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Cite this: *RSC Sustainability*, 2025, **3**, 112

Surfactant-influenced biosorption as a sustainable and effective way for the eradication of environmental pollutants: a review

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Received 16th September 2024
Accepted 11th November 2024

DOI: 10.1039/d4su00574k

rsc.li/rscsus

The biosorption process offers a sustainable and promising solution for treating wastewater contaminated with industrial effluents containing dyes, heavy metals, personal care products, pharmaceuticals, and phenolic compounds. Different types of biomass, such as agricultural waste products, animal waste, biopolymers, *etc.*, have been reported in contemporary times as environmentally friendly, low-cost, and efficient materials for treating different categories of wastewater. Many researchers often utilized surfactants to modify the surface properties of these biomaterials to enhance their removal efficiency. A considerable amount of research conducted on surfactant-modified biomaterials (SMBs) for treating wastewater in modern times has prompted us to prepare a review article on the same. The main aim of the current article is to focus on the recent developments that took place in this field, the behavior of different surfactants towards different categories of pollutants, and explore underlying mechanisms in depth. Notable advancements, such as the practice of new optimization techniques and the deployment of SMBs for real wastewater decontamination, have also been highlighted. The emergence of SMBs in accordance with the United Nations Sustainable Development Goals (UNSDGs) has been justified. Several current hindrances, along with future outlooks, are briefly presented before the conclusion. This review aims to be highly relevant in the present times, encouraging scientists and engineers to explore novel SMBs for industrial effluent clean-up programs.

Sustainability spotlight

The current review article describes recent advancements that took place globally regarding the application of different surfactant modified biomaterials for treating different kinds of wastewater. Biomaterials are environmentally friendly sustainable adsorbent materials of the new age. On the other hand, the inclusion of surfactants enhances the robustness of the pollutant trapping process and makes it more attractive to the scientific community. The creation of a micellar environment on the biomaterial surface helps to eradicate different kinds of water pollutants. This novel pollutant abatement technology is in concordance with UN SDG No. 6, *i.e.* clean water and sanitation and hence, we believe that the topic is highly suitable for the journal '*RSC Sustainability*'.

1. Introduction

The rapid increase in water pollution during the last few decades has forced environmental scientists and engineers to explore various advanced wastewater remediation techniques. Conventional biological wastewater treatment methods often fail to remove compounds such as dyes,[1] pharmaceutical compounds, phenolic products, and heavy metals from aqueous media. However, in the current age of industrialization, due to their wide industrial utility, these compounds often enter natural streams worldwide. For example, different categories of synthetic organic dyes are used for industrial purposes. Hence, a large quantity of dye residuals can be expected in the effluents coming out of these units. Studies have shown that more than 1000 tonnes of dyes are consumed globally per year, and 10–15% of these products are discharged into the wastewater stream.[1] Among heavy metals, Cr(VI) is widely used in the electroplating and tannery industries.[2] Nickel is utilized in the manufacture of stainless steel, alnico magnets, microphone capsules, *etc.*[3] Lead, another important heavy metal, is useful for battery production.[4] Therefore, a considerable amount of heavy metals is discharged from these units, and hence, they are expected to be present in the effluents. On the other hand, drug compounds or pharmaceutical compounds are often consumed in significant amounts in modern times to combat several diseases. However, these antibiotic compounds are recalcitrant in nature and often

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retain a considerable portion of their original molecular structure even after being metabolized inside the human body. For example, ibuprofen, one of the most commonly used non-steroidal anti-inflammatory drugs, is able to maintain 90% of its original molecular structure after being metabolized.[5] As the consistent accumulation of these compounds in the environment is hazardous, it is pertinent to develop new techniques for the abatement of such environmental pollutants from water bodies. Consequently, methods like adsorption,[6] advanced oxidation processes,[7] coagulation,[8] photodegradation,[9] membrane separation,[10] *etc.*, began to be explored for various types of wastewater treatment. Each method has its own pros and cons. For example, membrane separation is suitable for various types of wastewater treatment. But membrane fouling and the associated high cost of operation and maintenance are some of the major hindrances behind its large-scale application. The advanced oxidation process deals with the mineralization of recalcitrant pollutants by means of the application of novel catalysts. However, during the oxidation process, some toxic intermediates may be created. Among different commonly practiced remediation methods, adsorption has been accepted as one of the most convenient and versatile wastewater treatment techniques. The list of adsorbents available in the literature is quite long. Many promising adsorbents have also emerged in current times. Among different reported adsorbents, biomaterials are particularly noteworthy for various reasons.[11,12] Different functional groups are present on the surface, and they have been found to be useful for eliminating diversified categories of pollutants from water bodies. Moreover, these substances are environmentally friendly and hence can be considered as sustainable materials of the new age.

