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# Smart adsorbent frameworks enabling high-efficiency pharmaceutical degradation via adsorption

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Pharmaceutical residues are increasingly detected in aquatic systems and present ecological and human health concerns due to their biological activity, structural complexity, and limited biodegradability. Poor removal *via* conventional wastewater treatment processes drives the development of smart adsorbents that offer tailored chemistry and stimuli-responsive behavior to selectively capture and degrade pharmaceuticals. This review summarizes recent advances in functionalized carbons, stimuli-responsive polymers, metal–organic frameworks, magnetic composites, and hybrid nanozymes that interact with pharmaceuticals through  $\pi$ – $\pi$  stacking, electrostatic attraction, hydrogen bonding, and metal–ligand coordination. Special attention is paid to how surface functionalities, pore architectures, and pH-dependent speciation govern adsorption kinetics, isotherms, and selectivity. Coupling adsorption with catalytic degradation processes is highlighted as a synergistic strategy that can enable *in situ* transformation of adsorbed pharmaceuticals into less toxic products, overcoming drawbacks associated with adsorption-only systems, such as Fenton, photo-Fenton, or peroxymonosulphate activation. Key structure–property relationships, performance descriptors, and recyclability considerations are discussed in establishing a unified smart adsorbent design framework. Finally, critical knowledge gaps and future opportunities are identified, including scalable synthesis, selectivity tuning, regeneration, and integration into continuous treatment systems. This review offers guidelines for the rational development of next-generation smart adsorbents for efficient and sustainable removal of pharmaceutical pollutants.

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## Introduction

Pharmaceutical effluents (PEs) are wastewaters generated at different stages of pharmaceutical production, including the processes encompassing active pharmaceutical ingredient (API) synthesis, drug product formulation, and antibiotic production. Pharmaceutical effluents are categorized based on their origin or production methods. Among these categories are (A) chemical waste, (B) analysis residues and buffers, and (C) laboratory and surface cleaning waste.<sup>1</sup> Fig. 1(a) pharmaceutical pollution pathways.<sup>2</sup> Currently, the observed aqueous concentrations of different pharmaceutical compounds vary from nanograms to micrograms per liter.<sup>3</sup> The presence of heavy metals in drinking water is hazardous to consumers. Metal ions in water can originate from the leaching of ore waste and from anthropogenic resources, which mainly include industrial wastewater

and solid waste deposits. Currently, with the rapid development of industrial areas and the associated increase in heavy metal concentration in water systems, water pollution has substantially increased. Treatment of metal ions such as Pb, Cu, Hg, Cd, Cr, and Zn attracts particular attention because of their higher toxicity even at trace concentrations.<sup>4</sup> Fig. 1(b) hydroxyl radical generation.<sup>5</sup> Once administered, pharmaceuticals and personal care products (PCs) are incompletely metabolized by the body. Both original compounds and metabolites are subsequently released into the aquatic environment.<sup>6</sup> They pose a threat to human health due to their persistence in the ecosystem, bioaccumulation, and biomagnification in the food webs. These also lead to adverse effects on human health, which is why PCs are a major cause for concern globally.<sup>7</sup> Fig. 1(c) sources of pharmaceutical contamination.<sup>8</sup> Consequently, they are now categorized as emerging pollutants.<sup>9</sup> Fig. 1(d) general pathway of degradation. A huge quantity of waste is being produced worldwide, both solid and liquid. It has been estimated that the yearly production of waste will increase from 2.01 to 3.40 billion tonnes worldwide by 2050. However, a very small amount of waste is being recycled. The remaining waste is either disposed of improperly or left untreated, resulting in various forms of pollution, including land, water, and air pollution, as well as

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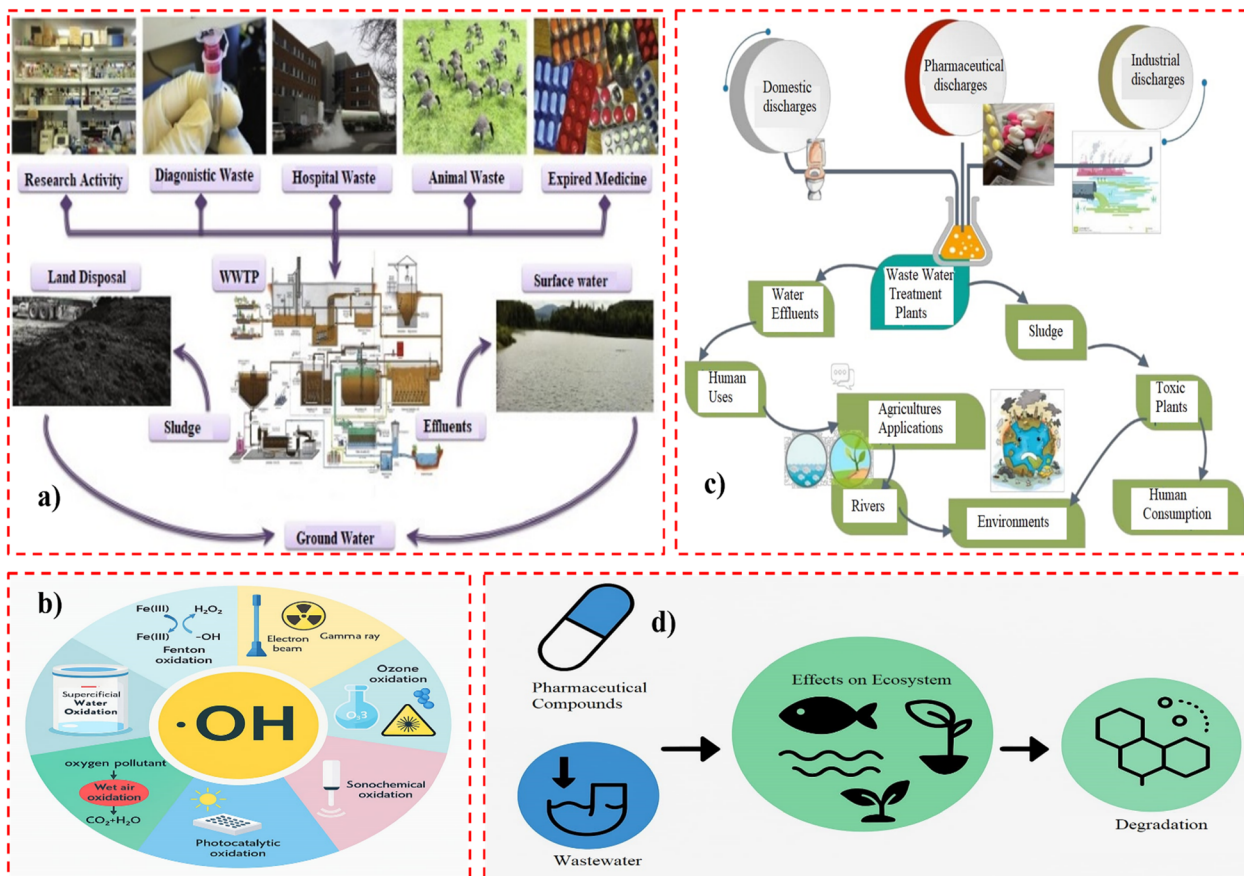



Fig. 1 (a) Pharmaceutical pollution pathways<sup>2</sup> (Adapted with permission from Elsevier (Tiwari, S. B., Ouarda, Drogui, Tyagi and Buelna, *Bioresour. Technol.*, 2017), copyright 2017). (b) Hydroxyl radical generation.<sup>5</sup> (Adapted with permission from Elsevier (Wang and Zhuan, *Sci. Total Environ.*, 2020), copyright 2020). (c) Sources of pharmaceutical contamination<sup>8</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Mansouri, F., C. K., Roche, N., Ksibi, M., removal of pharmaceuticals from water by adsorption and advanced oxidation processes: state of the art and trends, *Applied Sciences*, 2021, 11(14), 6659). (d) General pathway of degradation.

thermal and visual pollution, ultimately causing serious harm to both human health and the environment. Table 1 shows the pharmaceutical categories most often found in water.<sup>10</sup>

The efficiency of removal of pollutants, the low cost of adsorbents, and the possibility of regenerating or recycling the adsorbents are considered crucial. Various types of adsorbents, such as activated carbon, agricultural waste, and natural and synthetic polymers, and their composites, have been used to remove pollutants from water as well as wastewater.<sup>12</sup> Fig. 2(a)

conceptual overview of smart adsorbents in pharmaceutical wastewater treatment. The application of metal-organic framework materials as catalysts for decomposing organic pollutants has provided viable solutions for various environmental issues. Recent developments on the use of metal-organic frameworks for the removal and degradation of organic pollutants are discussed. These are classified according to the various applications that the metal-organic frameworks have been employed in, such as adsorbent materials, immobilized

Table 1 Pharmaceutical categories most frequently found in water, including the compounds discussed, fall into several key therapeutic categories<sup>11</sup> (Adapted with permission from Elsevier (Rivera-Utrilla et al., *Chemosphere*, 2013), copyright 2013)

Drug class	Examples
Anti-inflammatories and analgesics (pain and inflammation relief)	Acetylsalicylic acid (aspirin), diclofenac, ibuprofen, paracetamol
Antiepileptics (seizure control)	Carbamazepine
Antidepressants	Benzodiazepines
$\beta$ -Blockers (cardiovascular agents)	Metoprolol, atenolol, and propranolol
Lipid-lowering drugs (cholesterol management)	Fibrates
Antibiotics (a broad group for bacterial infection treatment)	Macrolides, penicillins, $\beta$ -lactams, quinolones, tetracyclines and sulphonamides
Antiulcer drugs and antihistamines (acid reduction)	Ranitidine and famotidine





Fig. 2 (a) Conceptual overview of smart adsorbents in pharmaceutical wastewater treatment. (b) From pollutant transfer to pollutant destruction: adsorption and catalytic degradation. (c) Smart adsorbent mechanism for pharmaceutical degradation via the adsorption–Fenton process. (d) Smart adsorbent–Fenton degradation flowchart.

enzymes, nanozymes, photocatalysts, and, finally, as components in Fenton and sulphate radical technologies.<sup>13</sup> Fig. 2(b) from pollutant transfer to pollutant destruction: adsorption and catalytic degradation. The smart adsorbent framework for pharmaceutical drug removal operates through a synergistic mechanism combining adsorption and Fenton-like catalytic degradation. Initially, the pharmaceutical molecules are selectively captured by the hydrochar-based smart adsorbent via hydrogen bonding,  $\pi$ - $\pi$  interactions, and electrostatic attractions between the drug functional groups and surface hydroxyl, carboxyl, and carbonyl groups of the adsorbent. This targeted adsorption enriches the pollutants in the vicinity of the bimetallic Fe/Cu active centers, enabling efficient generation of hydroxyl radicals ( $\cdot\text{OH}$ ) through the Fenton-like reaction, where  $\text{Fe}^{2+}/\text{Cu}^+$  reacts with hydrogen peroxide. The adsorbed drugs are subsequently degraded by these radicals into smaller intermediates, eventually leading to complete mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Spectroscopic analyses, such as FTIR and XPS, demonstrate modifications in functional group signals, confirming strong adsorption, while EPR studies detect the presence of  $\cdot\text{OH}$  radicals, evidencing catalytic activity. Complementary density functional theory (DFT) calculations further elucidate the adsorption energies and electron-transfer processes at the Fe/Cu sites, providing a molecular-level understanding of how the smart adsorbent framework enhances pharmaceutical degradation efficiency through the combined adsorption–Fenton process. Fig. 2(c) smart adsorbent

mechanism for pharmaceutical degradation via adsorption–Fenton process. Fig. 2(d) smart adsorbent–Fenton degradation flowchart.

Traditionally, antibiotics are chemical substances designed to suppress or eliminate microbial proliferation. Substances are derived from microbes, and some are semi-synthetic or entirely man-made.<sup>14</sup> The following key aspects should be considered: (1) the presence of antibiotics in various environmental locations, specifically surface water, soil and wastewater; (2) antibiotics exerting toxic effects on non-target lifeforms, affecting both aquatic and terrestrial species; and (3) current treatment methods for degrading and removing antibiotics, such as hydrolysis, oxidation, biodegradation and adsorption.<sup>15</sup> Fig. 3(a) Specific pathway of degradation through adsorption. Anaerobic bioprocessing is emerging as a potential opportunity to combat the issues associated with antibiotics-loaded pharmaceutical wastewater. The treatment of antibiotic wastewater is vital, and the operation of anaerobic treatment systems must be optimized.<sup>16</sup> Fig. 3(b) general mechanism for degraded products. Three structurally different families of antibiotics were screened for their efficiencies of degradation: *Amoxicillin* (beta-lactam), *Ciprofloxacin* (fluoroquinolone), and *Streptomycin* (aminoglycoside).<sup>17</sup> The direct dangers posed to human health by pharmaceutical residues present in untreated wastewater include their contamination of plants through irrigation and fish that are consumed by people.<sup>8</sup> Fig. 3(c) conversion process of degraded techniques. Most pharmaceuticals are only



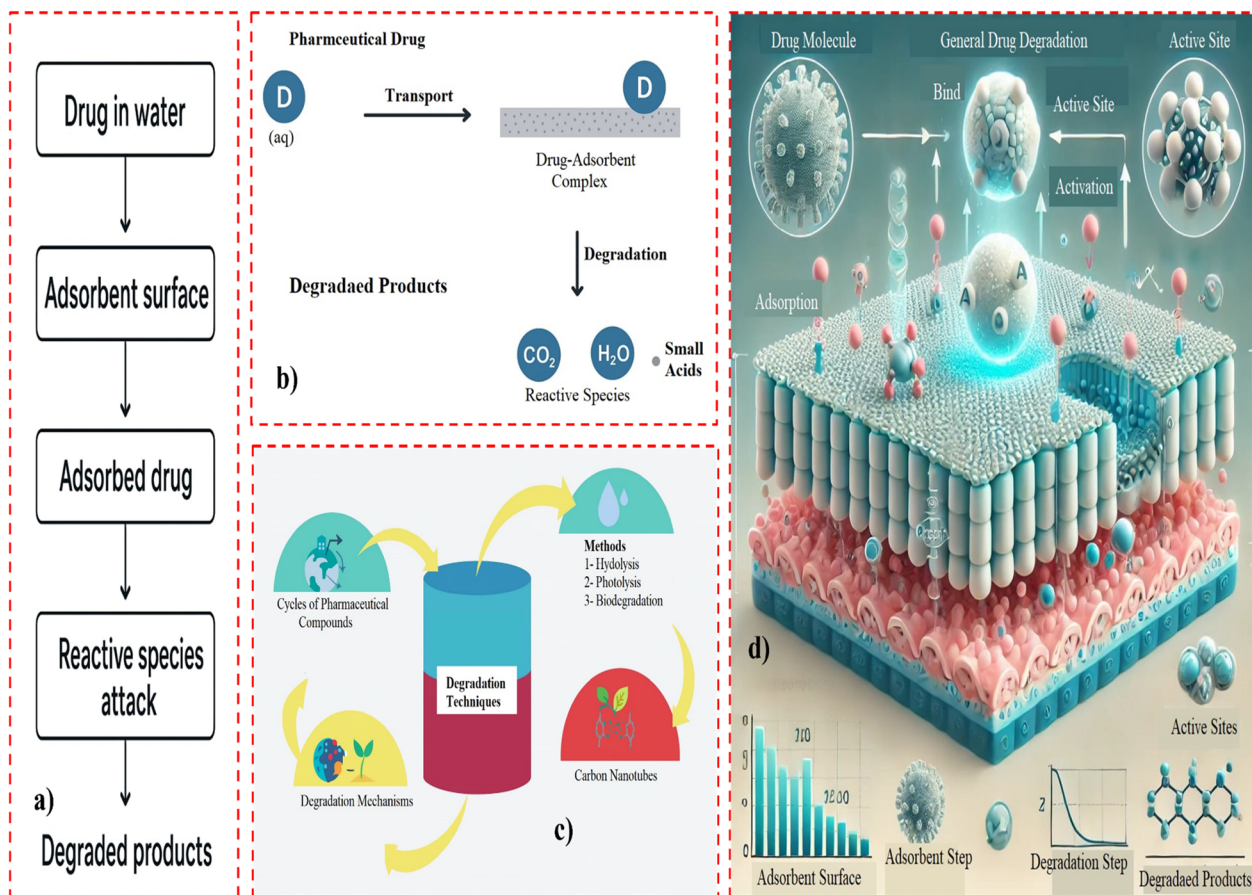


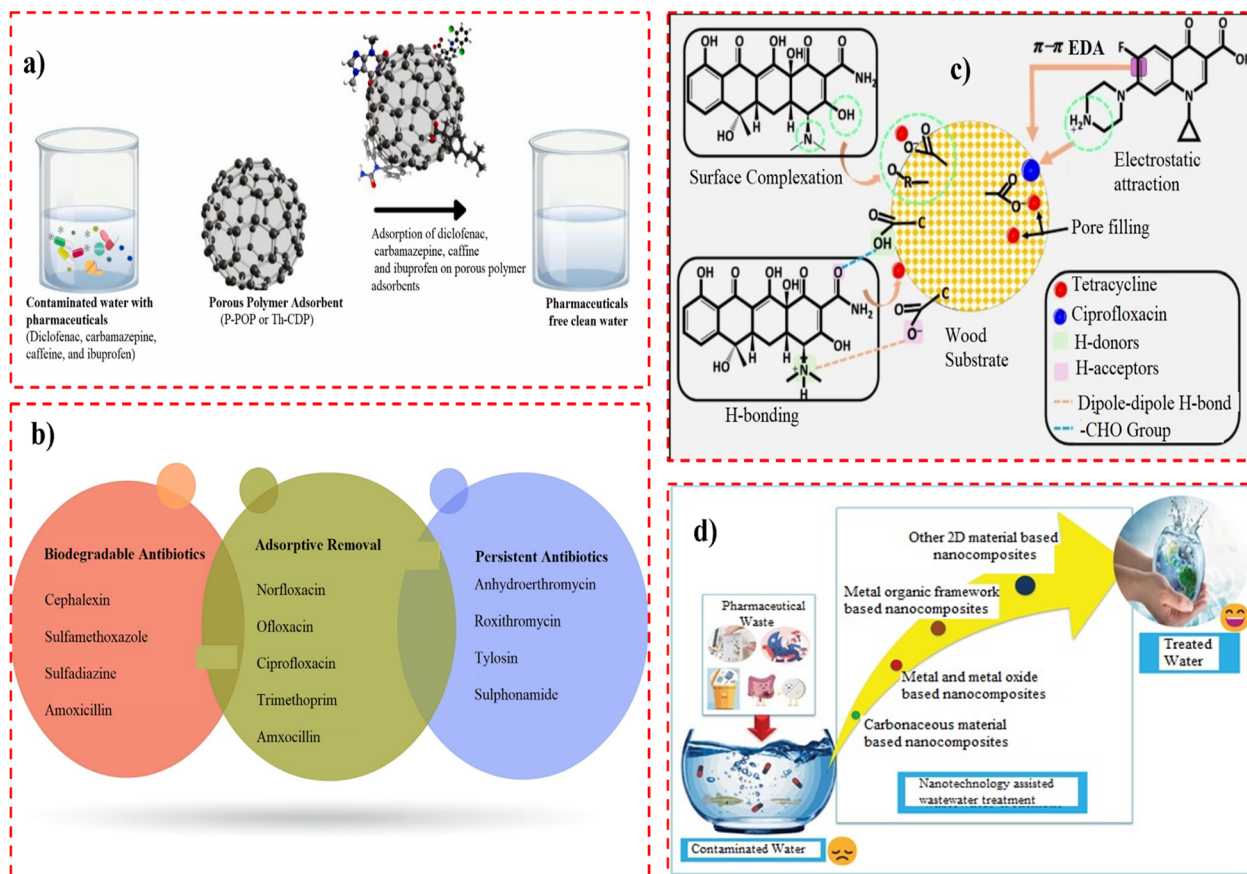
Fig. 3 (a) Specific pathway of degradation through adsorption. (b) General mechanism for degraded products. (c) Conversion processes in degradation techniques. (d) 3-D schematic of drug degradation reactions.

partially removed during standard wastewater treatment. After their entry into the environment, they also do not easily biodegrade.<sup>18</sup> Fig. 3(d). Ozonation, biodegradation, photocatalysis, and the Fenton process are the most explored methods for the elimination of pharmaceuticals from polluted water. Advanced oxidation processes (AOPs) are effective for degrading synthetic pollutants such as pharmaceuticals; however, they can sometimes result in the formation of more harmful intermediate compounds. Besides, AOPs are costly and challenging to operate, particularly when aiming for the complete degradation of persistent compounds. The nature of the selected adsorbent, however, plays a pivotal role in adsorption success.<sup>19</sup> Fig. 4(a) study of the elimination of key pharmaceutical contaminants (carbamazepine, caffeine, ibuprofen and diclofenac) utilizing Th-CDP and the P-POP adsorbents.<sup>20</sup> Fig. 4(b) successful removal techniques for different antibiotics. Advanced treatment technologies include a range of processes such as membrane-based filtration, granular activated carbon systems, biologically active porous media filters, ozonation, and advanced oxidation processes (AOPs), as summarized in Table 2 ref. 21.

