cd(II). The sorption data of Pb(II), Cd(II), Cu(II), and Ni(II) showed good fitness to the pseudo-second-order and Langmuir models, respectively. The Langmuir optimum uptake capacities of Ni(II), Cd(II), Cu(II), and Pb(II) by the adsorbent were found to be 0.700, 0.701, 0.615, and 0.620 mmol g⁻¹, correspondingly. The study revealed that the adsorbent is proficient in the uptake of heavy metals from wastewater.

4.8 Graphene-based adsorbents

Due to their exceptional electrical and thermal mobility, huge surface area, high mechanical strength, outstanding corrosion resistance, and configurable surface chemistry, graphene-based materials have recently attracted a lot of interest in the field of water and wastewater treatment. The renewability of the spent adsorbents and adsorbates recovery even after many life cycles is one of the key advantages of graphene-based adsorbents.

Fig. 19 shows the synthesis process of graphene-based adsorbent for the decontamination of adsorbate molecules.

Divalent cadmium [Cd(II)] and divalent lead [Pb(II)] ions in mono- and binary solutes aqueous media were decontaminated using nickel oxide-decorated reduced graphene oxide.²⁹ The results of the single metal sorption showed that Cd(II) and Pb(II) had sorption rates of about 725.00 and 890.00 mg g⁻¹, respectively. Additionally, the simultaneous sequestration of Cd(II) and Pb(II) from the binary metal systems triggered a rise in Pb(II) uptake rate and decreased the removal capacity of Cd(II). The maximum uptake efficiencies of Pb(II) and Cd(II) attained were 1000.00 and 580.00 mg g⁻¹, correspondingly. This suggested that the elimination of Cd(II) and Pb(II) were influenced by synergistic and antagonistic effects, respectively. The experimental data attained from both single- and binary-metal systems fitted the pseudo-second-order and Langmuir models.

A novel graphene-like biochar (GB)-supported nanoscale zero-valent iron (nZVI) and the underlying mechanisms of synergistic effects between GB and nZVI for the concurrent sorption of As(III) and Cd(II) were investigated.¹⁶⁵ It was observed that at pH 4.00 and 7.00, maximum depollution of Cd(II) and As(III) was realized. The study showed that GB has an efficient uptake capacity of 181.50 and 46.40 mg g⁻¹ for As(III) and Cd(II), correspondingly. While nZVI uptake capacity was 363.00 and 92.80 mg g⁻¹ for As(III) and Cd(II), correspondingly. The study indicated a strong synergistic effect between GB and nZVI, which promoted Cd(II) and As(III) ions removal. Therefore, GB and nZVI exhibited high performance and could be employed for the simultaneous depollution of other heavy metal ions from irrigation waters.

To examine the selectivity of Cu(II) ions in mixed multi-metal systems, graphene oxide (GO)-based hybrid membranes (GHMs) were produced.¹⁶⁶ The study showed that the Ni(II), Cu(II), and Co(II), were competitively adsorbed onto GHMs and

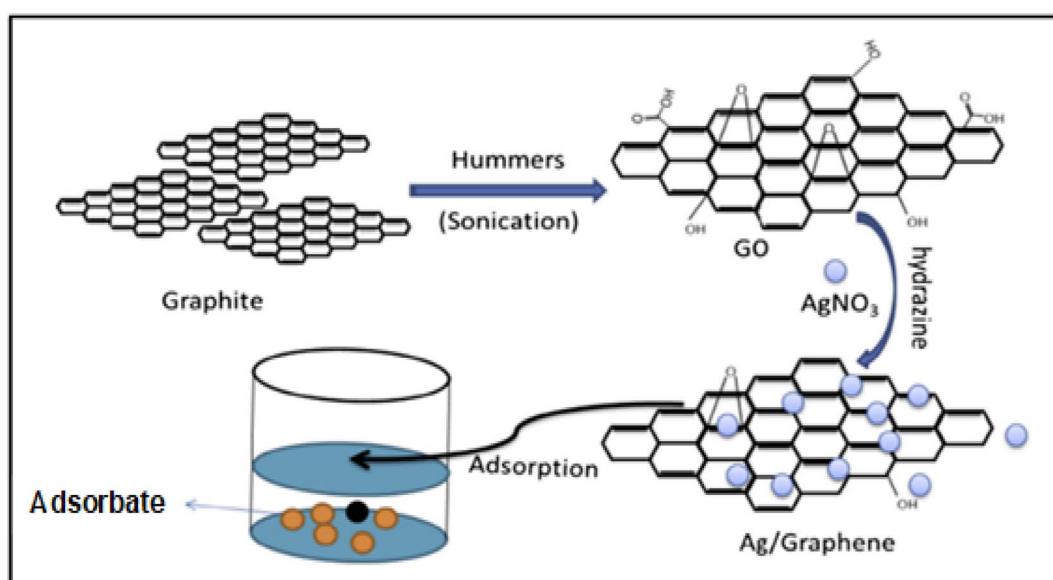


Fig. 19 A schematic diagram showing the synthesis process of graphene-based adsorbent for adsorbate molecules removal (this figure has been adapted from Qu *et al.*¹⁶⁴ with permission from Elsevier, copyright 2017).





Table 3 Decontamination of heavy metal ions from multicomponent adsorption systems with various adsorbents

Adsorbent	Heavy metals	Adsorption system(s)	Interaction effect(s)	Best-fitted adsorption model(s)	Adsorption capacity (mg g ⁻¹)	Reference
Sodium dodecyl sulfate	Cd(II), Pb(II), and Zn(II)	Binary	Synergistic and antagonistic	Competitive Langmuir	Pb(II) = 49.37 Cd(II) = 47.27 Zn(II) = 44.18	168
Modified zeolite	Hg(II) and Pb(II)	Binary	Antagonistic	Pseudo-second-order and Langmuir	Pb(II) = 12.02 Hg(II) = 6.68	169
Iranian scoria	Cd(II) and Cu(II)	Binary	Synergistic	Extended Freundlich and modified Langmuir	Cu(II) = 6.92 Cd(II) = 2.33	170
Modified mesoporous silica	Cd(II) and Ni(II)	Binary	Antagonistic	Pseudo-second-order, Langmuir, and Cd(II) = 156.00	Ni(II) = 139.70	171
Iron dust-zeolite composite	Cd(II) and Ni(II)	Binary	Both synergistic and antagonistic	Pseudo-second-order, Langmuir, and Cd(II) = 78.13	Ni(II) = 76.33	172
Leonardite	Cd(II) and Zn(II)	Binary	Antagonistic	Freundlich	Cd(II) = 23.89	173
Bottom ash	Cd(II) and Zn(II)	Binary	Antagonistic	Extended Freundlich	Zn(II) = 16.86	174
Modified beer lees	Pb(II) and Zn(II)	Binary	Antagonistic	Yoon-Nelson and bed depth service time	Zn(II) = 7.72	175
Termite mound	Pb(II) and Zn(II)	Binary	Antagonistic	Pseudo-second-order and Langmuir	Pb(II) = 6.06 Zn(II) = 5.43	176
Modified chitosan/CoFe ₂ O ₄ particles	Cu(II) and Pb(II)	Binary	Antagonistic	Pseudo-second-order and Langmuir	Zn(II) = 7.62 Pb(II) = 166.26	177
<i>Fumaria indica</i> biomass	Cu(II) and Pb(II)	Binary	Non-interaction and antagonistic	Freundlich	Cu(II) = 139.86 Pb(II) = 9.91	178
Straw/bentonite-g-poly(acrylic acid-co-acrylamide) resin	Cd(II) and Pb(II)	Binary	Synergism and antagonistic	Pseudo-second-order and Langmuir	Cu(II) = 4.08 Pb(II) = 355.50	179
Industrial chili seeds (<i>Capsicum annuum</i>) waste	Cd(II) and Pb(II)	Binary	Antagonistic	Modified Langmuir	Cd(II) = 315.10 Pb(II) = 8.78	180
Iranian hematite	Cd(II) and Pb(II)	Binary	Antagonistic	Langmuir, extended Freundlich, and Pb(II) = 17.86	Cd(II) = 7.32 Pb(II) = 17.86	181
<i>Salix matsudana</i> activated carbon	Cd(II) and Pb(II)	Binary	Antagonistic	extended Langmuir	Cd(II) = 1.89 Pb(II) = 31.09	182
Straw-derived biochar	Cd(II) and Co(II)	Binary	Antagonistic	Pseudo-second-order and Langmuir	Cd(II) = 25.32 Co(II) = 193.00	183
Sugarcane cellulose	Cu(II), Pb(II), and Zn(II)	Binary	Synergistic	Competitive Langmuir	Zn(II) = 934.60 Pb(II) = 621.10	184
Modified green tea waste	As(III) and Ni(II)	Binary	Antagonistic	Extended Langmuir and extended Freundlich	Cu(II) = 462.90 As(III) = 0.42 Ni(II) = 0.31	185
Ferrhydrite	As(III) and As(V)	Binary	Antagonistic	Freundlich	As(V) = 14.50	186
Modified <i>Luffa acutangula</i> peels	Cu(II) and Ni(II)	Binary	Antagonistic	Pseudo-second order, Langmuir and Cu(II) = 22.06	As(III) = 10.51 Ni(II) = 22.72	187
Polyamide	Cd(II), Ni(II), and Zn(II)	Binary and ternary	Antagonistic	Pseudo-second-order and Langmuir	Binary = 339.90-399.20	188
					Ternary = 275.60-314.30	