In 1903, Tswett's discovery of adsorption chromatography was developed as a novel analytical technique following the realization that adsorption processes exhibit selectivity. Tswett

advocated for its use in separating various mixtures.<sup>30</sup> Adsorption is a process in which pollutants, called adsorbates, transfer from a fluid (liquid or gas) and then interact or react on a solid surface, known as an adsorbent.<sup>31</sup> Fig. 4(c) promising innovations set to transform adsorption technology.<sup>32</sup> Adsorption is a well-established surface-based water-treatment technique, the effectiveness of which is determined by the available active sites, pore structure, surface area and various complex interactions.<sup>33</sup> Fig. 4(d) graphical representation showing water contamination and its treatment by nanotechnology assisted approach to obtain treated water.<sup>23</sup> Among water-treatment processes, adsorption presents the simplest design, with a small initial capital outlay for cost and space. Advantages include effectiveness at low adsorbate concentrations, low capital investment, the ability to reuse and regenerate adsorbents, and adaptability to both batch and continuous processes. Adsorption is an energy-saving technique that can achieve up to 90% removal under mild operating conditions. Photocatalysis generates acidic conditions, around pH 3.0, requiring a neutralizing stage after treatment, with considerable sludge production.<sup>34</sup> Fig. 5(a) this figure presents a schematic of pharmaceutical entry routes into surface water and the compositional distribution of these drugs found in U.S. surface water.<sup>35</sup> Regarding the removal of antibiotics from aquatic systems,





**Fig. 4** (a) Removal of pharmaceuticals (caffeine, diclofenac, carbamazepine, and ibuprofen) with the help of the P-POP and Th-CDP adsorbent<sup>20</sup> (Adapted with permission from Elsevier (Song *et al.*, *J. Hazard. Mater.*, 2024), copyright 2023). (b) Successful removal techniques for different antibiotics. Advanced treatment technologies include a range of processes such as membrane-based filtration, granular activated carbon systems, biologically active porous media filters, ozonation, and advanced oxidation processes (AOPs), as summarized in Table 2.<sup>21</sup> (Adapted with permission from Elsevier (Jumah *et al.*, *J. Environ. Chem. Eng.*, 2024), copyright 2022). (c) Key pharmaceutical adsorption mechanism using wood-based adsorbents<sup>22</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Godiya, C. B., Leiviskä, T., wood-derived adsorbents for the removal of pharmaceutical contamination from wastewater: a review, *Environmental Chemistry Letters*, 2025, 1–31). (d) Graphical representation showing water contamination and its treatment by a nanotechnology-assisted approach to obtain treated water<sup>23</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Saroa, A., *et al.*, Nanotechnology-assisted treatment of pharmaceuticals contaminated water, *Bioengineered*, 2023, 14(1), 2260919).

adsorption processes generally use either batch or continuous methods. A wide variety of adsorbents may be employed, such as biochar, activated carbons (ACs), ion exchange resins, zeolites, clay minerals, and carbon nanotubes (CNTs). Hybrid systems using a variety of membrane technologies in conjunction with traditional methods of filtration, sedimentation, ozonolysis, chlorination, and photocatalysis have been developed; these do not come without their own set of problems.<sup>21</sup> Fig. 5(b) exposure of pharmaceuticals in the environment.<sup>36</sup> The overall expense of an adsorption process is generally governed by three factors: capital investment, energy use, and chemical costs. One of the most promising methods to decrease such costs is the utilization of inexpensive adsorbents synthesized from waste.<sup>31</sup> Adsorption is considered a prime method for the eradication of antibiotics from contaminated water, as it has 90–100% efficiency for concentrations in the  $\text{mg L}^{-1}$  range.<sup>37</sup> Adsorptive separation and purification processes can occur through both steric (based on size and shape exclusion) and kinetic (based on differences in adsorption rates) mechanisms.<sup>30</sup> Fig. 5(d) competitive interaction of  $\text{H}_2\text{O}$  and

$\text{CO}_2$  on active sites. Table 3 shows a roadmap of adsorbent research for pharmaceuticals removal from water. Table 4 summarises basic types of adsorbents that can be used.<sup>38</sup>

The adsorption process falls into two distinct forms. Physical adsorption is influenced by van der Waals forces between the adsorbent and adsorbate molecules. Chemical adsorption involves reactions occurring directly at a molecular level between a substance (adsorbate) that is being adsorbed and the surface of the material doing the adsorbing (adsorbent).<sup>45</sup> Fig. 6(a) bio-regeneration of saturated adsorbents.<sup>46</sup> Membrane-based adsorption techniques allow greatly improved water purification by combining the best of both worlds: the ability of materials to adsorb pollutants and the selective separation of membranes.<sup>32</sup> Fig. 6(b) chemical modifications to biochar can improve the removal of pollutants and its reuse potential.<sup>47</sup>

Adsorption processes range from the nanometer scale of pores, through micrometer-sized crystals and millimeter-sized adsorbent particles.<sup>50</sup> Fig. 6(c) the main methods used for the adsorbent modification.<sup>48</sup> The adsorbent's cost makes up about



**Table 2** Advantages, drawbacks and removal efficiencies of different advanced wastewater treatment processes for pharmaceutical removal<sup>24</sup> (Adapted with permission from Elsevier (Stadlmair *et al.*, *Chemosphere*, 2018), copyright 2018)

Advanced treatment method		Typical removal efficiency	Main advantages	Main drawbacks	Typical pharmaceutical removal efficiency	References
Physical	Conventional activated sludge (CAS)	Minor to intermediate	No hazardous byproducts are produced	Competition reduces the overall adsorption capacity from dissolved organic carbon (DOC) and the issue of safe waste disposal	20–60%	25
	Activated carbon in powdered or granular form	Moderate to high		High energy intensity (energy-intensive operation), the issue of membrane fouling and the challenge of concentrate stream disposal		26
	High-pressure membrane filtration (nanofiltration, reverse osmosis)	Medium to high	No toxic byproducts		85–99%	27
Biological	Membrane bioreactor (MBR)	Limited to average	Absence of harmful byproducts	Membrane fouling and diminished adsorption capacity due to the aging of the MBR sludge	60–95%	28
	Biofiltration	Intermediate	Minimal energy usage and zero waste production	Large spatial requirements and performance variability	40–85%	26
	Enzymatic processes	Under review	No biological waste is generated	The system is characterized by high selectivity and durability, but suffers from unproven technical feasibility	50–95%	26
Chemical	AOP: different combinations of hydrogen peroxide, ozone and UV respectively	Moderate to high	Can oxidize a wide range of pharmaceuticals ( <i>i.e.</i> , it is non-selective)	High power consumption and the possibility of toxic by-product formation	60–99%	25 and 29

70% of the total expense, and developing adsorbents using inexpensive materials derived from waste and biomass provides a sustainable and economical solution. This is crucial because actual wastewater and effluents almost always contain multiple components that can compete for adsorption sites, which, in turn, lowers the ideal loading capacity for a pure substance in the adsorption system.<sup>51</sup> Fig. 6(d) indicate adsorptive removal of pharmaceutical pollutants using green-synthesized nanotube.<sup>49</sup> Smart adsorbents offer a novel technology for the removal of pharmaceutical pollutants, which not only provide high adsorption capacity but also promote the catalytic degradation of organic molecules. Current trends in research and development are oriented towards the use of functionalized carbons, metal-based hybrid adsorbents, and metal oxide-functionalized adsorbents, which provide multiple avenues for improvement in efficiency.

#### Fundamentals of adsorption in pharmaceutical degradation

Pharmaceuticals that are widely used in animal welfare (veterinary medicine) can enter the environment through various pathways. After being consumed, drugs such as antimicrobials are constantly released into natural ecosystems *via* excreta (urine and feces). Veterinary medicines encompass a wide spectrum of pharmacological classes. The extensive use of these compounds in livestock farming has led to growing concerns, as

agricultural practices increasingly serve as a significant pathway for pharmaceutical contaminants to enter the environment as shown in Table 5 ref. 52.

Several pharmaceuticals, including diclofenac, ibuprofen, phenazone, naproxen, ketoprofen, indomethacin, and acetylsalicylic acid, have been detected in overland water. This involves two aspects: the disposal of unwanted chemicals and metabolic excretion.<sup>59</sup> Pharmaceuticals enter the environment from two main types of sources. Point source pollution originates from distinct, identifiable points and, therefore, can be quantifiable for mathematical modeling. Prime examples are industrial and healthcare facility effluents, along with traditional wastewater treatment systems such as sewage treatment plants and septic tanks, all of which directly release pharmaceuticals into soil resources. Diffuse pollution is a lot more challenging to trace to a single source because it occurs across large areas.<sup>60</sup> Fig. 7(a) origin and routes of pharmaceutical products.<sup>61</sup> Pharmaceutical compounds in wastewater are effectively removable through various processes, including sorption, biodegradation, and abiotic transformation, such as photolytic degradation. Biodegradation may be complete (a process termed mineralization), yielding carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O), or incomplete/partial, where the pharmaceutical may be conjugated or degraded into a metabolite, somewhat similar to processes in the human body.<sup>62</sup> Antibiotics are



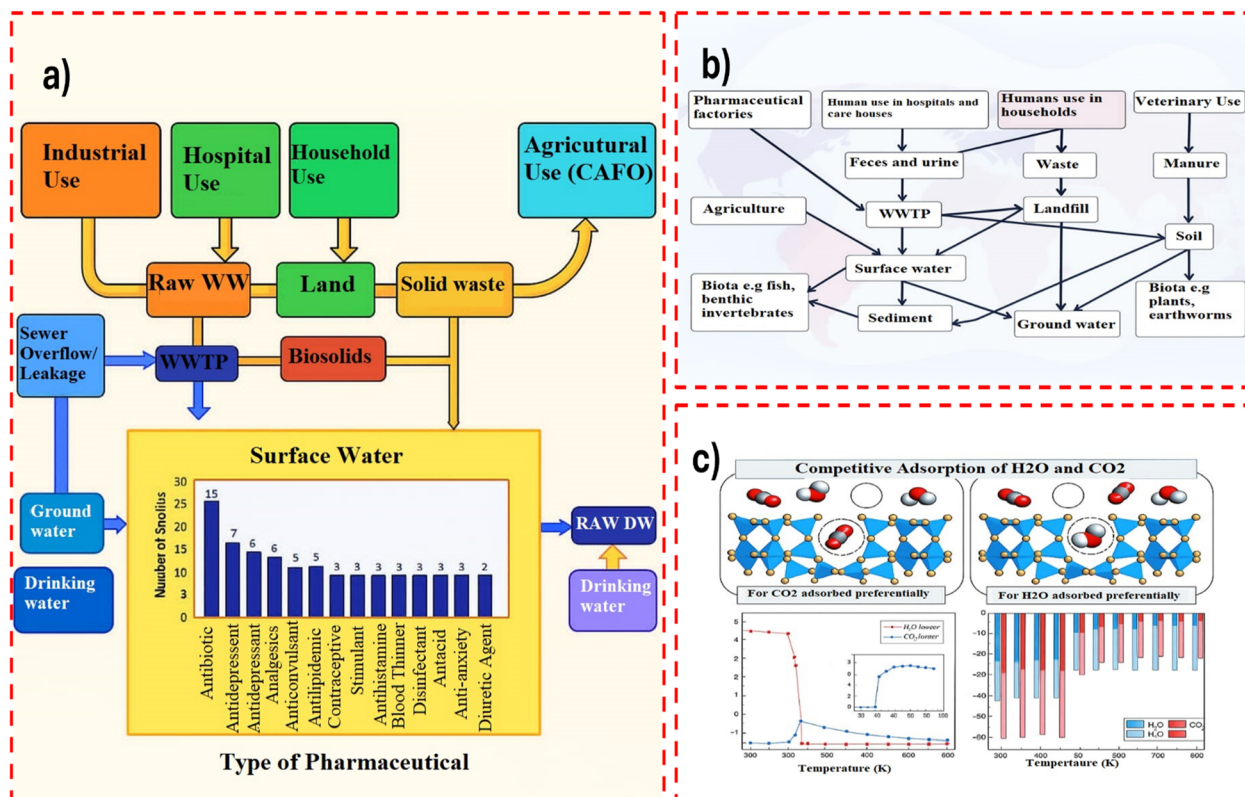


Fig. 5 (a) Schematic showing various pathways by which pharmaceuticals enter surface water, and distribution of the types of pharmaceuticals found in surface water of the USA. WW (wastewater); DW (drinking water); CAFO (concentrated animal feeding operation); WWTP (wastewater treatment plant); and DWTP (drinking water treatment plant)<sup>35</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, RP, D., Pharmaceuticals in the Surface Water of the USA: A Review, *Current Environmental Health Reports*, 2014, 1(2), 113–122). (b) Release of pharmaceuticals in the environment<sup>36</sup> (Adapted with permission from Elsevier (Kayode-Afolayan, Ahuekwe and Nwinyi, *Sci. Afr.*, 2022), copyright 2022). (c) Competitive interactions of H<sub>2</sub>O and CO<sub>2</sub> on active sites. Table 3 shows a roadmap of adsorbent research for pharmaceuticals removal from water. Table 4 summarises basic types of adsorbents that can be used.<sup>38</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Zhao, J., *et al.*, Understanding the effect of H<sub>2</sub>O on CO<sub>2</sub> adsorption capture: mechanism explanation, quantitative approach and application, *Sustainable Energy & Fuels*, 2020, 4(12), 5970–5986).

Table 3 Roadmap of adsorbent research for pharmaceutical removal

Time period	Adsorbent type	Advances	Pharmaceutical removal relevance	Limitations	References
1970s–1990s	Conventional materials: clays, zeolites	Basis of adsorption technology	Efficient for general organics used as baseline adsorbent	Low selectivity	39
1990s–2005	Modified carbons and natural sorbents	Surface functionalization	Enhanced electrostatic interaction	Limited target specificity	40
2005–2015	Nano-adsorbents: CNTs, metal oxides	Increased surface reactivity, faster kinetics	Nanomaterials show high capacity toward drugs	Aggregation cost	39
2015–2020	Functional MOFs and porous frameworks	Tunable porosity, functional design for selectivity	MOFs show high pharma uptake	Stability and regeneration still challenge	41
2020–2025	Hybrid and bio-derived: biochar, hydrochar	Combining adsorbent types: magnetic recovery	Good removal of antibiotics	Regeneration complexity	42
2023–present	Advanced nanostructure and specific adsorbents	Highest capacities and partition coefficients for drugs	Record adsorption capacity materials	Scalability	43
Future directions	Smart/selective and multifunctional systems	Stimuli-responsive, integrated adsorbent/catalyst	Toward simulation removal + degradation	Requires validation in real wastewater	44



Table 4 Basic types of adsorbents<sup>30</sup> (Adapted with permission from Elsevier (Dąbrowski, *Adv. Colloid Interface Sci.*, 2001), copyright 2001)

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Activated carbons	Silica gels	Synthetic polymers
Activated carbon fibres	Activated alumina	Composite adsorbents
Carbonaceous	Pillared clays	
Fullerenes	Zeolites	Mixed sorbents
Heterofullerenes	Clay minerals	
Mesocarbon microbeads	Hydroxides of metals	X-elutrilite, X = Zn, Ca
Molecular carbon sieves	Oxides of metals	Complex mineral carbons
Nanomaterials	Porous clay heterostructures (PCHs)	

also commonly detected in water matrices. Due to their anti-bacterial properties, it is not common that they are efficiently eliminated by wastewater treatment plants. Anti-inflammatory pharmaceuticals, such as diclofenac, naproxen, aspirin and ibuprofen, are among the dominant PPs detected in the environment, representing about 15% of all the PPs detected.<sup>63</sup> Fig. 7(b) routes of pharmaceutical contamination in aquatic environments and corresponding biological treatment

solutions (bioremediation).<sup>64</sup> Humans can be exposed to non-therapeutic or recreational drugs by two broad routes. (1) Environmental recycling: ingestion of minute amounts of drugs present in the surroundings may take place through contaminated drinking water and food. These are mainly residues coming out of drugs released into the environment and going into the food and water intake. (2) Drug waste: exposure may also take place from the intake of drug wastes, either accidentally

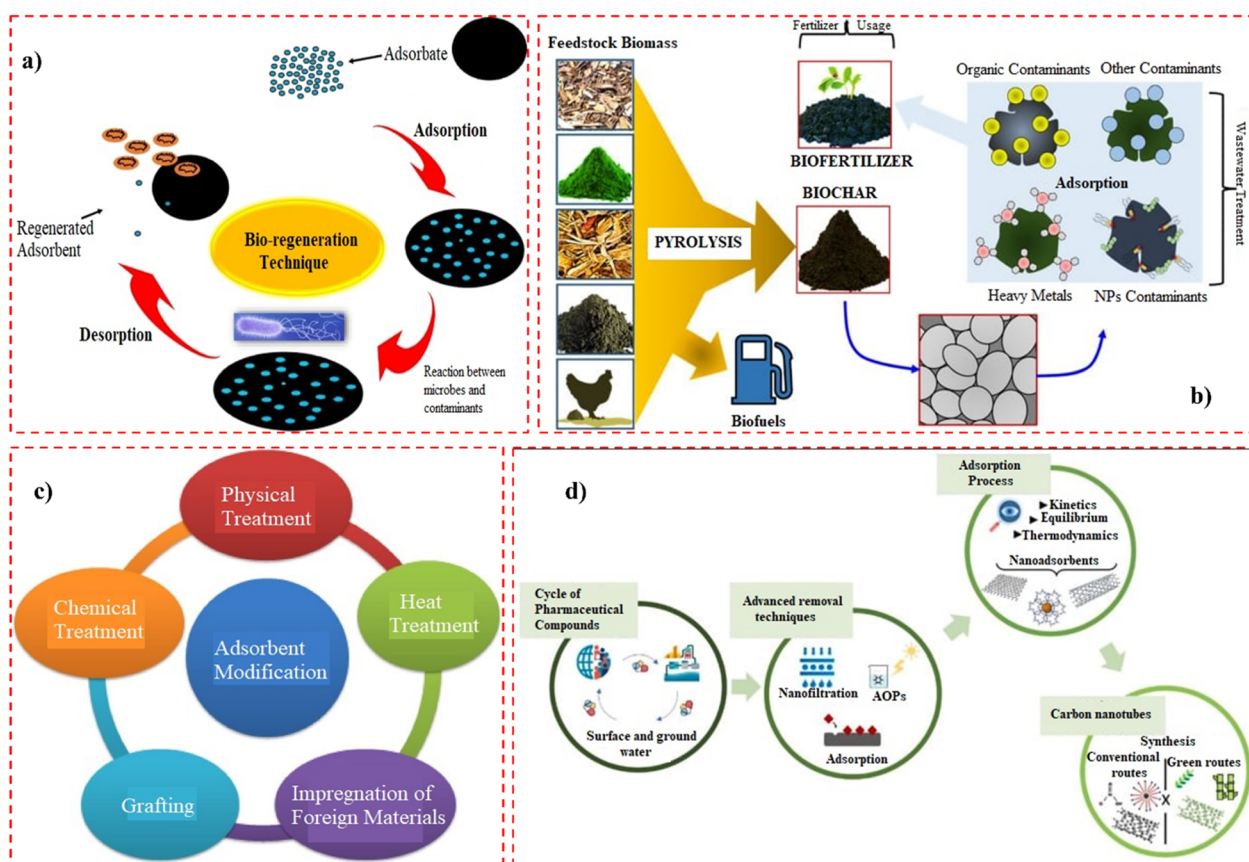


Fig. 6 (a) Bio-regeneration of saturated adsorbents<sup>46</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Yadav, S., et al., Cutting-edge regeneration technologies for saturated adsorbents: a systematic review on pathways to circular wastewater treatment system, *Environmental Monitoring and Assessment*, 2025, **197**(2), 215). (b) Chemical modifications of biochar improve the removal of pollutants and its reuse potential<sup>47</sup> (Adapted with permission from Elsevier (Alshehri and Pugazhendhi, *J. Hazard. Mater. Adv.*, 2024), copyright 2024). (c) Main methods used for adsorbent modifications<sup>48</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Dehghani, M. H., et al., Recent advances on sustainable adsorbents for the remediation of noxious pollutants from water and wastewater: A critical review, *Arabian Journal of Chemistry*, 2023, **16**(12), 105303). (d) Pharmaceutical adsorption processes using nanotubes obtained by green routes<sup>49</sup> (Adapted with permission from Elsevier (Alshehri and Pugazhendhi, *J. Hazard. Mater. Adv.*, 2024), copyright 2024).

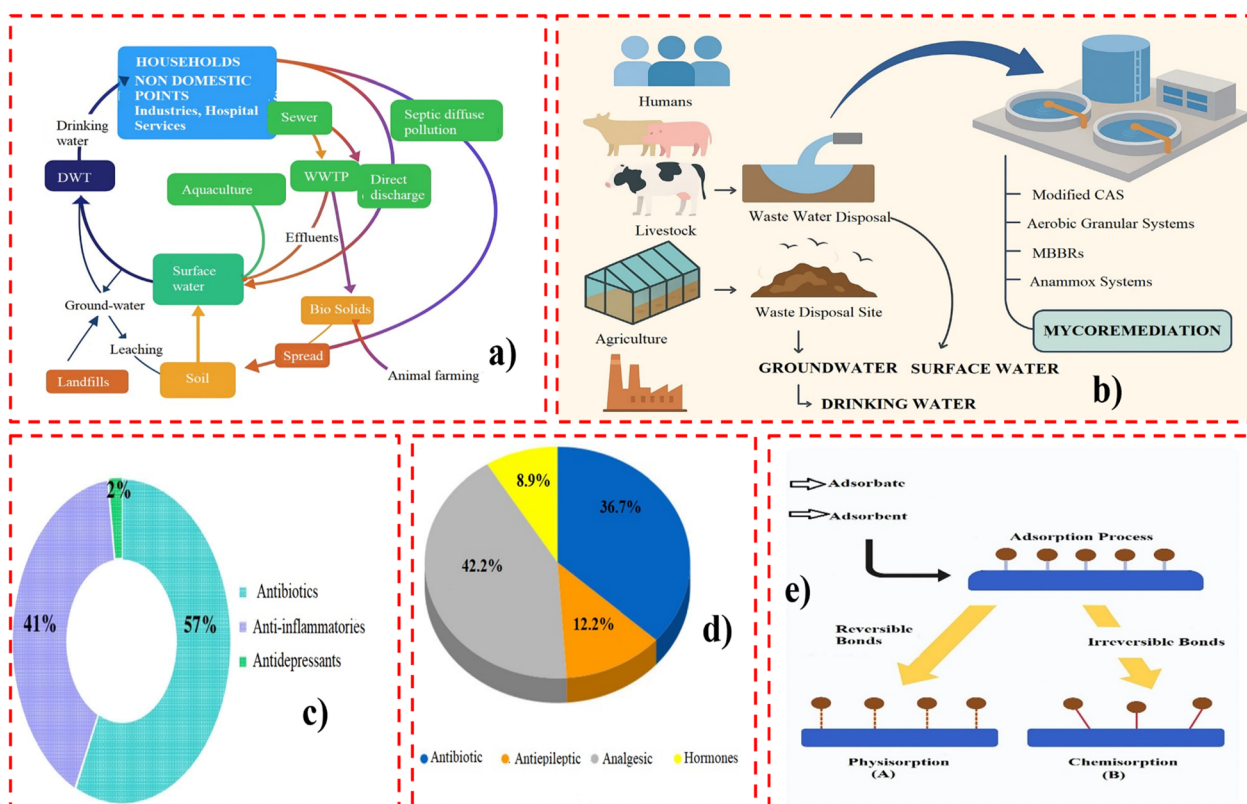


**Table 5** Categories of veterinary pharmaceuticals: these pharmaceuticals fall into a range of pharmacological categories<sup>52</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Wychodnik, K., *et al.*, Poultry farms as a potential source of environmental pollution by pharmaceuticals, *Molecules*, 2020, 25(5), 1031)

Major drug class	Specific sub-categories/types	Examples of agents	References
Antiparasitics	Endectocides, ectoparasiticides, endoparasiticides	Anthelmintics and antiprotozoals	53
Anti-infective agents	Antifungals, antimicrobials	General antibiotics, antifungals	54
Hormones	Various regulatory compounds	Estrogens, progestins, <i>etc.</i>	55
Anti-inflammatory drugs	Steroidal and non-steroidal types	Corticosteroids, NSAIDs	56
Central nervous system agents	Anesthetics, tranquilizers, sedatives	Agents affecting mood and consciousness	57
Gastrointestinal and other agents	Bronchodilators, antacids, diuretics, emetics	Drugs for respiratory, digestive, and fluid balance	58

(taking leftover drug wastes, for example) or intentionally (consuming leftover drug wastes).<sup>65</sup> Fig. 7(c) publication history of research on pharmaceutical pollutants between 2010 and 2021.<sup>63</sup> Fig. 7(d) main therapeutic categories.<sup>66</sup> Pharmaceuticals present in the environment can affect human health, mainly through our drinking water and food. Both surface and

groundwater, which we rely on for our water supply, can become contaminated with these drugs. Despite the fact that pharmaceutical concentrations in drinking water and food are typically low, the possibility of prolonged, continuous exposure is a significant concern.<sup>67</sup> Among the many types of drug residues found, certain pharmaceuticals are frequently detected. These



**Fig. 7** (a) Origin and routes of pharmaceutical products<sup>61</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Gupta, N., *et al.*, Pollution by pharma industries: an overview, *Environmental Remediation Technologies, Regulations and Safety*, 2023, 55). (b) Routes to pharmaceutical contamination in aquatic environments and corresponding biological treatment solutions (bioremediation)<sup>64</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Ortúzar, M., *et al.*, Pharmaceutical pollution in aquatic environments: a concise review of environmental impacts and bioremediation systems, *Frontiers in Microbiology*, 2022, 13, 869332). (c) Publication trends in the period of 2010–2021 of pharmaceutical pollutants<sup>63</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Bustos Bustos, E., *et al.*, Detection and treatment of persistent pollutants in water: general review of pharmaceutical products, *ChemElectroChem*, 2022, 9(12), e202200188). (d) Main therapeutic categories<sup>66</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Rodríguez-Serin, H., *et al.*, Literature review: Evaluation of drug removal techniques in municipal and hospital wastewater, *International Journal of Environmental Research and Public Health*, 2022, 19(20), 13105). (e) Mechanisms of various kinds of adsorptions: (A) physisorption and (B) chemisorption<sup>70</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, AlAqad, K. M., *et al.*, Adsorbent materials for water treatment: a review of current trends and future challenges, *Environmental Pollution and Management*, 2025, 2, 1–3).



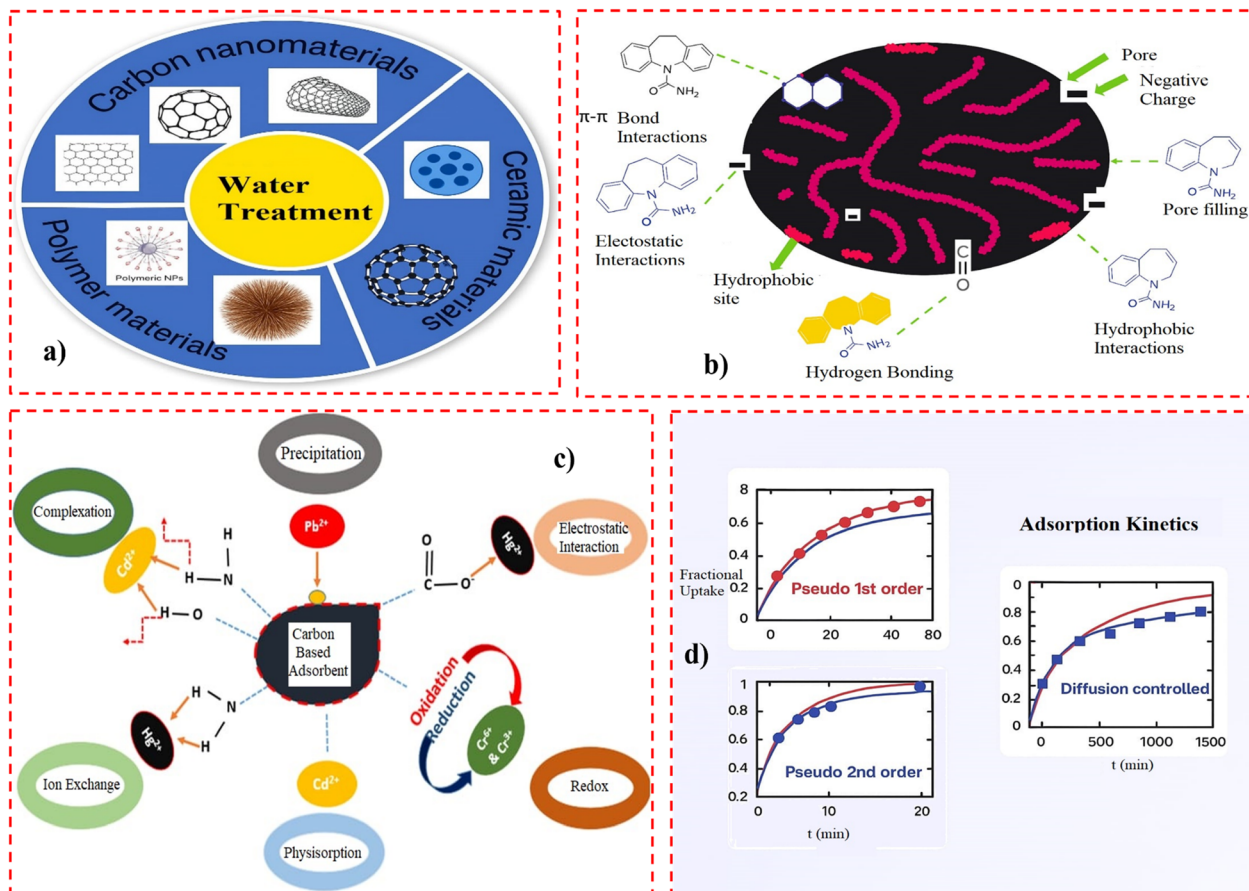


Fig. 8 (a) Nanomaterials used in water treatment applications<sup>70</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, AlAqad, K. M., *et al.*, Adsorbent materials for water treatment: a review of current trends and future challenges, *Environmental Pollution and Management*, 2025, 2, 1–3). (b) Drug (Carbamazepine) adsorption mechanisms onto activated carbon and biochar<sup>72</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Décima, M. A., *et al.*, A review on the removal of carbamazepine from aqueous solution by using activated carbon and biochar, *Sustainability*, 2021, 13(21), 11760). (c) Mechanism of adsorption of heavy metals on carbon-based adsorbents<sup>73</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Sheraz, N., *et al.*, Comprehensive assessment of carbon-, biomaterial- and inorganic-based adsorbents for the removal of the most hazardous heavy metal ions from wastewater, *RSC Advances*, 2024, 14(16), 11284–11310). (d) Evaluation of adsorption kinetics<sup>74</sup> (Adapted with permission from Elsevier (Simonin, J.-P., *Chem. Eng. J.*, 2016), copyright 2016).

commonly reported categories include: antibiotics, lipid-regulating agents, *e.g.* statins, anti-inflammatory drugs, beta-blockers, contrast media, and contraceptives.<sup>68</sup> Antibiotics have been widely used for infectious disease therapy since the 1940s. In addition to human medicine, they are also used to enhance growth in fish farms and livestock. A major source of environmental contamination by antibiotics is hospitals.<sup>69</sup> Fig. 7(e) mechanisms of various kinds of adsorptions: (A) physisorption and (B) chemisorption.<sup>70</sup> Essentially, the removal of pharmaceutical compounds is achieved through three main routes involving physical, biological, and chemical methods. Most WWTPs apply a primary system, which relies on physical and chemical methods of treatment. In this manner, some pharmaceuticals could be adsorbed and thus removed, but many still remain in the water. This is because most pharmaceutical compounds cannot be easily metabolized as a carbon source by the microorganisms in the activated sludge. Furthermore, these compounds can sometimes suppress the

effectiveness of these beneficial microorganisms or potentially build up (bioaccumulate) within the food chain. Tertiary water treatment methods offer advanced solutions for further purification. These can include, biological systems for removing nitrogen compounds, ion exchange processes to eliminate various ions, chemical precipitation to specifically target and remove phosphorus, distillation to remediate volatile organic compounds, liquid–liquid extraction for separating pollutants, adsorption onto activated carbon to effectively eliminate both organic and inorganic contaminants, and advanced oxidation processes (AOPs), which are highly efficient in decomposing toxic and bio refractory persistent organic contaminants.<sup>71</sup> Fig. 8(a) application of nanomaterials for water treatment.<sup>70</sup> The key step during the degradation of pharmaceuticals, as it enriches pollutants on the adsorbent surface and creates efficient interaction with reactive sites. Adsorption behavior has recently been determined by surface functionality, porosity, and surface charge to have a direct impact on degradation kinetics.



Therefore, a clear understanding of adsorption fundamentals provides a key basis for designing high-performance smart adsorbents for pharmaceutical removal.

### Smart adsorbent frameworks

Adsorption is the reversible process in which fluid molecules stick to a solid surface, forming a thin layer. The subsequent detachment of these molecules from the surface is desorption.<sup>75</sup> Fig. 8(b) drug (Carbamazepine) adsorption mechanisms onto biochar and activated carbon.<sup>72</sup> This is driven by the same weak intermolecular forces that cause vapors to condense. The energy involved is rather low, less than 40 kJ mol<sup>-1</sup>. Because the forces are weak in physisorption, it proceeds under mild thermal conditions, demanding little energy activation. It occurs naturally at low temperatures. Unlike chemical adsorption (chemisorption), physisorption can create more than a monolayer of adsorbate on the surface. Chemical adsorption (or chemisorption) is a form of adsorption where a reaction mechanism takes place between the adsorbent (surface) and the adsorbate (substance being adsorbed). This process requires a high activation energy and occurs at high temperatures, often with an energy change greater than 40 kJ mol<sup>-1</sup>.<sup>76</sup> Fig. 8(c) mechanism of adsorption of heavy metals on carbon-based adsorbents.<sup>73</sup> Adsorption isotherm models, which consider both equilibrium data and adsorbent properties, describe the fundamental interaction mechanisms that occur between pollutants and adsorbent materials. This system is useful for defining the fundamental behavior of the adsorption process.<sup>77</sup> Fig. 8(d) evaluation of adsorption kinetics.<sup>74</sup> Rationally designed frameworks incorporate surface functionalization, metal active sites, and hybrid architecture to promote synergistic adsorption-degradation pathways. In this way, smart adsorbents represent a promising and sustainable platform for next-generation pharmaceutical wastewater treatments. A comprehensive overview of theoretical isotherm and kinetic models employed to interpret adsorption behavior in biochar-assisted removal of pharmaceutical contaminants from aqueous systems as represented in Table 6 ref. 78.

### Engineering high-efficiency adsorption systems

(1) Langmuir isotherm: the Langmuir theory, one of the earliest explanations for adsorption, is based on a kinetic approach and the following core assumptions: (i) the adsorption process occurs with uniform, equivalent sites. (ii) Every site can only hold a single adsorbate molecule (monolayer adsorption). (iii) The bonds are strong enough to keep the adsorbate attached, and there are no interactions (attraction or repulsion) between them. A significant limitation of the Langmuir isotherm is its unrealistic premise that the heat of adsorption remains constant and does not depend on how much of the surface is covered by the adsorbate. (2) Freundlich isotherm: this isotherm is a popular experimental framework frequently employed to characterize adsorption processes occurring on heterogeneous surfaces. The model contains two parameters,  $K_F$  and  $n$ . Parameter  $n$  is a measure of surface heterogeneity,

meaning it tells how far the surface binding locations are from having the same adsorption energy. The linear form is:<sup>89</sup>

$$\ln q_e = \ln K_F + 1 + \frac{1}{n} \ln P_e \quad (1)$$

(3) Langmuir–Freundlich isotherm: the Langmuir–Freundlich isotherm represents a highly effective and functional model for adsorption equilibrium studies, as it incorporates some aspects of both Langmuir and Freundlich models. Though the original model was developed for gas adsorption on solids, a similar equation is presently used extensively in adsorption from liquid phases.<sup>89</sup>

$$\theta_e = \left( \frac{(K_{LF} C_e)^{1/n}}{1 + (K_{LF} C_e)^{1/n}} \right) \quad (2)$$

The rate of adsorption is crucial because it directly influences how efficient the process is.<sup>90</sup> The thermodynamic parameters change with the temperature variation in an adsorption process, as it is sensitive to temperature. (4) Gibbs free energy of change ( $\Delta G^\circ$ ):  $\Delta G^\circ$  demonstrates whether an adsorption process will occur and if it is viable. A negative value of  $\Delta G^\circ$  represents that the process is spontaneous, whereas a positive  $\Delta G^\circ$  reveals the opposite: one that will not occur spontaneously.<sup>91</sup>

$$\Delta G^\circ = -RT \ln K_C \quad (3)$$

where  $R$  is the universal gas constant (J mol<sup>-1</sup> Kg<sup>-1</sup> K<sup>-1</sup>),  $T$  is the temperature (K), and  $K_C$  is the equilibrium constant. For example, a comprehensive thermodynamic investigation revealed that the adsorption entropies and enthalpies for CO<sub>2</sub> and H<sub>2</sub>O are temperature dependent. This dependence causes a switch in the relative Gibbs free adsorption energy order among the two molecules.<sup>38</sup> Fig. 9(a) studies on dye removal utilizing a range of synthesized adsorbents.<sup>92</sup> The adsorption of pharmaceuticals occurs because of particular interaction mechanisms. Aromatic pharmaceuticals have a high interaction with  $\pi$ -rich materials, such as graphene oxide and biochar. The interaction occurs because of the  $\pi$ - $\pi$  stacking interaction. Pharmaceutical polar groups such as the carboxylate ion and primary or secondary amines can form hydrogen bonds with the oxygen- or amine-functionalized surfaces. In cases where metal ions are present in adsorbent material, such as those with Fe- or Cu-based adsorbent surfaces, the carboxylate and heterocyclic groups can form inner-sphere complexes with the metal ions. Ionic strength and pH conditions can modulate the adsorption. However, the interaction mechanisms at the molecular scale are often inadequately described in the context of adsorption. The knowledge gap in this aspect is critical. Fundamental molecular interactions between drug molecules and the surface of adsorbent media (Table 7) and, four adsorption isotherm models were employed, and their corresponding parameters were evaluated as shown in Table 8.<sup>93</sup> A comparative evaluation of adsorption kinetics and isotherm models for pharmaceutical contaminants is shown in Table 9. The major types of





**Table 6** Summary of different theoretical models applied for predicting isotherm and kinetic data of biochar-mediated adsorption of PCs<sup>78</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Chauhan, S., et al., Biochar-mediated removal of pharmaceutical compounds from aqueous matrices via adsorption, *Waste Disposal & Sustainable Energy*, 2023, 5(1), 37–62)

Models	Equations	Model parameters	Biochar precursor	Pharmaceutical compounds	References
Langmuir	$q_e = \frac{1}{k_1 q_L} + \frac{c_e}{k_1 q_L q_L}$	$q_e$ ( $\text{mg g}^{-1}$ ) = equilibrium adsorption capacity $q_L$ ( $\text{mg g}^{-1}$ ) = maximum adsorption capacity $K_L$ ( $\text{L mg}^{-1}$ ) = Langmuir isotherm constant	Banana stem fibers Date stone seeds Pomelo peel	Carbamazepine (CBZ) Ibuprofen (IBF) Amoxicillin (AMX)	79
Freundlich	$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$	$C_e$ ( $\text{mg L}^{-1}$ ) = equilibrium adsorbate concentration in solution $K_F$ [ $\text{mg g}^{-1}$ ( $\text{L mg}^{-1}$ )] = Freundlich isotherm constant $n$ = heterogeneity factor	Municipal solid waste (MSW) <i>Gliricidia sepium</i> Gooseberry seed shells Giant reed MSW	Tetracycline (TC) Caffeine (CAF) Naproxen (NPX) Amoxicillin (AMX)	80
Sips	$q_e = \frac{q_s K_S C_e^{1/m}}{1 + K_S C_e^{1/m}}$	$q_s$ ( $\text{mg g}^{-1}$ ) = maximum uptake of adsorbate per unit mass of adsorbent $K_S$ ( $\text{L mg}^{-1/m}$ ) = Sips constant related to energy of adsorption $m$ = Sips parameter characterizing the system heterogeneity	Bovine bone Pure glucose Pine sawdust Cherry stalk Pomelo peel	Ciprofloxacin (CFX) Sulfamethoxazole (SMX) Paracetamol (PRC) Caffeine (CAF) Ciprofloxacin (CFX)	82
Redlich–Peterson (R–P)	$\ln \left( \frac{C_e}{k_R q_e} \right) - 1 = \ln(\alpha_R) + \beta \ln(C_e)$	$\alpha_R$ and $\beta$ are constants used for fitting the model	Pure glucose Cherry stalk Pomelo peel	Carbamazepine (CBZ)	83
Dubinin–Radushkevich (D–R)	$\ln q_e = \ln q_D - B \epsilon^2$ $\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)$	$B$ ( $\text{mol}^2 \text{kJ}^{-2}$ ) = Dubinin–Radushkevich isotherm constant $\epsilon$ ( $\text{kJ mol}^{-1}$ ) = adsorption potential derived from Polanyi adsorption potential theory $R$ = universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )	Pomelo peel waste Pure glucose	Carbamazepine (CBZ)	84
Temkin	$q_e = \frac{RT}{b} \ln k_T + \frac{RT}{b} \ln C_e$	$T$ (Kelvin) = temperature $k_T$ ( $\text{L g}^{-1}$ ) = equilibrium binding constant corresponding to the maximum binding energy $b$ = Temkin isotherm constant	Corn husk <i>Gliricidia sepium</i> Cherry stalk	Paracetamol (PRC) Caffeine (CAF) Tetracycline (TC) Ciprofloxacin (CFX) Tetracycline (TC) Amoxicillin (AXM)	85
Pseudo-first-order (PFO)	$\ln(q_e - q_i) = \ln q_e - k_1 t$	$q_i$ ( $\text{mg g}^{-1}$ ) = amount of adsorbate adsorbed at any time $t$ (min) $k_1$ ( $\text{min}^{-1}$ ) = PFO rate constant $k_2$ ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) = PSO rate constant	Pure glucose Giant reed Gooseberry seed shells	Paracetamol (PRC) Amoxicillin (AXM)	81

Table 6 (Contd.)