Table 3 (Contd.)

Adsorbent	Heavy metals	Adsorption system(s)	Interaction effect(s)	Best-fitted adsorption model(s)		Adsorption capacity (mg g ⁻¹)	Reference
				Langmuir	Pseudo-second-order and Langmuir		
Sunflower plant biomass-based carbons	Cd(II), Cr(VI) and Ni(II)	Binary and ternary	Antagonistic	Langmuir	Cu(II) = 0.12–0.05	189	
Carbonaceous nanofibers	Cu(II), Ni(II) and Pb(II)	Binary and ternary	Antagonistic	Langmuir	Ternary = 0.08–0.03		
Granular Fe–Mn binary oxide	Cd(II), Cu(II), and Zn(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Zn(II) = 88.62–665.11	190	
C-phenylcalix[4]pyrogallolarene material	Cr(III), Cu(II), Ni(II), and Pb(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Cd(II) = 0.055	470.34	
Dithizone (DZ) and mesoporous Bifunctional graft copolymer	Cd(II), Cu(II), and Hg(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Ni(II) = 60.97	50	
Modified graphene oxide	Co(II), Ni(II), and Zn(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Pb(II) = 16.36	191	
Endoskeleton biomass	As(III), Cd(II), and Hg(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Cr(II) = 14.31	192	
Chitosan-pyromellitic dianhydride modified biochar	Cd(II), Cu(II), and Pb(II)	Ternary	Non-interaction	Pseudo-second-order and Langmuir	Cu(II) = 8.14	193	
Olive stones activated carbon	Cd(II), Cu(II), and Ni(II)	Ternary	Antagonistic	Pseudo-second-order and Langmuir	Cd(II) = 30.30	194	
Arborvitae leaves	Co(II), Cu(II), and Pb(II)	Ternary	Both synergistic and antagonistic	Pseudo-second-order, Langmuir, and Sips	Hg(II) = 25.04	195	
Date stones activated carbon	Cu(II), Ni(II), and Zn(II)	Ternary	Antagonistic	Langmuir	Zn(II) = 68.00	196	
Chicken bone biochar	Cd(II), Cu(II), and Zn(II)	Ternary	Antagonistic	Langmuir	Cd(II) = 122.00	197	
BiPO ₄ /FePO ₄ /CSG nano-adsorbent	Cd(II), Cu(II) Ni(II), and Pb(II)	Quaternary	Antagonistic	Pseudo-second-order, intraparticle diffusion and Langmuir	Cu(II) = 285.71	201	



Table 3 (Contd.)

Adsorbent	Heavy metals	Adsorption system(s)	Interaction effect(s)	Best-fitted adsorption model(s)	Adsorption capacity (mg g ⁻¹)	Reference
Iron oxide-coated gravel	Al(II), Cd(II), Cu(II), Fe(II), and Pb(II)	Quinary	Antagonistic	Pseudo-second-order and Freundlich	Pb(II) = 99.72 Cu(II) = 99.61 Cd(II) = 99.51 Fe(II) = 99.30 Al(II) = 93.30	202
Coal fly ash	Cd(II), Cu(II), Ni(II), Mn(II), and Pb(II)	Quinary	Antagonistic	Pseudo-first-order, pseudo-second-order and Langmuir	Pb(II) = 45.30 Cu(II) = 32.86 Cd(II) = 26.93 Ni(II) = 16.25	203
Sesame straw biochar	Cd(II), Cr(III), Cu(II), Pb(II), and Zn(II)	Quinary	Antagonistic	Freundlich and Langmuir	Mn(II) = 14.63 Pb(II) = 83.00 Cu(II) = 40.00 Cr(III) = 21.00 Zn(II) = 7.00 Cd(II) = 5.00	204

the competitive elimination of Cu(II) in mixed multi-metal solutions demonstrated that Cu(II) ions uptake by the GHMs was higher. According to the sorption data, the adsorptive elimination of Ni(II), Cu(II), and Co(II) was well-described by the diffusion-chemisorption and pseudo-second-order models, respectively. Furthermore, according to the Langmuir model, the uptake rates of Cu(II), Co(II), and Ni(II) on the surface of GHMs were 4.338, 3.339, and 3.160 mg g⁻¹, respectively. These findings demonstrated that GHMs may have potential uses in heavy metals separation and recycling.

A glutathione-functionalized NiFe₂O₄/graphene oxide composite is employed in the single and competitive detoxification of Hg(II), Pb(II), and Cu(II) from aqueous systems.¹⁶⁷ The removal rate of these heavy metal ions showed dependence on pH, agitation time, and concentration. In the single system, the optimum pH of 5.00 was attained for Pb(II) and a pH of 6.00 was optimum for both Hg(II) and Cu(II) ions removal with a removal efficiency of 94.00% at an equilibrium time of 90.00 min. The kinetic data were well explained by both pseudo-second-order and Elovich models as well as the Freundlich isotherm. In the bicomponent system, the percentage removal of Cu(II) and Pb(II) decreased in the presence of Hg(II), Mn(II), and Cd(II) by competition. The study indicated that the adsorbent is efficient in the decontamination various of heavy metals from groundwater samples.

The summaries of other studies on the decontamination of heavy metals from multi-metal sorption systems (binary, ternary, quaternary, and quinary solutions) using various adsorbents are presented in Table 3.

5. Conclusion and future perspectives

The present study systematically and particularly reviews the multicomponent adsorption of heavy metals from various multicomponent systems such as binary, ternary, quaternary, and quinary solutions using different kinds of adsorbents. This is necessary because the adsorption of a specific heavy metal in complex wastewater may be affected by the other components and the adsorbent properties including surface charge, structure, size, functional groups, porosity, and active sites present on the adsorbent surface. Therefore, it is imperative to review the adsorption of different heavy metals from multicomponent systems using different kinds of adsorbents to elucidate the interactive behaviors among co-existing pollutants by using multicomponent adsorption isotherm models.

The systematic review revealed that adsorbents derived from naturally and locally available materials including biomasses, agricultural, and industrial wastes are more promising and efficient in the decontamination of heavy metals from multicomponent systems. It was also discovered that numerous studies evaluate the adsorption characteristics of an adsorbent in a multicomponent system using various important independent adsorption parameters. These independent adsorption parameters include reaction time, solution pH, agitation speed, adsorbent dosage, initial metal ion concentration, ionic

strength as well as reaction temperature, which were found to significantly affect the multicomponent adsorption process. Furthermore, through the utilization of the multicomponent sorption isotherm models, the competitive adsorption mechanisms of the heavy metals were found to be characterized by three primary kinds of interactive effects including synergism, antagonism, and non-interaction. Generally, the review conducted on the different kinds of adsorbents indicates that the competitive effects for heavy metal ions become more recognized with the increase in the number of solutes in the aqueous systems where the sorption of one metal ion usually interferes with that of another.