Models	Equations	Model parameters	Biochar precursor	Pharmaceutical compounds	References
Pseudo-second-order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$		Giant reed	Paracetamol (PRC)	
Intra-particle diffusion (IPD)	$q_t = k_t t^{1/2}$	$k_t$ (mg g <sup>-1</sup> min <sup>-1/2</sup> ) = IPD rate constant	Cherry stalk Textile effluent sludge Corn husk	Ciprofloxacin (CFX) Ofloxacin (OFL) Tetracycline (TC) Levofloxacin (LEV)	86
Boyd's film diffusion	$2\pi - \pi^2 \frac{F(t)}{3} - 2\pi \left(1 - \pi \frac{F(t)}{3}\right)^{1/2}$ $B_t = -0.4977 - \ln(1 - F(t))$ $q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$	$F(t)$ = ratio of $q_t$ to $q_e$ corresponding to fractional achievement of equilibrium $B_t$ = mathematical function of $F$ $\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> ) = rate of adsorption during the initial phase $\beta$ (g mg <sup>-1</sup> ) = desorption constant	Bagasse biomass Cherry stalk Raw bamboo	Tetracycline (TC) Ciprofloxacin (CFX) Sulfamethoxazole (SMX)	87 88
Elovich			Pure glucose	Paracetamol (PRC)	

adsorbents used in industrial applications are presented in Table 10.<sup>94</sup>

Activated carbon (AC) possesses high porosity and an extensive surface area; thus, the material is very effective at adsorption. Due to its unique properties, it can function as a catalyst or serve as a substrate for other catalysts. These characteristics, such as high porosity and catalytic and adsorptive capabilities, result directly from the activation it undergoes. Activated carbon is the most popular material used to remove dyes from wastewater. Dyes are commonly used in the textile industry, and colored wastewater is a significant problem. One of the characteristic features of activated carbon is its adsorption capacity, which refers to the amount of dye that it can remove.<sup>109</sup> Renewable, biodegradable and nontoxic precursors are mainly used to develop bio-derived carbon nanostructures. Some examples of bio-derived carbon nanostructures are cellulose, graphene obtained from lignin, fullerene, and carbon nanodots derived from plant extracts.<sup>110</sup> Fig. 9(b)) Pharmaceutical waste: sources and consequences.<sup>43</sup> Biochar is produced *via* the fast pyrolysis of biomass, which can be sourced from various quarters, including forest materials such as sawdust, bark, wood shavings, and agricultural waste, such as bagasse and wheat straw. It is a solid biofuel that possesses a high heat value and serves as fuel in kilns and boilers.<sup>111</sup> Fig. 9(c) preparation process of solidification methods for composite adsorbents.<sup>95</sup> There are several carbonization processes by which biochar may be prepared. Among them, well-known techniques involve pyrolysis, pyro-gasification, and gasification. Various techniques used to synthesize the material include hydrothermal carbonization, torrefaction, and microwave pyrolysis. The material structure, surface chemistry, and operational conditions are optimized to maximize pharmaceutical uptake and stability. Thus, rational system engineering is of critical importance in translating advanced adsorbent materials into effective pharmaceutical treatment technologies in a scalable way.

### Adsorption kinetic models

Adsorption kinetics are crucial because they determine how fast adsorption proceeds and help identify the main factors controlling the rate. (a) Pseudo-first-order: the PFO model, developed by Lagergren, is a non-reversible kinetic model. This model assumes a direct proportionality between the rate of adsorption and the number of unoccupied active sites on the adsorbent. The model is represented by the following non-linear equation:<sup>72</sup>

$$q_t = q_e (1 - e^{-k_1 t}) \quad (4)$$

where  $q_t$  is the amount of adsorbate adsorbed at time  $t$ ,  $q_e$  is the amount of adsorbate adsorbed at equilibrium, and  $k_1$  is the pseudo-first-order rate constant.

$$\ln(q_e - q_t) = q_e - k_1 t \quad (5)$$



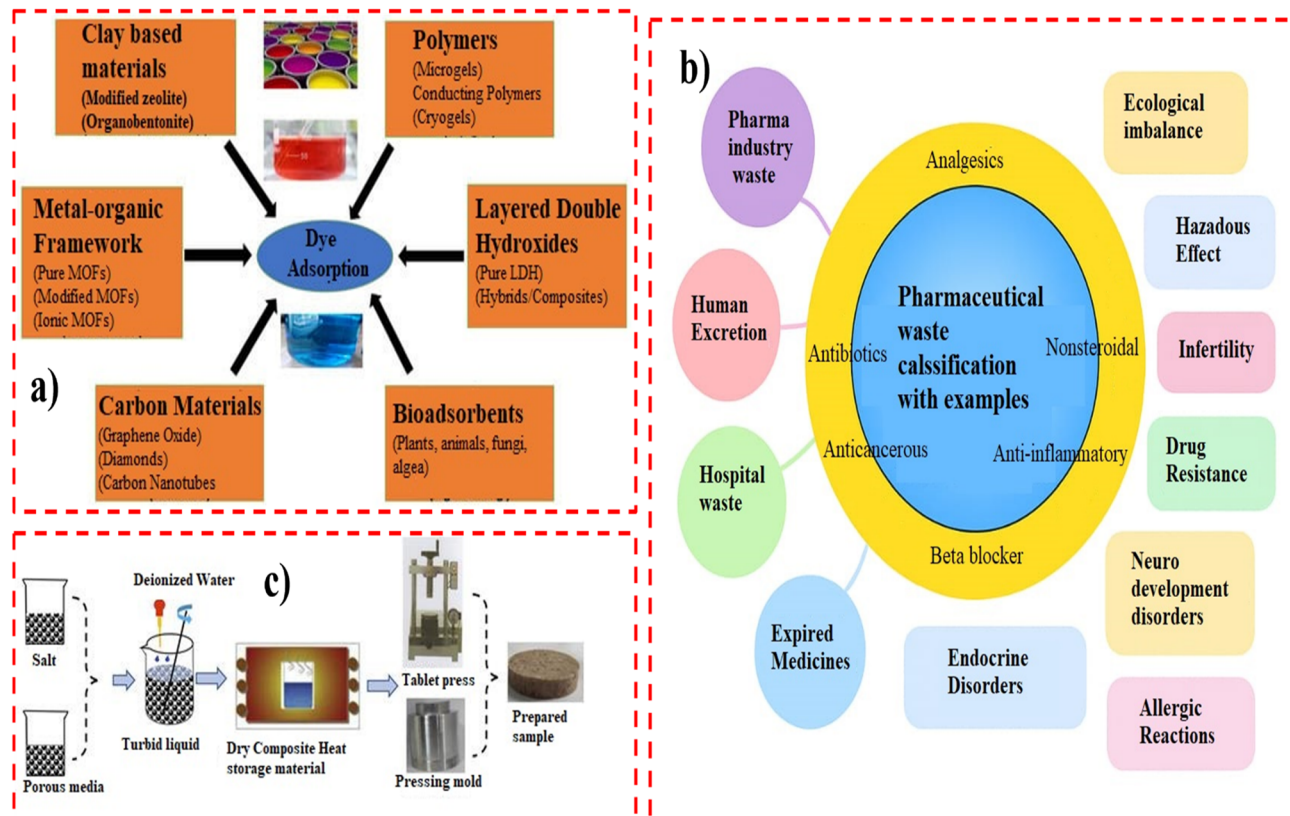


Fig. 9 (a) Dye adsorption over different kinds of designed materials<sup>92</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Haleem, A., *et al.*, A comprehensive review on adsorption, photocatalytic and chemical degradation of dyes and nitro-compounds over different kinds of porous and composite materials, *Molecules*, 2023, **28**(3), 1081). (b) Pharmaceutical waste: sources and consequences<sup>43</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Aziz, K., *et al.*, Recent advances in nanomaterial-based adsorbents for removal of pharmaceutical pollutants from wastewater, *Materials Horizons*, 2025). (c) Preparation process involving solidification methods for composite adsorbents<sup>95</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Zhang, X., *et al.*, Influential factors and optimization analysis of adsorption refrigeration system performance, *AIP Advances*, 2020, **10**(10)).

Table 7 Molecular-level interactions between pharmaceuticals and adsorbent surfaces

Drug functional group	Representative drugs	Adsorbent surface site	Dominant interaction type	pH/ionic strength influence	References
Aromatic rings	Diclofenac, ibuprofen, ciprofloxacin	Graphene-basal planes, biochar	$\pi$ - $\pi$ stacking	Weak pH dependence, minimal ionic strength	96
Carboxylate ( $-\text{COO}^-$ )	Diclofenac, ibuprofen, naproxen	$-\text{OH}$ , $-\text{COOH}$ , metal sites	Electrostatic interaction	Strongly pH-dependent	97
Amine	Ciprofloxacin, amoxicillin	$-\text{COOH}$ , $\text{NH}_2$ groups	Hydrogen bonding	Enhanced low pH	98
Heterocyclic	Sulfonamides, fluoroquinolones	Fe/MOF metal sites	Metal-ligand coordination	Favored around neutral pH	99
Hydroxyl	Tetracycline	$-\text{OH}$ , $-\text{COOH}$	Hydrogen bonding	Best near neutral pH	100
Multiple functional group	Ciprofloxacin, tetracycline	GO-chitosan, Fe-Cu hybrids	Synergistic electrostatic coordination	Narrow optimal pH	97

where  $k_1$  is the apparent rate constant ( $\text{L min}^{-1}$ ),  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the adsorption capacity at time  $t$  and at equilibrium. Its linearized form is also presented below:<sup>72</sup>

(b) Pseudo-second-order: the PSO model of Ho and McKay is based on the premise that chemisorption, a chemical mechanism involving the sharing or exchanging of electrons, is the

rate-determining step in adsorption. The PSO model equation can be expressed in eqn (6).<sup>72</sup>

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} \quad (6)$$



**Table 8** Four isotherm models adopted in this work and their parameters<sup>93</sup> (Adapted with permission from Elsevier (Özkaya, J. *Hazard. Mater.*, 2006), copyright 2005)

Isotherm	Model
Freundlich	$q_e = k_f \cdot C_e^{1/n}$
Langmuir	$q_e = \frac{Q_0 \cdot k_L \cdot C_e}{1 + k_L \cdot C_e}$
Redlich–Peterson	$q_e = \frac{r_e \cdot C_e}{1 + p_e \cdot C_e^g}$
Toth	$q_e = \frac{A \cdot C_e}{(B + C_e^D)^{1/D}}$

The pseudo-second order and intraparticle diffusion models are the most commonly applied because they reflect the combined effects of surface reactions and mass transfer. In this respect, appropriate kinetic modeling is an important step, allowing a valid comparison between different adsorbents and enabling the selection and design of an efficient adsorption system. Due to outstanding physicochemical properties, MOFs and COFs have received multidisciplinary research interests. The excellent properties of COFs and MOFs and their derivatives are represented in CO<sub>2</sub> reduction reactions and environmental pollutant treatments through strategies on sorption, photocatalysis, and electrocatalysis.<sup>112</sup> Metal organic frameworks (PCPs), are a novel class of crystalline porous materials. They can be formed by the linkage of metal ions with organic molecules (ligands) to give a unique, highly structured framework.<sup>113</sup>

Fig. 10(a) Properties and applications of multifunctional MOFs.<sup>114</sup> Of all the applications of MOFs, catalysis is one of the most extraordinary and fastest-growing areas. This is mainly due to several advantages of MOFs as catalysts. It is possible to design the framework to contain various types of active sites, metal centers, and functional groups on the organic ligands. The active sites are densely and homogeneously distributed within the whole material, which significantly enhances the activity and lifetime of the catalyst. The extensive network of pores and open channels allows reactants to reach every single active site, increasing efficiency. It is easy to control how the reactant molecules interact with the MOF. Having the form of a solid porous material, MOFs could easily be recovered and reutilized, making them an excellent choice for use as a recyclable catalyst.<sup>115</sup> Fig. 10(b) various strategies for the synthesis of MOFs/Polymer composites.<sup>116</sup> Several approaches are adopted to synthesize MFCs from the Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles and metal–organic frameworks, resulting in materials with unique design principles. Composites created from various combinations of nanomaterials and MOFs offer a huge range of functions and characteristics. This is the capability that makes MOF-based composites of interest for a variety of purposes. The large surface area makes MOF-based composites ideal for catalysis and adsorption processes. Porous MOF-based composites are excellent for gas storage and separation. MOF-based composites are often very chemically stable and can be effectively used in harsh conditions. The properties and performance of MOF-based composites are directly defined by the MOFs from which they were made.<sup>117</sup> MOFs are crystalline, three-

**Table 9** Comparative overview of kinetic and isotherm models for pharmaceutical adsorption

Adsorbent	Pharmaceutical compounds	Kinetic model	Rate constant	Isotherm model	$q_{\max}$ (mg g <sup>-1</sup> )	References
Activated carbon (AC)	Tetracycline	PSO	$k_2 \sim 0.001\text{--}0.01 \text{ g mg}^{-1}$	Langmuir	200–450	101
Metal–organic framework (MOF-235)	Ciprofloxacin	PSO	$k_2 \sim 0.005\text{--}0.02 \text{ g mg}^{-1}$	Langmuir	300–600	102
Graphene oxide (GO)	Amoxicillin	PSO	$k_2 \sim 0.002\text{--}0.015 \text{ g mg}^{-1}$	Langmuir	50–200	103
Biochar	Sulfamethoxazole	PSO	$k_2 \sim 0.001\text{--}0.015 \text{ g mg}^{-1}$	Langmuir	150–200	103
Magnetic nanocomposite	Diclofenac	PSO	$k_2 \sim 0.003\text{--}0.012 \text{ g mg}^{-1}$	Langmuir	180–400	103
Zeolite	Ibuprofen	PFO/PSO	$k_2 \sim 0.01\text{--}0.05 \text{ min}^{-1}$	Langmuir	40–150	104

**Table 10** Basic types of industrial adsorbents<sup>94</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Crini, G., *et al.*, Conventional and non-conventional adsorbents for wastewater treatment, *Environmental Chemistry Letters*, 2019, 17(1), 195–213)

Carbon adsorbents	Mineral adsorbents	Other adsorbents	Target pharmaceuticals	Adsorption capacity (mg g <sup>-1</sup> )	References
Activated carbon	Silica gels	Synthetic polymers	Diclofenac, ibuprofen	120–350	105
Activated carbon fiber	Activated alumina	Composite adsorbents (mineral carbons)	Mixed pharmaceuticals	150–400	106
Carbonaceous materials	Zeolites, clay minerals, pillared clays and inorganic nanomaterials		Antibiotics, NSAIDs, ciprofloxacin Quinolones	30–210 50–300	107
Fullerenes	Metal hydroxides	Mixed adsorbents	NSAIDs, antibiotics	100–260	107
Molecular carbon sieves	Metal oxides		Tetracycline, SMX	60–240	108



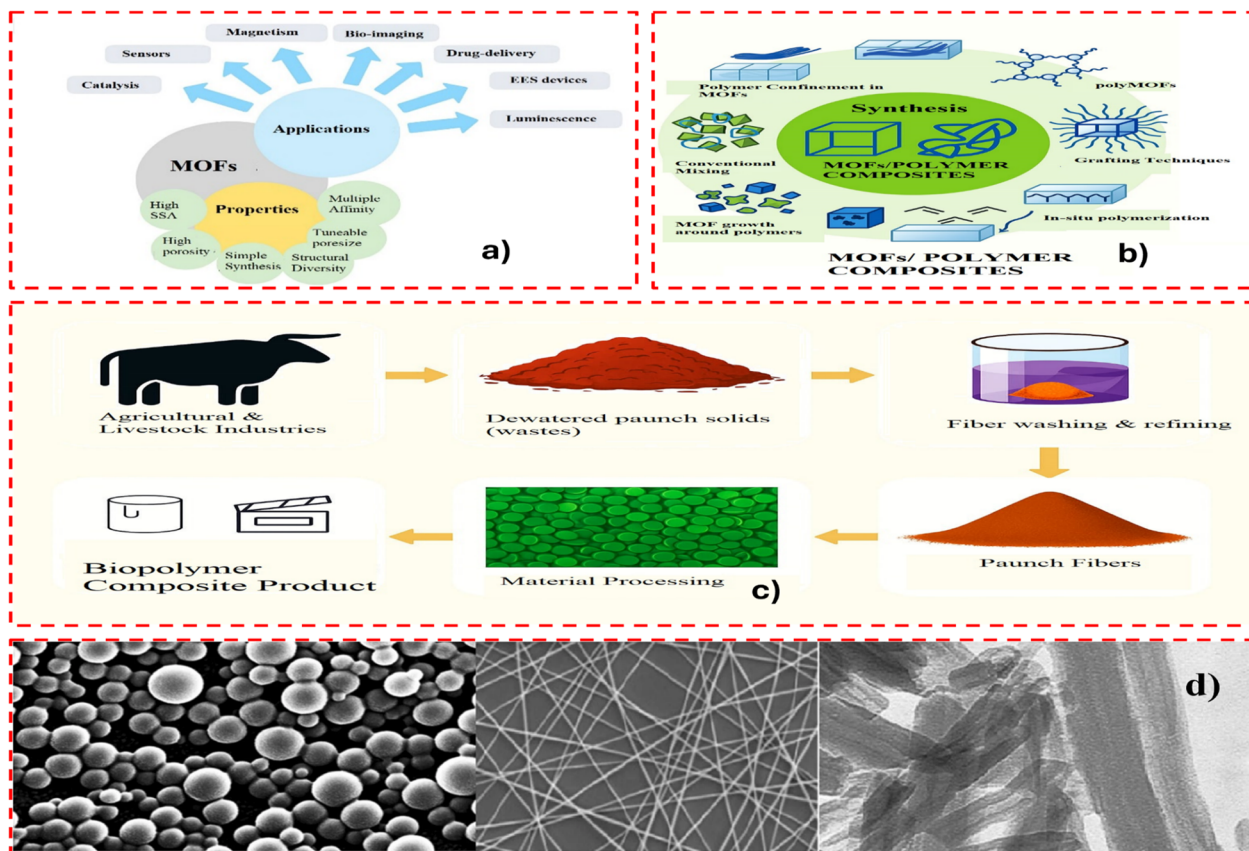


Fig. 10 (a) Properties and applications of multifunctional MOFs<sup>114</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Prajapati, M., *et al.*, Recent advancement in metal–organic frameworks and composites for high-performance supercapacitors, *Renewable and Sustainable Energy Reviews*, 2023, **183**, 113509). (b) Various strategies for the synthesis of MOFs/Polymer composites<sup>116</sup> (Adapted with permission from Elsevier (Deeraj, J. S. J., Raman, Asok, Paul, Saritha, and Joseph, *Surfaces Interfaces*, 2023), copyright 2023). (c) Biopolymer-based composite from agricultural waste biomass.<sup>120</sup> Molecular-level strategies for elucidating the mechanisms of pharmaceutical pollutant removal are summarized in Table 11. The benefits and drawbacks of commonly used materials for removing pharmaceutical contaminants are presented in Table 12. Additionally, Table 13 outlines various agricultural wastes utilized for biochar production and their effectiveness in adsorbing antibiotics from water, as well as approaches for the removal of pharmaceuticals from surface water.<sup>121</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, TG, Y. G., *et al.*, Biopolymer-based composites: an eco-friendly alternative from agricultural waste biomass, *Journal of Composites Science*, 2023, **7**(6), 242). (d) Nanoparticles, nanofibers and nanoclays<sup>122</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Omanović-Miklićanin, E., *et al.*, Nanocomposites: a brief review, *Health and Technology*, 2020, **10**(1), 51–59).

Table 11 Molecular-level approaches for understanding pharmaceutical pollutant removal mechanisms

Approach	Techniques	Insights provided	References
Molecular-level interaction mechanism	Molecular interaction	Explains pollutant-adsorbent catalyst interactions in detail	123
Spectroscopic characterization	FTIR, XPS, NMR, UV-Vis	Functional group changes, surface interactions, oxidation states	124
Theoretical calculations	DFT simulations	Adsorption sites, binding energies, and electronic interactions	125
Combined approach	Experimental + computational	Comprehensive understanding of interaction mechanisms	126

dimensional structures composed of organic ligands and metal ions. Because of the unique hybrid structure comprising inorganic and organic components, MOFs have become highly tunable. For this reason, they find applications in catalysis, water purification, and the removal of gases and toxic chemicals. Because of the crystalline, porous, and fragile nature of MOFs, their properties are very different from those of

polymers, which are pliable, malleable solids that are processed by processing routes. Recently, crystalline MOFs have been hybridized with flexible polymers to create new materials with combined features of both.<sup>116</sup> Covalent organic frameworks (COFs) are crystals made from light elements (such as carbon, hydrogen, oxygen, nitrogen, and sulfur) and are characterized by their long-range ordered structure, controlled pore sizes,



Table 12 Advantages and limitations of common materials for pharmaceutical pollutant removal

Material type	Key advantages	Key limitations
Activated carbon (AC)	High surface area, strong adsorption, widely available	Costly regeneration, nonselective, potential secondary pollution
Biochar/hydrochar	Renewable, low-cost, tunable surface chemistry	Variable quality, lower adsorption than AC
Metal oxides (Fe, Cu, TiO <sub>2</sub> , etc.)	Effective catalytic degradation, reusable, stable	Agglomeration, limited selectivity, possible metal leaching
Bimetallic composites (FE-CU, FE-NI, and ETC)	Synergistic effects, enhanced catalytic activity, fast removal	Complex synthesis, higher cost, metal leaching risk
Polymeric adsorbents	Selective adsorption, functional group tunability	Limited thermal/chemical stability, expensive, slower kinetics
Magnetic nanomaterials	Easy magnetic separation, high surface area	Synthesis cost, aggregation, potential toxicity

Table 13 Agricultural wastes used for biochar production and the adsorption of antibiotics from water<sup>221</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Onyekachukwu, E., et al., Low-Cost Adsorbents for the Removal of Pharmaceuticals from Surface Waters, *Water*, 2025, 17(17), 2619)

Biochar feedstock	Antibiotic	Modification agent	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	pH	Adsorption capacity (mg g <sup>-1</sup> )	References
Banana	Furazolidone	FeCl <sub>2</sub> ·4H <sub>2</sub> O	116.97	7.5	37.45	127
Bamboo	Sulfamethoxazole	Fe <sub>2</sub> O <sub>3</sub>	61.48	6	212.8	128
Corn stalk	Enrofloxacin	KOH	22.69	3	58.29	129
Pine wood	Daptomycin	Fe <sub>3</sub> O <sub>4</sub>	634.218	4	212.77	130
Poplar	Tetracycline	KOH	1.61	5	21.17	131
Reed stalk	Florfenicol	FeSO <sub>4</sub> ·7H <sub>2</sub> O	254.6	6	9.29	132

high degree of crystallinity, good thermal stability, large specific surface area, and low density, and they have received considerable attention for applications in various areas. However, their application and large-scale synthesis are hindered because the powdered materials are not recyclable.<sup>118</sup> The biocomposites are considered efficient adsorbents to remove contaminants from wastewater. Bentonite showed good removal behavior for most common industrial pollutants due to its surface being negatively charged. It is generally functionalized with other materials so that the drawbacks can be overcome and its adsorption efficiency performance can be enhanced.<sup>119</sup> Fig. 10(c) biopolymer-based composite from agricultural waste biomass.<sup>120</sup> Molecular-level strategies for elucidating the mechanisms of pharmaceutical pollutant removal are summarized in Table 11. The benefits and drawbacks of commonly used materials for removing pharmaceutical contaminants are presented in Table 12. Additionally, Table 13 outlines various agricultural wastes utilized for biochar production and their effectiveness in adsorbing antibiotics from water, as well as approaches for the removal of pharmaceuticals from surface water.<sup>121</sup>

Some of the vital parameters that need to be tested are as follows: (1) batch-to-batch consistency. (2) Testing for hazards and risks. (3) Testing the robustness of the process under variable conditions. (4) Yield or the extent of the reaction regarding the conversion of reactants to products.<sup>133</sup> The formed composite material has been successfully used in drug delivery and demonstrated to be biocompatible.<sup>133</sup> Fig. 10(d) nanoparticles, nanofibers and nanoclays.<sup>122</sup>

Nearly half of the studies (45%) focused on using natural clay minerals as adsorbents. The other 55% were dedicated to creating new, enhanced adsorbents by modifying or combining clay minerals using different techniques. This included: biopolymers (16%), metal pillared-clay minerals (11%), and organocations (17%).<sup>134</sup> Fig. 11(a) sources and chemical structures of natural biopolymers used in bionanocomposite fabrication.<sup>135</sup> In a water purification system, clay can remove about 70% of the waste. Removal of the final 30% can be achieved by utilizing activated carbon.<sup>136</sup> The mechanisms of adsorption of the clay minerals through liquid and gaseous phases are: (i) physical and nonionic adsorption: weak physical forces are involved, such as van der Waals interactions. (ii) Ion exchange: an electrostatic process in which ions from the clay structure are exchanged with ions of the substance. (iii) Zeolite action: the ability of the porous clay to selectively trap and release molecules, similar to the actions of a zeolite.<sup>137</sup> Such modifications render them very effective for the adsorption of organic molecules. Because of this, they are used to clean up organic-contaminated soils and water.<sup>138</sup> Soil clay minerals act as a natural filter, cleaning water by removing pollutants through ion exchange and adsorption. This makes them effective and tough enough for use in a variety of environmental conditions.<sup>139</sup> By changing the reaction conditions, many types of organoclays have been prepared.<sup>140</sup> Pillared clays are another type of heterogeneous catalyst prepared from clays. Their wide applications in various organic reactions are due to their enhanced reactivity, porosity, thermal stability, reactivity and selectivity.<sup>141</sup>



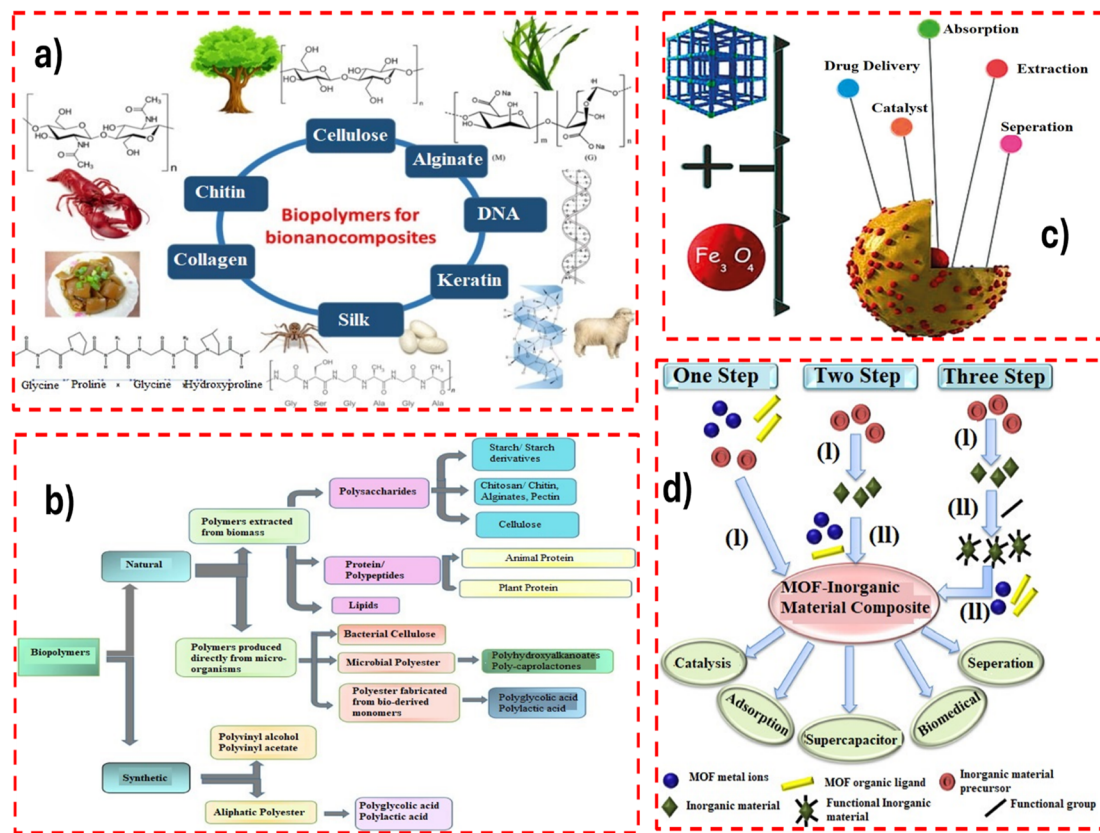


Fig. 11 (a) The molecular structures and sources of naturally derived biopolymer components for bionanocomposites<sup>135</sup> (Adapted with permission from Elsevier (Xiong *et al.*, *Mater. Sci. Eng., R*, 2018), copyright 2018). (b) Broad biopolymer classifications<sup>142</sup> (Adapted with permission from Elsevier (Sharma, Malik and Jain, *Mater. Today Commun.*, 2018), copyright 2018). (c) Synthesis of metal-organic frameworks<sup>143</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Aghayi-Anaraki, M., Safarifard, V., *Fe<sub>3</sub>O<sub>4</sub>@ MOF magnetic nanocomposites: Synthesis and applications*, *European Journal of Inorganic Chemistry*, 2020, 2020(20), 1916–1937). (d) Schematic of the synthesis and application of a MOF-inorganic material composite framework<sup>144</sup> (Adapted with permission from Elsevier (Rani, Kasnerky and Opanasenko, *Appl. Mater. Today*, 2022), copyright 2022).

### Limitations of surfactant-modified clay

Despite these advantages, surfactant modification of clay has certain disadvantages, including contaminant specificity, concentration dependency, and an unclear impact on surface area.<sup>145</sup> Any polymer that is synthesized biologically or produced from biological materials is a biopolymer. Such polymers are biodegradable and often biocompatible. Microorganisms break these materials down completely into harmless natural elements, such as biomass, water and carbon dioxide, without producing any harmful byproducts during the process. Biopolymers may be divided into three types: (1) polysaccharide-based: examples include starch, chitosan and cellulose. (2) Protein-based: examples include whey protein, gelatin, and soy protein. (3) Microbial-derived: examples include polylactic acid and polyhydroxyalkanoates.<sup>146</sup> Fig. 11(b) depicts the general categories of biopolymers.<sup>142</sup> Agricultural byproducts and non-food waste materials form substantial feedstock for producing bioplastics. Manufacturing bioplastics from waste will increasingly enhance the sustainability of the agricultural economy, thus providing additional economic, social, and environmental benefits.<sup>147</sup> Fig. 11(c) synthesis of

metal-organic frameworks.<sup>143</sup> Biocomposites derived from biopolymers are perfect for the creation of non-structural interior auto parts. In general, this creates the possibility to solve some of the most pressing environmental and economic problems.<sup>148</sup> Fig. 11(d) schematic summary of the MOF inorganic material composite framework synthesis and application.<sup>144</sup> Reinforcement is critical because these bio-based polymers naturally have high rates of water permeability and are biodegradable, which can limit their durability in construction applications. More than 100 types of agricultural waste are capable of generating a broad spectrum of biopolymers.<sup>149</sup> Fig. 12(a) synthesis and types of chemically altered clay minerals used for the adsorption and removal of pollutants.<sup>145</sup>

The application of innovative technologies must be stimulated for processing the bio-based raw materials (agricultural waste) into valuable biofertilizers.<sup>151</sup> Fig. 12(b) Impact of heavy metals on the human body.<sup>150</sup> Sustainable agriculture in the 21st century will have to depend on research and development of new, renewable feedstocks for biopolymers in farming situations.<sup>152</sup> Owing to their outstanding characteristics, bio-based polymers are widely utilized in various aspects. In medicine, they are commonly applied in regenerative medicine, bone



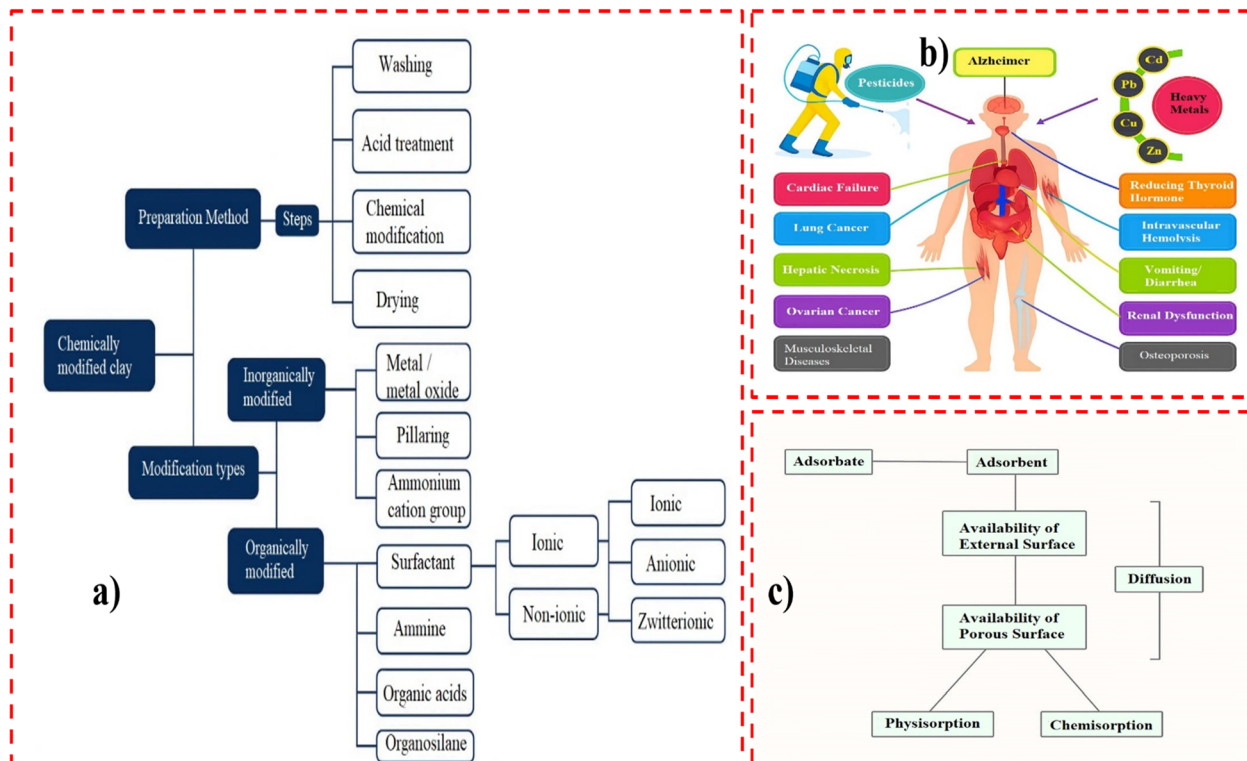


Fig. 12 (a) Modification types and synthesis steps of chemically modified clay minerals and adsorption of contaminants<sup>145</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Alomari, A. D. A., Chemically modified clay for adsorption of contaminants: trends, advantages and limitations—a concise review, *International Journal of Environmental Analytical Chemistry*, 2025, **105**(10), 2302–2325). (b) Impact of heavy metals on the human body<sup>150</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Maftouh, A., et al., Comparative review of different adsorption techniques used in heavy metals removal in water, *Biointerface Research and Applied Chemistry*, 2023, **13**(4)). (c) Schematic of the adsorption pathway and techniques<sup>150</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Maftouh, A., et al., Comparative review of different adsorption techniques used in heavy metals removal in water, *Biointerface Research and Applied Chemistry*, 2023, **13**(4)).

implants, drug delivery, tissue engineering and regenerative medicine.<sup>153</sup> The development of regenerative and clean sources of energy is an imperative approach to satisfy the increasingly growing demand for energy worldwide and to address the ecological concerns arising from the overexploitation of different resources.<sup>154</sup> Fig. 12(c) illustrative flowchart of adsorption pathways and techniques.<sup>150</sup> Surfactant-modified clays have enhanced affinity toward pharmaceutical pollutants; however, limited stability and risk of surfactant leaching reduce their practical use, and a decrease in performance is observed when the water matrices become more complex. Recent investigations have demonstrated that these constraints can adversely affect reusability and long-term operational efficiency. Thus, overcoming these limitations is still integral to developing surfactant-modified clays into effective pharmaceutical wastewater remediators.

### Factors affecting adsorption efficiency

The effectiveness of liquid phase adsorption and, thus, the best way to run a water treatment process, is affected by various key factors. Adsorption efficiency is governed by several physico-chemical parameters, including the surface chemistry and pore structure of the adsorbent, the nature of adsorbent–adsorbate

interactions, solution pH, temperature, contact time, pressure, particle size, and the presence of competing ions or other co-existing species.<sup>155</sup> Fig. 13(a) graphical representation of factors affecting adsorption efficiency.

(1) Effect of solution pH: the pH is a crucial factor for effective adsorption because it influences how the adsorbent (the material doing the adsorbing) and the adsorbate interact. The optimal pH is necessary to achieve maximum extraction percentage for a given antibiotic. (2) Effect of contact time between adsorbate and adsorbent: With respect to this parameter, despite the goal of reducing operational time, a sufficiently long optimum contact time is necessary to attain maximum removal efficiency. This ensures that a sufficient amount of the substance, such as antibiotics, is removed. (3) Effect of the initial concentrations of adsorbate and adsorbent: the initial amounts of both the adsorbate (the substance being removed) and the adsorbent (the material doing the removal) determine when the system becomes saturated, a point known as breakthrough. Once breakthrough occurs, the adsorbate starts to pass through without being treated. Conversely, increasing the adsorbent dosage results in better removal, although this will also raise the operational cost.<sup>156</sup> Fig. 13(b) factors affecting on adsorption process. (4) Surface chemistry: a key factor is surface



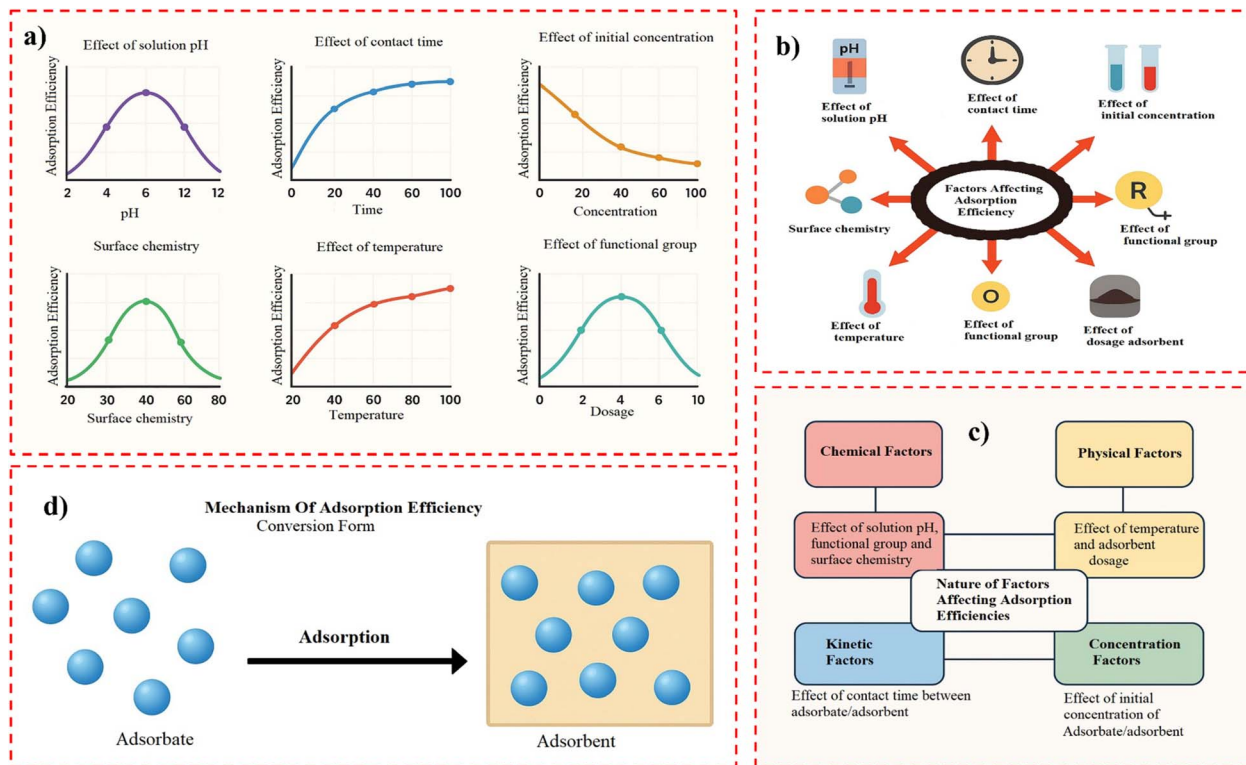


Fig. 13 (a) Graphical representation of factors affecting the adsorption efficiency. (b) Factors affecting the adsorption process. (c) Flowchart of the nature of factors affecting adsorption. (d) Mechanism of adsorption.