Despite the enormous amount of research and extensive data on the capability of different adsorbents, several significant drawbacks hinder adsorbents from being used practically and economically to remove heavy metal ions from multicomponent systems. As a result, the current systematic review provides the following insights and perspectives for further studies through the thorough and reliable analysis of the relevant literature on heavy metals removal from multicomponent systems.

(1) Due to the non-biodegradable nature of heavy metal ions, they can cause both indirect and direct health-related problems to humans and other lifeforms when released into water resources. Several adsorbents are being used nowadays to remove harmful metal ions from drinking water, wastewater, and groundwater to preserve water systems due to their efficiency. Future studies are therefore recommended to develop non-toxic, secure, high-performing green adsorbents using environmentally friendly processes.

(2) The application of biochar for the adsorptive decontamination of heavy metals from multicomponent systems has been recognized to be very proficient. However, further investigations are required on various types of biochar derived from locally and naturally available materials as well as different synthesis conditions to actually know and select a reliable biochar that could effectively eliminate several heavy metal ions concurrently from the complex wastewater.

(3) In addition, it is important to first assess the effectiveness of adsorbents in a multicomponent adsorption system before deploying them for industrial use. Therefore, choosing the appropriate sorbent material for the type of adsorbate in the aqueous solution is crucial from the perspective of practical applications. Hence, future studies should not only focus on the presence of the adsorbates in the multi-solute system but also their baseline concentration, pH, and other vital independent adsorption factors.

(4) During the field and laboratory studies, several other variables, like cost and time that are significant in industrial and commercial applications are sometimes overlooked. The expenditures should include the cost of producing the adsorbent and byproduct disposal in addition to the cost of the raw materials. According to this systematic review, surface modifications of the adsorbents improved their adsorption capacity but increased the cost of the adsorption process.

(5) There has been limited research on the renewability and reuse of exhausted adsorbent after the adsorption process, and this approach is not financially feasible. However, due to their

capacity to both adsorb and desorb heavy metals from aqueous systems, adsorbents can be regarded as dual-functional materials. Particularly in real-scale applications, the regeneration and reusability of adsorbents heavily influence their economic worth and efficiency. Unfortunately, while adsorption is the subject of in-depth analyses in the literature, very few studies address the regeneration of spent adsorbents. Hence, in future studies, attention should be focused on the regeneration of the exhausted adsorbents as well as the recovery of precious metal ions from the sorbent surface after the sorption process to understand the worth of low-cost adsorbents. After the adsorption process, the exhausted adsorbents must be removed from the medium, renewed, reused, and subsequently disposed of appropriately. Therefore, in addition to desorption studies, regeneration capability is crucial when choosing a promising adsorbent for the adsorptive decontamination of heavy metals from single and multicomponent systems.

(6) Future research ought to focus on reducing the antagonistic effects of one heavy metal over other heavy metal ions in multicomponent systems. Additionally, research should be conducted to determine whether there are any synergistic effects of water contaminants in the multicomponent systems using various competitive adsorption isotherm models.

(7) More so, there is limited research on the optimization of competitive sorption process and concurrent removal of more than one heavy metal ion in the coexistence of other cations or anions in multi-solute systems. Therefore, more attention should focus on the optimization of heavy metals removal from multicomponent systems using the design of experiments and statistical packages including Design Expert of Stat-Ease. It is essential to identify optimum operating conditions for the efficient sequestration of heavy metals from multi-solute systems and determine the types of interactive effects among the heavy metals.

Author contributions

Jonas Bayuo: conceptualization, investigation and writing – original draft. Mwemezi Rwiza: reviewing, editing, and supervision. Mika Sillanpää: reviewing and editing. Kelvin Mark Mtei: reviewing, editing and supervision.

Conflicts of interest

The authors declare no conflict of interest.

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