chemistry, specifically the types and number of functional groups present. Surface functional groups form when unsaturated carbon atoms on a material's surface bond with atoms such as sulfur, hydrogen, oxygen, halogens and nitrogen. This process takes place during carbonization. (5) Effect of temperature: upon elevating the temperature within the adsorbent bed, the adsorption capacity decreases. This happens because the adsorbed molecules acquire more energy, allowing some to overcome the weak van der Waals forces. To reduce the risk of fire, continuous monitoring is required for carbon monoxide concentrations and temperature, as well as any operating parameters that directly impact thermal conditions.<sup>157</sup> Fig. 13(c) flowchart of nature of factors affecting on adsorption. Fig. 13(d) mechanism of adsorption. (6) Effect of functional groups: a larger charge transfer shows a stronger interaction, corresponding to a higher adsorption energy. Despite the fact that no atomic rearrangement or destruction was observed, some models still showed adsorption energies higher than  $-50 \text{ kJ mol}^{-1}$ . When two functional groups are located next to each other on a surface, the combined effect generally results in a higher adsorption energy than that of a single, isolated functional group.<sup>158</sup> Fig. 14(a) various forms of adsorbent-adsorbate interactions.<sup>159</sup> (7) Effect of dosage of adsorbent: adsorption efficiency was measured at set time intervals for each dose, while all other conditions remained constant. The adsorption efficiency was evaluated as a function of time by systematically varying the adsorbent dosage.<sup>160</sup> Fig. 14(b) analysis of experimental variables affecting adsorption capacity: this

includes (a) pH, (b) adsorbent dose (at  $50 \text{ mg L}^{-1}$ , 30 min, and  $25 \text{ }^\circ\text{C}$ ), (c) contact time (at  $20 \text{ mg}$  dose, pH 9, and  $25 \text{ }^\circ\text{C}$ ), and (d) initial CV concentration (at  $20 \text{ mg}$  dose, pH 9, and 30 min).<sup>161</sup> Fig. 14(c) results of adsorption kinetics model fitting compared with the experimental kinetic data for (a) benzene and (b) toluene on activated carbon (AC). (Experimental conditions: 10–70 min adsorption time,  $100 \text{ mL min}^{-1}$  gas flow rate,  $0.07 \text{ g}$  adsorbent amount, and optimized initial concentration and temperature).<sup>162</sup> Adsorption efficiency in pharmaceutical removal can be affected by the properties of the material itself, such as surface area, functional groups, and charges on the surface, and by the operational conditions, which include pH, contact time, temperature, and concentration of the substance to be removed. It has been revealed that significant roles are played by these factors in determining the efficiency of the adsorption process. Table 14 show the adsorption capacities and kinetic parameters and Table 15 represented recyclability and reusability of adsorbents.<sup>163</sup>

### Target pollutants and adsorption behavior

The widespread use of pharmaceuticals and dyes poses a global environmental risk with respect to their discharge. Annually, approximately 7 million tons of dyes and 100 000 to 200 000 tons of antibiotics are used worldwide.<sup>170</sup> The primary routes of pharmaceutical contamination into water bodies are discharges from drug production plants and municipal sewage systems, and from hospital effluents. These compounds are considered hazardous. Advanced oxidation processes (AOPs), which



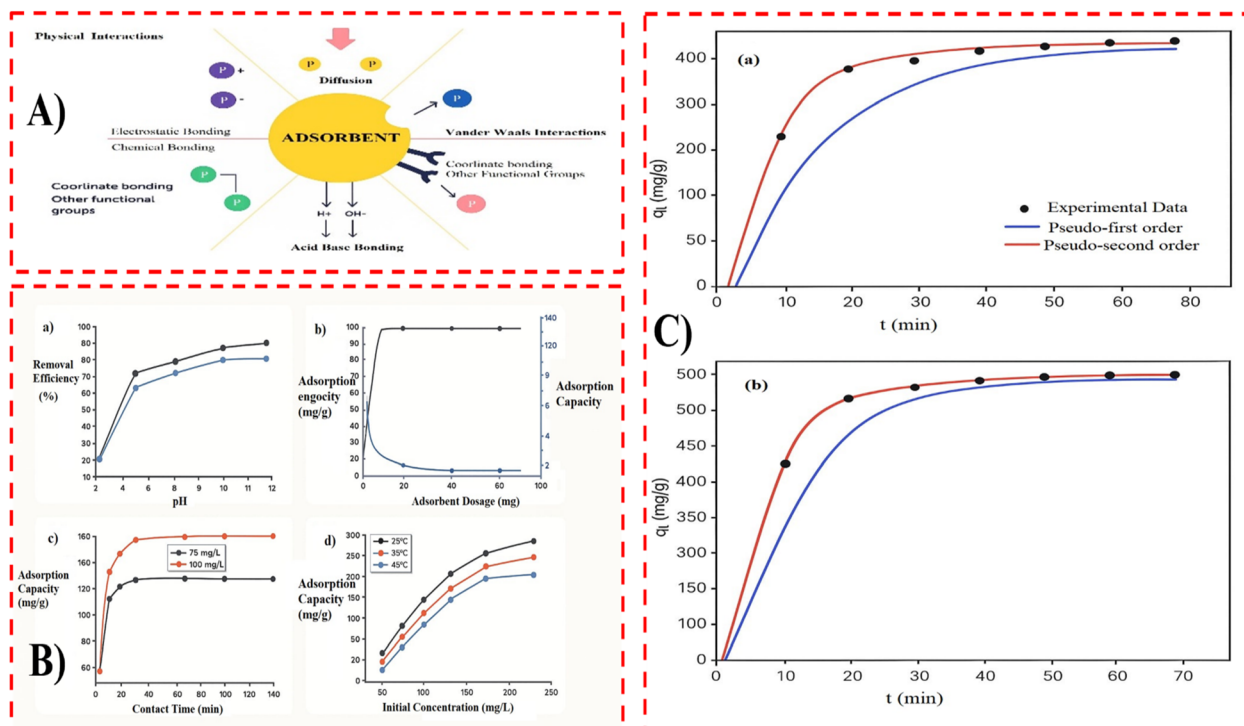


Fig. 14 (A) Various forms of adsorbent–adsorbate interactions<sup>159</sup> (Adapted with permission from Elsevier (Natarajan *et al.*, *Chemosphere*, 2022), copyright 2022). (B) Analysis of experimental variables affecting adsorption capacity: effects of pH (a), adsorbent dose ( $C_0$ –50 mg L; time–30 min; and  $T$ –25 °C) (b), contact time (dose–20 mg; pH–9; and  $T$ –25 °C) (c) and initial CV dye concentration (dose – 20 mg; pH–9; and time–30 min) (d) on adsorption capacity<sup>161</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Al-Shehri, H. S., *et al.*, Effective adsorption of crystal violet from aqueous solutions with effective adsorbent: equilibrium, mechanism studies and modeling analysis, *Environmental Pollutants and Bioavailability*, 2021, 33(1), 214–226). (C) Adsorption kinetics model fitting results and experimental kinetics of benzene<sup>162</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Baytar, O., *et al.*, High-performance gas-phase adsorption of benzene and toluene on activated carbon: response surface optimization, reusability, equilibrium, kinetic, and competitive adsorption studies, *Environmental Science and Pollution Research*, 2020, 27(21), 26191–26210).

Table 14 Adsorption capacities and kinetics

Adsorbent type	Pharmaceutical targets	Max adsorption capacity ( $\text{mg g}^{-1}$ )	Kinetic model	References
Wood-derived engineered sponge	Tetracycline	~863.8	Pseudo second order	22
Wood-derived biochar	Diclofenac	~350.0	Pseudo second order	22
Activated biochar (ASBS)	Tetracycline	~402.7	Pseudo second order	164
Nitrogen-doped graphene	Diclofenac	~278	Pseudo second order	103
Graphene oxide (GO)	Trimethoprim	~218	Pseudo second order	103
Activated carbon	Tetracycline	~909	Pseudo first order	103
Activated carbon (walnut)	Diclofenac and others	~2.5–3.0	Pseudo first order	103
Chitosan-GO hydrogel	Diclofenac	~129–131	Pseudo second order	165
Magnetic chitosan composites	Carbamazepine	~95% removal in 25 min	Pseudo second order	165
MOF-derived adsorbents	Gemifloxacin	~876	Pseudo second order	103

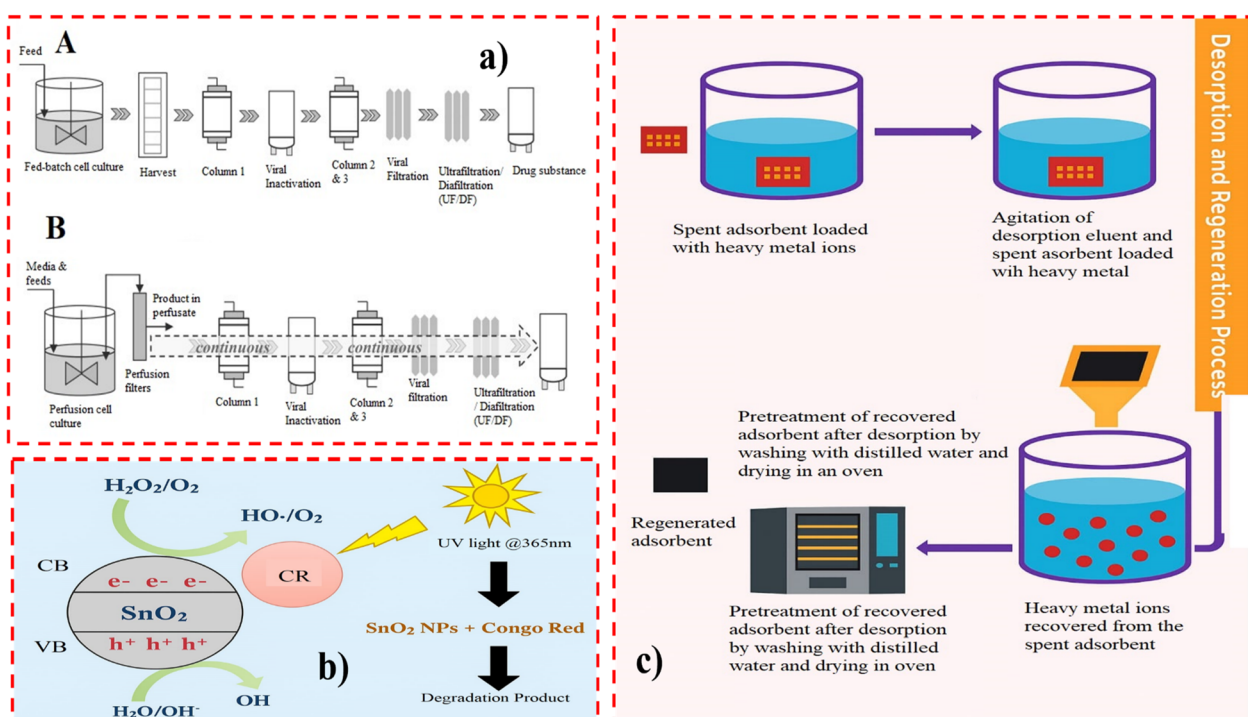
include methods such as ozonation, the Fenton process, and photocatalysis, have been shown to effectively degrade synthetic contaminants.<sup>171</sup> This has led to an increased focus on finding adsorbents that are highly efficient, safe, and affordable.<sup>172</sup> Antibiotics are a type of pharmaceutical that often ends up in the environment, contaminating water and soil. Bacterial resistance occurs when bacteria that were once vulnerable to an antibiotic become resistant to it. This can be caused by the overuse of antibiotics and improper treatment of wastewater.<sup>173</sup> As a result, the contaminated adsorbents then become

a disposal concern, meaning that adsorption alone is not a complete solution for the issue of antibiotic residue.<sup>174</sup> Continuous processes are typically more cost-effective than batch processes because batch processes have higher energy consumption due to start-up times and increased raw material costs, since materials are recycled less frequently. However, a key advantage of batch processing is the ability to combine multiple tasks into a single, larger unit.<sup>175</sup> Continuous technology is considered advantageous for commercial production because it allows for flexible changes in production quantities



**Table 15** Regeneration and reuse performance<sup>163</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Siyal, A. A., et al., A review of the developments in adsorbents for the efficient adsorption of ibuprofen from wastewater, *RSC Advances*, 2025, 15(23), 17843–17861)

Adsorbent	Regeneration method	Number of cycles tested	Retention	References
Graphene oxide nanoparticles (GONPs)	Methanol	10	~95.9%	166
Carbon nanospheres (CNs)	DW wash	6	~16.9%	167
Pepper stem biochar	NaOH	4	~22%	168
PMLE-E adsorbent	Methanol	8	~22%	169



**Fig. 15** (a) Schematics of monoclonal antibody manufacturing processes: (A) traditional fed batch process, and (B) continuous manufacturing process<sup>177</sup> (Adapted with permission from Elsevier (Madabhushi, Pinto and Lin, *New Biotechnol.*, 2022), copyright 2022). (b) Possible mechanism of photocatalytic degradation<sup>186</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Titus, D., Samuel, E. J. J., Photocatalytic degradation of azo dye using biogenic SnO<sub>2</sub> nanoparticles with antifungal property: RSM optimization and kinetic study, *Journal of Cluster Science*, 2019, 30(5), 1335–1345). (c) Desorption and regeneration processes.<sup>195</sup> Table 16 presents fundamental mechanisms involved in the adsorption of heavy metals onto engineered adsorbents.<sup>194</sup> (Adapted with permission from Elsevier (Bayuo et al., *Adv. Colloid Interface Sci.*, 2024), copyright 2024).

and is easy to scale up. The use of continuous technology is expanding to include the production of active pharmaceutical ingredients (APIs) for both small molecules and biopharmaceuticals.<sup>176</sup> The product is continuously harvested by removing the old medium and replacing it with fresh medium.<sup>177</sup> Continuous production dramatically enhances the efficiency of the primary capture resin, resulting in a substantial 68% decrease in consumable costs.<sup>178</sup> One advantage of batch processing is its flexibility. Conversely, continuous processes must operate year-round at a large scale to be profitable.<sup>179</sup> Fig. 15(a) comparative schematics of monoclonal antibody production methods: illustrating the (A) traditional fed-batch process versus the (B) continuous manufacturing process.<sup>177</sup> Used adsorbents are often treated as waste, but their disposal

can be harmful to the environment because they may contain toxic, adsorbed compounds. To address this, an environmentally friendly alternative is to desorb the pollutants and regenerate the adsorbents for reuse.<sup>180</sup> Saturated adsorbents can be regenerated, and pollutants recovered using several methods, including chemical (acids, alkalis, other chemicals) regeneration. The maximum desorption capacities for these techniques were found to be 99.5%, 92.6%, 284%, 150%, and 66.61%, respectively.<sup>181</sup> Adsorption using activated carbon is considered a superior way to treat both water and wastewater. It stands out from other chemical and physical techniques because of its highly efficient adsorption of diverse pollutants, its rapid adsorption rate, and its simple design.<sup>182</sup> Adsorption techniques are particularly advantageous for environmental cleanup and



**Table 16** Adsorption mechanisms of heavy metals onto adsorbents<sup>194</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Wang, J., Guo, X., Adsorption kinetics and isotherm models of heavy metals by various adsorbents: An overview, *Critical Reviews in Environmental Science and Technology*, 2023, 53(21), 1837–1865)

Adsorption mechanism	Adsorption process	References
Ion exchange	Specific examples include the adsorption of modified biochar onto nanostructured zeolites	194
Electrostatic interaction	Specific examples of adsorption applications include the removal of Cr onto protonated Fe <sub>2</sub> O <sub>3</sub> surfaces, Cd onto MoS <sub>2</sub> and metals onto specialized chelating resins and magnetic chitosan composites	195
Van der Waals interaction	Specific adsorption applications include the removal of Cd onto MoS <sub>2</sub> composites	195
Hydrogen bonding	Specific applications demonstrated the adsorption of microplastics onto a chitosan magnetic composite	196
Establishment of strong bonds	Specific applications demonstrated the adsorption of brown algae and fungi onto graphene oxide	197

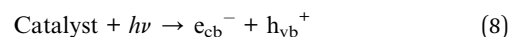
sustainability because they utilize common and effective materials such as activated carbon, clay minerals, silica gel, zeolites, and polymers.<sup>183</sup> In this regard, graphene materials are also very promising as next-generation conventional adsorbent replacements for the control of environmental pollution, representing very important scientific values. They feature strong adsorption capability and excellent recyclability.<sup>184</sup> Regeneration processes allow used adsorbents to be retrieved and reused multiple times with no significant drop in performance. Reuse and regeneration, often achieved through an inexpensive process such as desorption, is crucial when adsorbents are used for wastewater treatment outside of their original location. Reusing adsorbents is beneficial because it reduces costs and the need for material disposal.<sup>185</sup> Fig. 15(b) Possible mechanism of photocatalytic degradation.<sup>186,187</sup> The repeatability and reusability tests demonstrate that the photocatalyst exhibits high structural and catalytic stability.<sup>188–190</sup> Regeneration is a crucial part of the adsorption process from both economic and environmental perspectives. There are several regeneration methods that have yielded mixed results, including solvent washing, and thermal, chemical, and electrochemical regeneration. To make adsorption a more economical, valuable, and important method for treating wastewater, it is crucial to focus on regenerating and reusing the adsorbent, as well as recovering the solute.<sup>191</sup> Percentage desorption was calculated as:<sup>192</sup>

$$\text{Desorption efficiency(\%)} = \frac{C_{\text{de}}}{C_{\text{ad}}} \times 100 \quad (7)$$

where  $C_{\text{ad}}$  denotes the amount of metal ions adsorbed, and  $C_{\text{de}}$  is the concentration of metal ions desorbed.<sup>192</sup> Fig. 15(c) desorption and regeneration process.<sup>193</sup> Table 16 presents fundamental mechanisms involved in the adsorption of heavy metals onto engineered adsorbents.<sup>194</sup>

Photocatalytic degradation (PCD) is an increasingly important method for treating wastewater, particularly for water containing small amounts of stubborn organic pollutants. It offers several key advantages over other processes. Complete mineralization: it can break down pollutants entirely. No waste: it does not create a secondary waste disposal problem. Low cost:

it is an economical option. Mild conditions: it operates effectively under mild temperatures and pressure. A good photocatalyst needs to have several key qualities: it must be photoactive, meaning it can be activated by light (either visible or near UV light), and it should be cheap and nontoxic.<sup>198</sup> Fig. 16(a) basic process flow for common biochar modification techniques.<sup>199</sup> Photocatalysis proven to be an effective method for the reduction of high-valent metal ions to their low-valent states as well as the degradation of organic pollutants under irradiation. Besides the selective interaction between target molecules and porous materials, other important parameters that can enhance the efficiency of photocatalysis include strong light absorption ability and efficient separation of electron-hole pairs.<sup>200</sup> Photocatalytic reactions initiate a reaction when the catalyst absorbs a photon that has an energy higher than or equal to the band-gap energy ( $E_{\text{bg}}$ ) of the catalyst.<sup>201</sup> When a photocatalyst is exposed to UV light, an electron in the valence band gets a boost of energy and jumps to the conduction band, leaving behind a positively charged “hole” in the valence band. This process creates an electron-hole pair and is the initial step in the photocatalytic discoloration of a dye.<sup>202</sup>



Here,  $e_{\text{cb}}^-$  = electrons in the conduction band and  $h_{\text{vb}}^+$  = electron vacancy in the valence band.<sup>202,203</sup> AOPs developed for treating drinking water in the 1980s are today applied to a broad range of wastewaters. In AOP treatment, hydroxyl radicals ( $\text{OH}^\bullet$ ) or sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) are generated. These powerful radicals can remove recalcitrant organic pollutants, trace contaminants, and even some inorganic substances.<sup>204</sup> These two main steps are common to all advanced oxidation processes, namely, *in situ* production and their subsequent reaction with target pollutants.<sup>205</sup> Various techniques have been developed within this area of AOP, enabling the most appropriate options to be selected for particular treatment needs. Currently available cost analyses indicate that AOP systems are no more expensive than conventional pollutant removal technologies.<sup>206</sup> Fig. 16(b) mechanisms of biochar adsorption of pollutants in wastewater.



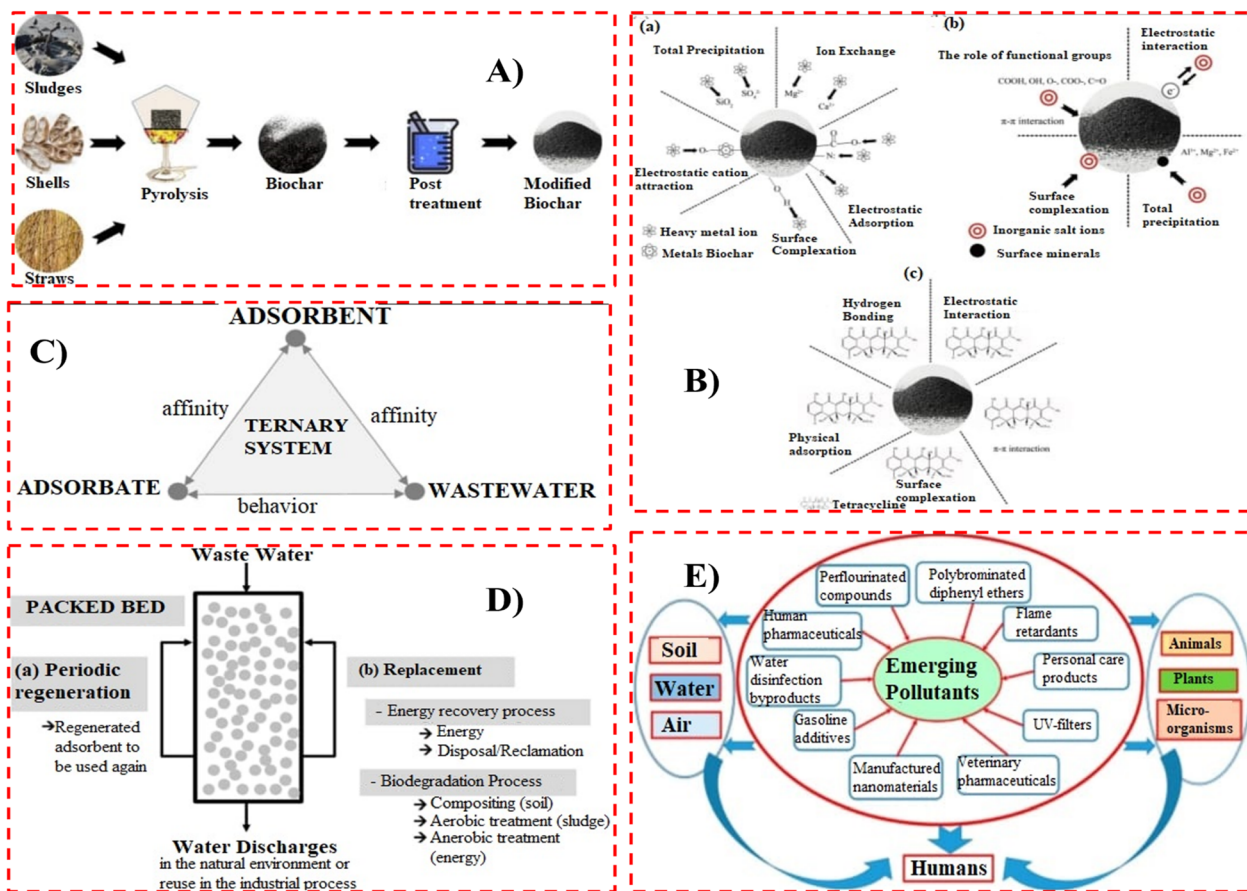


Fig. 16 (A) Simplified process scheme for common modified biochar preparation<sup>199</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Wang, Y., et al., Research status, trends, and mechanisms of biochar adsorption for wastewater treatment: a scientometric review, *Environmental Sciences Europe*, 2024, 36(1), 25). (B) Mechanisms of biochar adsorption of pollutants in wastewater. (a) Mechanisms of biochar adsorption of heavy metals. (b) Mechanisms of inorganic salt adsorption by biochar. (c) Mechanisms of tetracycline adsorption by biochar<sup>199</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Wang, Y., et al., Research status, trends, and mechanisms of biochar adsorption for wastewater treatment: a scientometric review, *Environmental Sciences Europe*, 2024, 36(1), 25). (C) Relationships between the three components of an adsorption system<sup>94</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Crini, G., et al., Conventional and non-conventional adsorbents for wastewater treatment, *Environmental Chemistry Letters*, 2019, 17(1), 195–213). (D) The two main strategies, regeneration step and replacement, that can be used to treat spent adsorbent after its usage<sup>94</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Crini, G., et al., Conventional and non-conventional adsorbents for wastewater treatment, *Environmental Chemistry Letters*, 2019, 17(1), 195–213). (E) Classifications of EPs that influence soil, atmosphere, aquatic life, animals, microbes, and people<sup>211</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Hashmi, Z., et al., Comparative analysis of conventional to biomass-derived adsorbent for wastewater treatment: a review, *Biomass Conversion and Biorefinery*, 2024, 14(1), 45–76).

Table 17 Representative reactions involving advanced oxidation process (AOP) mechanisms<sup>210</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Silva, J. A., Advanced Oxidation Process in the Sustainable Treatment of Refractory Wastewater: A Systematic Literature Review, *Sustainability*, 2025, 17(8))

AOP method	Representative reaction	References
Ozonation	$O_3 + H_2O \rightarrow 2OH + O_2$	212
Fenton reaction	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$	213
Photo Fenton reaction	$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \cdot OH + H^+$	214
UV/H <sub>2</sub> O <sub>2</sub> process	$H_2O_2 + h\nu \rightarrow 2OH$	215
Photocatalysis (TiO <sub>2</sub> -based)	$TiO_2 + h\nu \rightarrow e^- + h^+ + H_2O \rightarrow \cdot OH e^- + O_2 \rightarrow \cdot O^{2-}$	216

(a) Mechanisms of biochar adsorption of heavy metals. (b) Mechanisms of inorganic salt adsorption by biochar. (c) Mechanisms of tetracycline adsorption by biochar.<sup>199</sup>

Application development has been driven by a combination of the following: stricter regulations, pollution of water resources from agricultural and industrial activities, and the need for



industries to meet effluent discharge standards.<sup>207</sup> Advanced oxidation processes (AOPs) encompass a range of techniques, including nonthermal plasmas, UV/O<sub>3</sub>, photo-Fenton, UV/H<sub>2</sub>O<sub>2</sub>, supercritical water oxidation, radiolysis, sonolysis, Fenton and photocatalysis. In contrast, photochemical methods, such as photo-Fenton processes, generally require a precursor (catalyst) to generate these radicals.<sup>208</sup> Fig. 16(c) relationships between the three components of an adsorption system.<sup>94</sup> The ultimate goal is to fully mineralize the substances, yielding nontoxic final products such as carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and mineral acids (in cases where halogens are part of the pollutant).<sup>209</sup> Many municipalities employ AOPs as a supplementary step to eliminate persistent organic and inorganic contaminants. This helps traditional wastewater treatment plants comply with increasingly stringent environmental regulations.<sup>210</sup> Fig. 16(d) Management of spent adsorbents involves either regeneration to restore adsorption capacity or complete replacement of the material once adsorption sites are irreversibly exhausted.<sup>94</sup> Table 17 summarises representative chemical reactions involving advanced oxidation processes (AOPs).<sup>210</sup>

The two primary natural processes for eliminating hazardous compounds from water are photodegradation and biodegradation. Specifically, biodegradation involves the breakdown of pollutants, predominantly using bacteria and fungi naturally present in aquatic and soil environments.<sup>217</sup> Biological treatment, utilizing microorganisms rather than chemicals, is more eco-friendly. However, it can only be used to treat particular types of organic pollutants effectively. Because of this limitation, combining different treatment methods is frequently essential to attain the required level of water purity. Bioremediation, a common biological wastewater treatment method, uses organisms, such as plants, fungi, and algae, to remove emerging contaminants.<sup>218</sup> This metabolic activity enables the effective removal of a broad spectrum of contaminants.<sup>219</sup> Fig. 16(e) classifications of EPs that influence soil, atmosphere, aquatic life, animals, microbes, and people.<sup>211</sup>

The Fenton process is recommended only for highly concentrated dimethyl sulphoxide (DMSO) pre-treatment or for the final polishing after biological treatment, especially when excess hydrogen peroxide is present.<sup>220</sup> Fig. 17(a) the categorization of advanced oxidation processes is based on their

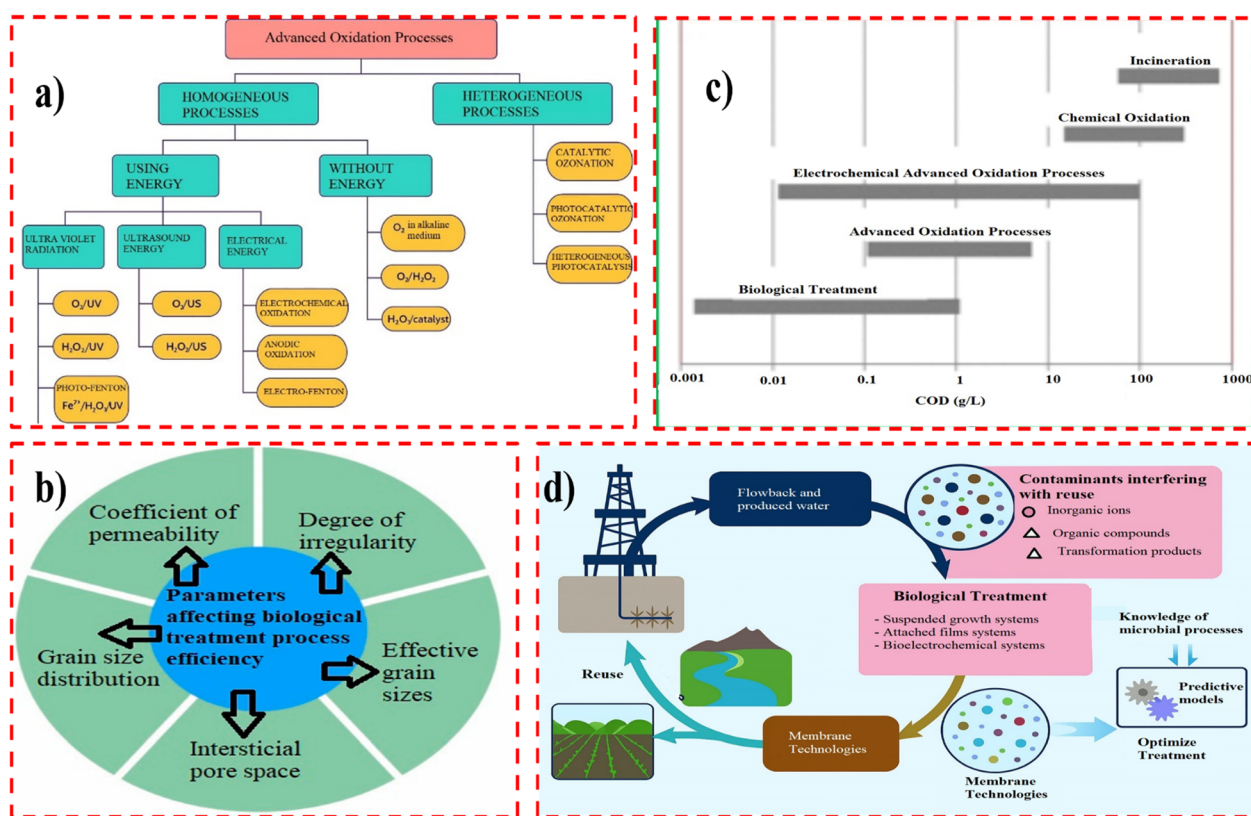


Fig. 17 (a) Advanced oxidation processes (AOPs) classification. Abbreviations used: O<sub>3</sub> ozonation; H<sub>2</sub>O<sub>2</sub> hydrogen peroxide; UV ultraviolet radiation; US ultrasound energy; Fe<sup>2+</sup> ferrous ion<sup>221</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Poyatos, J. M., et al., Advanced oxidation processes for wastewater treatment: state of the art, *Water, Air, and Soil Pollution*, 2010, **205**(1), 187–204). (b) Physical parameters affecting biological treatment efficiency<sup>218</sup> (Adapted with permission from Elsevier (Singh et al., *J. Cleaner Prod.*, 2024), copyright 2024). (c) Applicability of water treatment technologies based on the amount of organic load<sup>223</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Sirés, I., et al., Electrochemical advanced oxidation processes: today and tomorrow, *Environmental Science and Pollution Research*, 2014, **21**(14), 8336–8367). (d) Improvements in biological treatment of flowback and produced water will require a thorough understanding of contaminants and microbial processes involved<sup>224</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Acharya, S. M., Chakraborty, R., Tringe, S. G., Emerging trends in biological treatment of wastewater from unconventional oil and gas extraction, *Frontiers in Microbiology*, 2020, **11**, 569019).



**Table 18** Summary of the wide array of pharmaceutical compounds (PCs), their use, and environmental effects in aqueous matrices<sup>78</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License. Chauhan, S., et al., Biochar-mediated removal of pharmaceutical compounds from aqueous matrices via adsorption. *Waste Disposal & Sustainable Energy*, 2023, 5(1), 37–62)

Pharmaceutical class	PCs	Therapeutic use	Adverse effects when left untreated in the environment	References
Analgesic	Ibuprofen (IBP)	Analgesic drug and NSAID	Endocrine-disrupting effects and neurological system damage in organisms, along with degradation of freshwater and groundwater quality	225 and 226
	Ketoprofen (KETO) Naproxen (NPX)	Analgesic drug and NSAID	Aggregation in soil is a concern. Even more critically, aquatic organisms suffer long-term detrimental effects from continuous exposure to concentrations as low as nanograms to micrograms	
	Diclofenac (DFC)	NSAID	Poisonous or damaging effects on a wide range of organisms	
	Acetaminophen (ACE)	Antipyretic analgesic	Due to the shedding of diverse metabolites, aquatic ecosystems face acute toxicity. A further significant consequence is the promotion of antibiotic resistance in bacterial populations	
Antibiotic	Ciprofloxacin (CFX) Sulfamethoxazole (SMX)	Synthetic antibiotic Veterinary antibiotic and human	Adversely impacts surface quality Bioaccumulation in aquatic life drives the emergence of antibiotic-resistant genes throughout the ecosystem	227 and 228
	Chlortetracycline (CTC)	Veterinary antibiotic	The effects include histological alterations in the gills of fish, often resulting from pro-oxidative activity (a stress response). Additionally, there is concurrent growth	
Antimicrobial	Levofloxacin (LEV)	Bacterial antibiotic	The rise of antibiotic-resistant pathogens in humans and animals	229 and 230
	Triclosan (TCS)	Antimicrobial ingredient	Human impacts involve disorders of the endocrine system, the development of cancerous growths, and disturbances in thyroid hormone regulatory pathways	
Anticonvulsant	Carbamazepine (CBZ)	Antiepileptic	Its minimal degradation capacity results in its bioaccumulation and, consequently, its toxic effects	231 and 232
Stimulant drug	Caffeine (CAF)	Stimulant drug	The substance negatively affects diverse marine and aquatic species, including sponges, bivalves, microalgae and corals	233 and 234
Antihypertensive	Propranolol (PRO)	Beta-blockers	Due to the challenges associated with limiting its mobility in natural soil and sediment environments	235
	Atenolol (ATO)		The compound bioaccumulates in aquatic organisms and induces alterations in testosterone levels in male individuals	
	Metoprolol (MTP)			

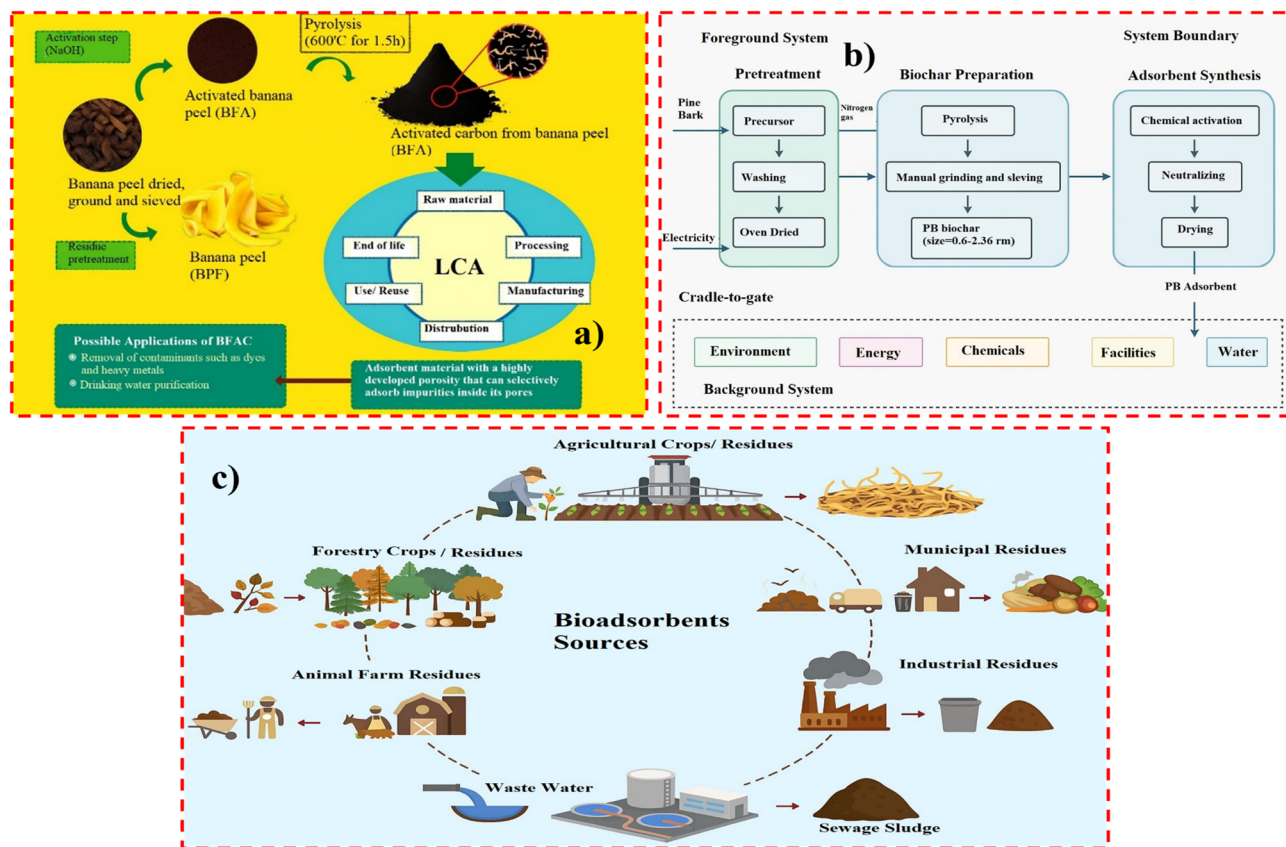


Fig. 18 (a) Interpretation of life-cycle assessment<sup>240</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Pereira, P. H. F., *et al.*, Prospective life cycle assessment (LCA) of activated carbon production, derived from banana peel waste for methylene blue removal, *Adsorption*, 2024, **30**(6), 1081–1101). (b) System boundary for the cradle-to-gate LCA modelling of the present study<sup>241</sup> (Adapted with permission from Elsevier (Nandikes *et al.*, *J. Ind. Eng. Chem.*, 2025), copyright 2025). (c) Source of biosorbents<sup>248</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Almeida-Naranjo, C. E., *et al.*, Transforming waste into solutions: Raw and modified biosorbents for emerging contaminant removal, *Journal of Environmental Chemical Engineering*, 2025, **13**, 116720).

primary components. Key abbreviations used in this classification are: ozonation, hydrogen peroxide, ultraviolet radiation, ultrasound energy and ferrous ion.<sup>221</sup> Biological methods are the most effective for treating this type of wastewater. The use of a combination of anaerobic digestion followed by an aerobic system improves treatment efficiency while reducing both energy consumption and sludge production.<sup>222</sup> Fig. 17(b) physical parameters affecting biological treatment efficiency.<sup>218</sup> Fig. 17(c) applicability of water treatment technologies based on the amount of organic load.<sup>223</sup> Adsorption behavior strongly depends on the physicochemical properties of the target pharmaceutical pollutants, including molecular structure, charge, and hydrophobicity. These properties govern interaction mechanisms such as electrostatic attraction,  $\pi$ - $\pi$  interactions, and hydrogen bonding with adsorbent surfaces. Therefore, understanding pollutant-specific adsorption behavior is crucial for designing selective and high-performance adsorption systems. Table 18 presents a comprehensive summary of various pharmaceutical compounds, their applications, and their environmental impacts in aquatic systems.<sup>78</sup>

### Environmental and economic sustainability

The conversion of agricultural and biomass waste into valuable products is an important step within a circular bioeconomy for the sustainable use of resources. There is a need to evaluate these waste products to quantify their environmental impact and benefits.<sup>236</sup> Fig. 17(d) effective advancement in the biological treatment of flowback and water necessitates a comprehensive understanding of the pollutants and the associated microbial processes.<sup>224</sup> A life cycle assessment has been systematically used. This LCA was specifically designed to compare the environmental outcomes associated with producing adsorbents from different types of algae for producing specific adsorbents.<sup>237</sup> The main aim was to find which life stages or processes for each adsorbent contributed the most to negative environmental impacts. The Life Cycle Assessment (LCA) in this study is based on specific assumptions regarding packaging, energy losses, transportation, bone sourcing, and alum waste management.<sup>238</sup> In an LCA, the conclusions from the life cycle inventory (LCI) are organized into impact categories to assess environmental concerns: (1) climate change: this is a common impact category, especially in this case, because the production of both nanoadsorbents



requires significant amounts of electricity. (2) Water use: this category accounts for total water required across the life cycle of the adsorbents, encompassing both primary production/application and all upstream activities (indirect processes). (3) Cumulative energy demand: the total energy required for both the foreground and background systems can change significantly as a product matures.<sup>239</sup> Fig. 18(a) interpretation of life-cycle assessment.<sup>240</sup> Scalability is a system's ability to grow in scale, magnitude, extent, and dimensions. The ability of a solution to be successfully duplicated elsewhere or later is known as replicability. Therefore, a scalability and replicability analysis for a smart grid solution is a predictive tool for forecasting implementation outcomes when the solution is applied to a larger scale (scalability) or transferred to a new location or time period (replicability). SRA analysis in smart grid projects highlights how the specific context of a solution influences its outcomes. SRA is a crucial tool for understanding how a smart grid solution's specific environment affects its outcomes. A full SRA involves: (i) identifying key contextual factors, and (ii) investigating the implications of their variation. Fig. 18(b) defining the scope of the current life cycle assessment model (cradle-to-gate).<sup>241</sup> A number of dimensions can be considered in SRA analysis, including scalability in density, intranational replicability, scalability in size, and international replicability.<sup>242</sup> With increased scalability, a system can exhibit improved stability and performance, coupled with reduced operational costs.<sup>243</sup> Several metrics have been developed for distributed and parallel computing to quantify scalability.<sup>244</sup> Based on the life cycle approach, the framework is supported by environmental indicators commonly adopted within a life cycle assessment study. Human toxicity potential measures toxicity to organisms on land.<sup>245</sup> The interaction between humans and the environment is mainly symbiotic, and this stability has to be maintained. The relation among the parameters used for treatment showed a high significance level.<sup>246</sup> Substantial work has been carried out to understand the specific mechanisms by which antibiotics attach to natural soils.<sup>247</sup> Fig. 18(c) source of biosorbents.<sup>248</sup> Surfactant-modified clays and smart adsorbents have high potential regarding their environmental and economic stability and could serve, therefore, as sustainable alternatives for the removal of pharmaceutical pollutants.

### Current challenges and research groups

In real-world applications, competitive adsorption is a common occurrence that significantly impacts an adsorbent's overall effectiveness. Even with competitive adsorption, the total amount of each metal ion adsorbed decreases, but the order of adsorption capacity remains the same as in single-metal systems. It is also considered that each metal species exhibits a different degree of penetrability into the porous structure of the adsorbent.<sup>249</sup> Due to the challenges of experimentally measuring simultaneous adsorption of several substances, the ideal adsorbed solution theory (IAST) was developed.<sup>250</sup> The major perspectives are: (i) characterize raw feedstock and CBB (biochar-based material). (ii) Contrast single and ternary metal adsorption patterns and characteristics. (iii) Evaluate the heavy

metal adsorption capacities using both Freundlich and Langmuir models on data from single- and ternary-metal adsorption isotherms. (iv) Select the most accurate adsorption model to predict CBB's heavy metal retention capacity. (v) Create three-dimensional simulation graphics based on the experimental data to visualize heavy metal adsorption behaviors under different conditions.<sup>251</sup> MOFs have the ability to selectively adsorb certain kinds of molecules because of their central metal ions and organic ligands of different types and structures. This means we can control the way substrate molecules bind to the MOF by controlling these components.<sup>252</sup> Poor isolation and removal of target ions are mainly due to competitive adsorption in such systems where the concentration of coexisting salt cations is high.<sup>249</sup> Different methods have been used to enhance wastewater's biodegradability and decrease its organic load through a combination of oxidation and coagulation before subsequent biological treatment. The combined Fenton and biological treatment process showed no toxicity to the microbes that were used.<sup>253</sup> The growing occurrence of pharmaceuticals in wastewater is a concern because they are difficult to biodegrade. These compounds are considered emerging contaminants (ECs) because conclusive evidence linking them to long-term health effects in wildlife and humans is still lacking.<sup>254</sup> The mechanical properties of ice are evaluated using standardized testing procedures. It is important to note that these recommendations are subject to change as new ice-testing methods are developed.<sup>255</sup> Although standardizing antibiotic susceptibility testing is challenging due to several factors, an ideal testing medium has yet to be established. There is ongoing debate regarding the optimal methods for determining inoculum size, selecting disk content, controlling incubation conditions, and accurately interpreting results for both laboratory and clinical applications.<sup>256</sup> When a test is given, it involves two steps: measurement and classification. Measurement is simply the process of giving numerical values to something. The quality of a measurement tool is determined by the reliability and validity of its scores. Reliability is about consistency: it is how consistently a tool measures a specific idea or concept. Validity is about accuracy: it is how well the tool actually measures what it is supposed to measure.<sup>257</sup> Fig. 19: challenges and research group about adsorption. Despite the remarkable advancements achieved, areas that still need improvement include the recyclability of the adsorbent materials to some extent, the efficiency of the adsorption process to remove the pollutants, and scalability.

### Future perspectives

Among the available techniques, adsorption is widely used and considered an effective removal method of contaminants from wastewater due to several advantages: it is easy to use, highly efficient, and often involves the use of low-cost materials. Furthermore, many adsorbents can be renewed and recycled. Commonly used adsorbents include activated carbon, agricultural residues, and a variety of both natural and man-made polymers and their composites. While current adsorbents can be highly effective at removing pollutants, most of them have



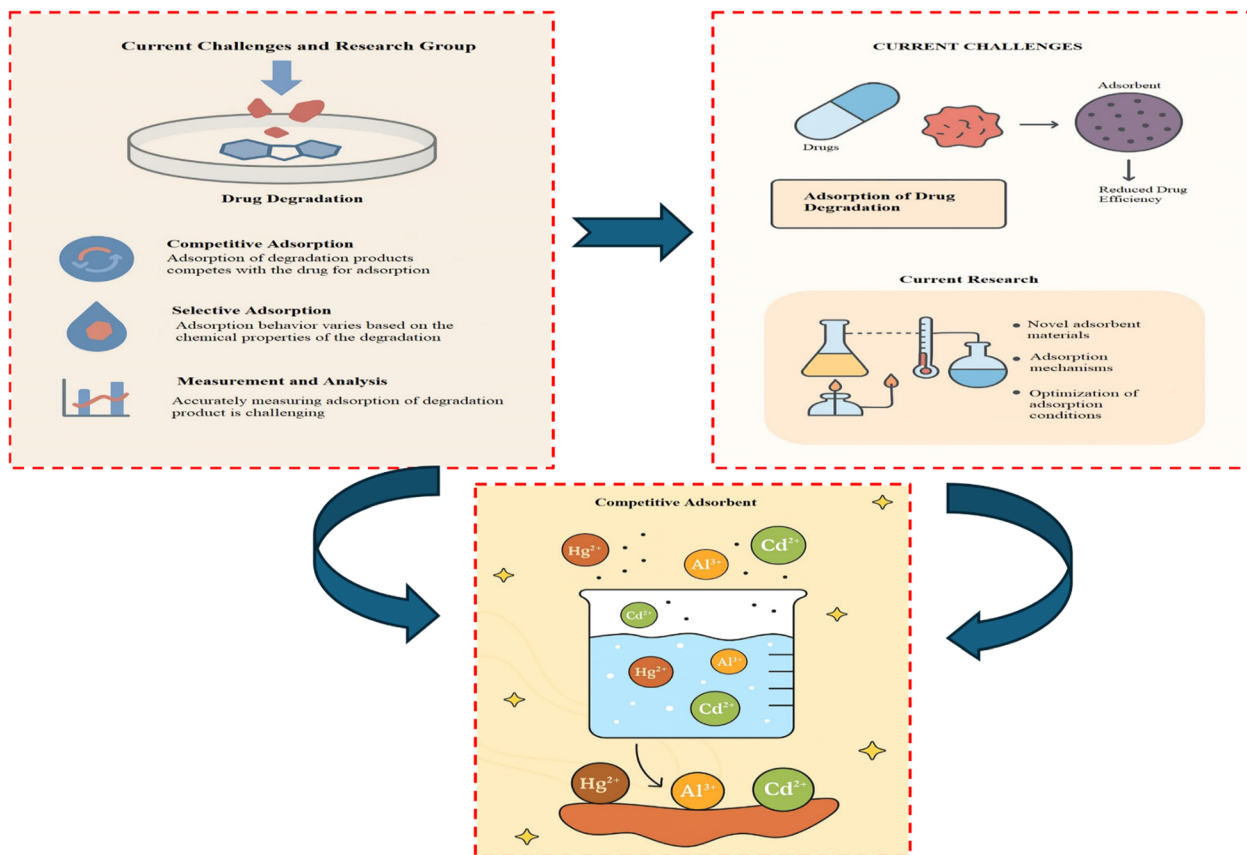


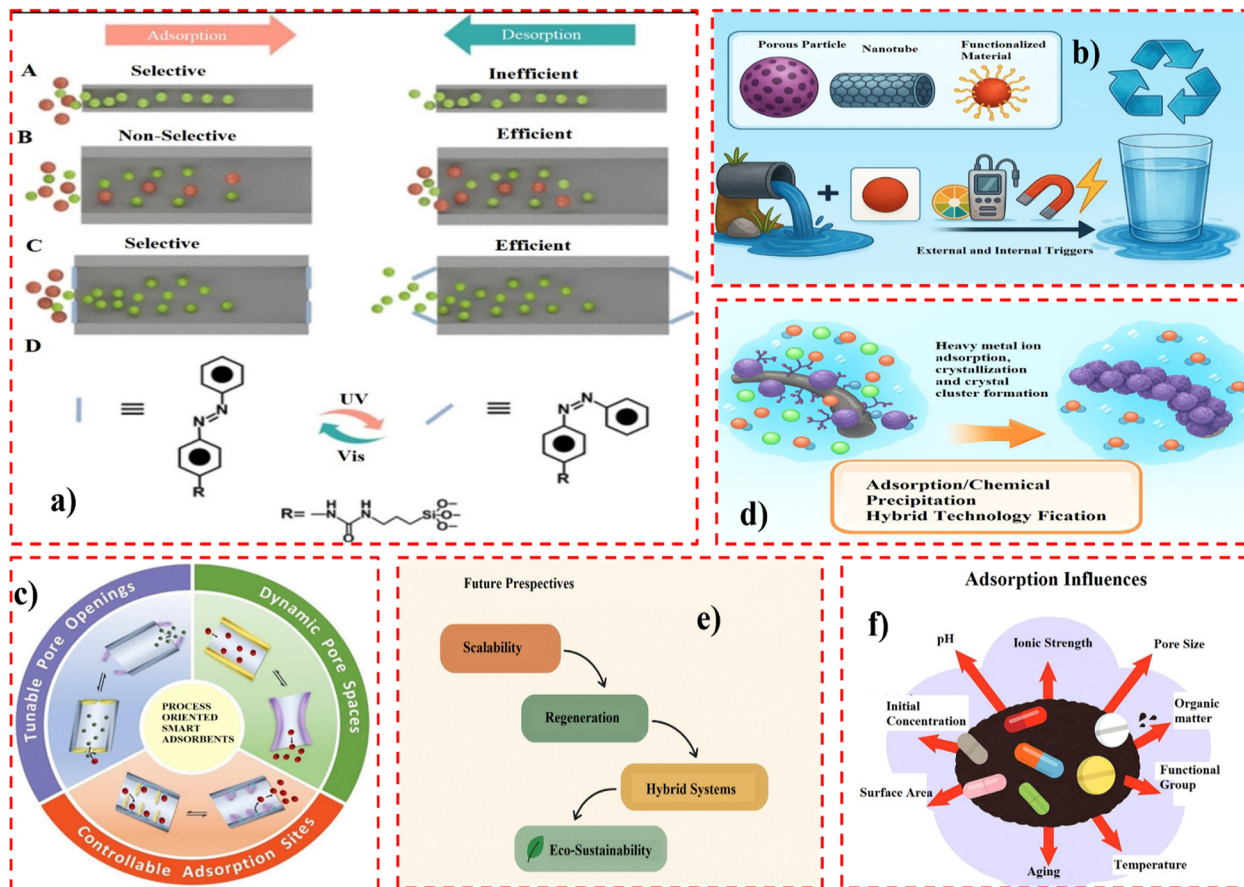
Fig. 19 Challenges and research focus of the group on adsorption.

limitations such as low selectivity and low adsorption capacity, which restrict their real-world application. Because these traditional adsorbents do not consistently provide the necessary pollutant removal effectiveness, there is a need to develop smart adsorbents that can efficiently capture pollutants even at trace concentrations.<sup>12</sup> Fig. 20(a) schematic comparison of adsorbent types: (A) display high selectivity but poor desorption efficiency, (B) offer efficient desorption but compromise adsorption selectivity, (C) smart adsorbents with molecular gates: achieve the dual benefits of selective adsorption, (D) gate operation: an illustration of the molecular gates reversibly opening and closing *via* the photoisomerization of the AB component.<sup>258</sup> Fig. 20(b) Remediation through smart adsorbent.<sup>12</sup> Fig. 20(c) process oriented smart adsorbents.<sup>259</sup> Adsorptive separation is a key process in many areas, including the chemical, food, and environmental sectors. Adsorbents are essential to this process because they perform separation tasks by undergoing adsorption (taking up substances) and desorption (releasing them). Process-oriented smart adsorbents (POSAs) are designed and developed based on the specific needs of adsorption and desorption processes. The goal is to develop highly efficient adsorbents and promote their use in practical industrial separation processes.<sup>259</sup> Conventional adsorbents featuring static pore structures cannot achieve the two critical challenges in adsorptive separation, namely energy-efficient regeneration and selective adsorption. Smart adsorbents, unlike conventional

adsorbents with fixed pores, can tune their pore properties in response to a particular condition of interest. This enables them to achieve the two critical objectives in adsorptive separation; that is, selective adsorption and energy-saving desorption, which is not possible with conventional materials.<sup>260</sup> In water treatment, a hybrid method combining adsorption and chemical precipitation has been proposed. Although adsorption is an effective technique on its own, its extraction capability of heavy metals is restricted based on the surface area provided for adsorption. This new hybrid approach has successfully delivered excellent performance. In this hybrid approach, the shape of the adsorbent material is critical for the separation of heavy metals. The key to this hybrid approach is that heavy metal ions form crystals on the adsorbent, which significantly increases the removal capacity. However, a major limitation is that this crystal growth can block the pores of the adsorbent, preventing heavy metal ions from entering and ultimately reducing the overall removal effectiveness.<sup>261</sup> Fig. 20(d) integration with hybrid technologies.<sup>261</sup> Fig. 20(e) future aspects Fig. 20(f) adsorbent influence.

Hybrid adsorption cooling systems are more effective than standalone systems. A hybrid system combines different cooling techniques, such as an adsorption cycle with a compression cycle, to improve overall efficiency.<sup>262</sup> A hybrid approach that includes adsorption and membranes could have complementary effects that solve problems associated with individual





**Fig. 20** (a) (A) Schematic of traditional microporous adsorbents possessing excellent performance in selective adsorption but inefficient during desorption; (B) schematic of traditional mesoporous adsorbents possessing excellent performance in desorption but at a cost in adsorption selectivity; (C) after anchoring photoregulated molecular gates, smart adsorbents with the benefit of selective adsorption and efficient regeneration; and (D) schematic of molecular gates that can reversibly close/open through photoisomerization of AB<sup>258</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Cheng, L., Yan, N., Shan, S. F., Liu, X. Q., Sun, L. B., Smart adsorbents with photoregulated molecular gates for both selective adsorption and efficient regeneration, *ACS Applied Materials & Interfaces*, 2016, 8(35), 23404–23411). (b) Remediation through smart adsorbents<sup>52</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Nazarzadeh Zare, E., et al., Smart adsorbents for aquatic environmental remediation, *Small*, 2021, 17(34), 2007840). (c) Process-oriented smart adsorbents<sup>259</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Jiang, Y., T. P., Liu, X. Q., Sun, L. B., Process-oriented smart adsorbents: tailoring the properties dynamically as demanded by adsorption/desorption, *Accounts of Chemical Research*, 2021, 55(1), 75–86). (d) Integration with hybrid technologies<sup>261</sup> (Adapted with permission from Elsevier (YG and K., *Chemosphere*, 2024), copyright 2024). (e) Future aspects. (f) Adsorbent influence.

processes, such as the inability to remove anions and dissolved organic matter (DOM) from water, due to the advantages of the hybrid method regarding its smaller footprint and better

performance towards water and wastewater treatment. The most favored hybrid systems are membrane adsorbents and membrane-adsorption bioreactors due to their unique

**Table 19** Factors affecting adsorption capacity and their effects<sup>266</sup> (Adapted under a Creative Commons CC BY Attribution 4.0 International License, Satyam, S., P.S., Innovations and challenges in adsorption-based wastewater remediation: A comprehensive review, *Heliyon*, 2024, 10(9))

Factor	Effect	References
Surface area	Increases the adsorption capacity by raising the number of available active sites	267
Porosity	Increases the capacity by providing more physical space for the molecules	268
Functional groups	Capacity is enhanced <i>via</i> specific interactions with the intended target molecules	269
Molecular size	Adsorption is favored for smaller molecules because they have better access to the adsorption sites	270
Polarity	Adsorption capacity is higher for polar molecules when the adsorbent is also polar	271
Concentration	Capacity increases directly with higher concentration until saturation is reached	272
Temperature	Although elevated temperatures may boost capacity, the actual effects are highly variable	273
pH	Impacts capacity by modifying the charge and the ionization ratio of the target molecule	274



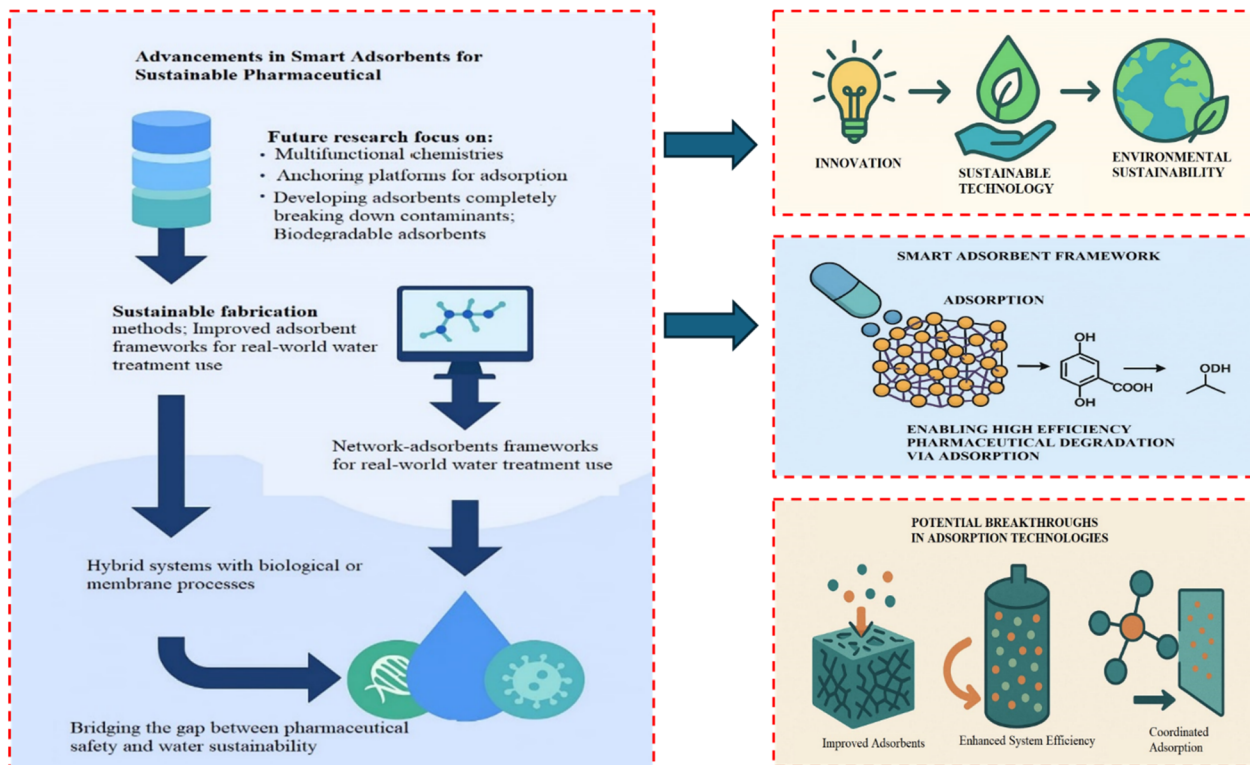


Fig. 21 Advancements in sustainable technologies in smart adsorbents for environmental and pharmaceutical remediation.

operational benefits.<sup>263</sup> Despite all this research, these new materials rarely result in commercial products. In this respect, the opportunities and challenges of commercializing adsorbent materials were assessed following an analysis of the current status of companies that were interviewed.<sup>264</sup> The primary commercialization barriers for adsorbents include (1) material properties: quality, availability, lifetime, and adaptability; (2) economic considerations: costs of regeneration, disposal, and transportation are unacceptably high; and (3) the costs of regeneration, disposal, and transportation are unacceptably high, legal and testing requirements: difficulties around environmental legislation, testing, and validation.<sup>265</sup> Factors influencing adsorption capacity and their impacts are presented in Table 19.<sup>266</sup>

Effective regulatory policies regarding adsorbent safety are important for a number of reasons: they instill public confidence through transparency in communications to stakeholders and the public, they protect public health and ecological systems, they allow innovation to occur since the rules are responsive to new technologies, and they help to certify the responsible and eco-friendly usage of technology in society. These policies also promote safe innovation and responsible development. They ensure that the benefits of new technologies are maximized while their potential risks are minimized.<sup>275</sup> Fig. 21: advancements in sustainable technologies in smart adsorbent for environment and pharmaceutical remediation. The following are directions for advancing smart adsorbent designs by including hybrid degradation strategies and optimizing cost-effective and environmentally sustainable

approaches to removing pharmaceutical pollutants in future research.

## Conclusion

The application of smart adsorbents for pharmaceutical removal and degradation has enormous potential but still faces issues such as scaling up, fouling by complex water sources, regeneration costs, and proper disposal. The focus for future research work could include data-driven design and fabrication, the development and application of adsorption-coupled advanced oxidation processes, and the utilization of biodegradable and waste materials as raw materials. Validating their application and designing regeneration processes that are less energy-intensive will be imperative for practical applications. Application and implementation of smart adsorbents within existing treatment plants through tertiary units or membrane-based adsorption systems can be one practical method to fill the widespread application gaps for pharmaceutical wastewater treatment. By doing so, smart adsorbents can lead to efficient and economically feasible pharmaceutical waste treatment.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



## Data availability

Since this manuscript is a review paper, no new experimental data were generated or analyzed in the course of this work. All data supporting the findings of this study are available within the cited references, which have been duly acknowledged in the manuscript.

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