Apart from using raw biomaterials as suitable adsorbents, surface modification is often practiced to enhance their uptake capacity. Surfactants are one of the notable surface modifiers. In contemporary periods, SMBs have become promising systems in the field of wastewater remediation. Various articles have been reported in the present decade, where novel SMBs have been explored for wastewater treatment. The introduction of surfactants in the biosorbent matrix can change the surface properties and drastically enhance the removal efficiency. The formation of micellar structures on solid surfaces especially helps in solubilizing different pollutants from wastewater. Saxena *et al.*, in one of their latest articles, described various useful aspects of surfactant-based environmental remediation. The authors clearly mentioned that diversified categories of pollutants, including heavy metals, dyes, pesticides, petroleum products, *etc.*, could be eradicated *via* a micellar environment. Further, surfactant-mediated techniques can be easily applied for large-scale wastewater decontamination.[13] Recently, we developed a novel cationic surfactant-modified alginate–xanthan biomaterial-based surface that is effective in trapping different types of dyes from wastewater followed by selective recovery of the desired dye.[14] Bilayers of cationic surfactant on the solid surface play a crucial role in dye uptake and recovery.

Some latest review articles emphasized the exploitation of the amphiphilic characteristics of surfactants for pollutant removal. Reeve and Fallowfield reviewed recent advances in the application of surfactant-modified zeolites to combat multiple pollutants that are commonly encountered.[15] Tamjidi *et al.*, in one of their articles,[16] presented promising performance of different types of surfactant-modified adsorbents utilized for heavy metal removal. Saxena *et al.* and Rasheed *et al.*, in their reviews, discussed several beneficial aspects of surfactant-assisted wastewater remediation.[13,17] However, we have not come across any article describing the specific application of SMBs regarding decontamination of wastewater. Hence, the main focus of this current review article is to highlight the latest advances that took place in the surfactant-assisted biosorption process. Surfactant modification enhances the selectivity and versatility of clean-up technologies. Reported studies on the application of various types of SMBs deployed for pollutant removal are first described briefly. Pollutants have been categorized into dyes, heavy metals, and other emerging pollutants of high concern. On the other hand, biomaterials are classified mainly as agro-waste-based products and biopolymers. Different mechanisms involved in pollutant uptake have been covered in depth with comparative analysis among other similar types of materials. Optimization techniques and the feasibility of application of these materials for real wastewater treatment are also dealt with concisely. Characterization techniques, often explored to get in-depth knowledge about the adsorption phenomenon, are also covered. The feasibility of large-scale application of SMBs in the light of UNSDGs has also been justified. Lastly, current challenges and future outlooks are highlighted before concluding the article.

2. Synthesis of different SMBs

In recent years, different SMBs have been tried out by researchers for the eradication of various categories of pollutants from water media. Out of the different biosorbents, the lion's share is occupied by agro-waste-based materials. Owing to the possession of distinguished functional groups, researchers often explore different fruit peels for pollutant abatement studies.[18,19] Dovi *et al.* reported the successful application of CTAB-modified walnut shells for the adsorptive eradication of CR dye and BPA from wastewater.[20] Some biopolymers such as alginate and chitosan have also been immensely explored for wastewater treatment. Pal and Pal applied SDS-modified chitosan hydrogel beads for the removal of Pb(II) and Cd(II) from water medium.[4,21,22] Apart from these, some other biomaterials such as ostrich bone waste have been utilized by Shakeri *et al.* for the adsorptive elimination of BTEX from aqueous medium.[23] Arshadi *et al.* applied CTAB-modified ostrich bone waste as an effective biosorbent for MO removal from wastewater.[24] Amiri *et al.* explored anionic and cationic surfactant modified ostrich bone waste for heavy metal (Pb(II) and Hg(II)) uptake from aqueous media.[25] The current section deals with the synthesis of different surfactant-modified adsorbents reported in the literature for pollutant removal purposes.

2.1. Biopolymer-based adsorbents

Biopolymers are naturally occurring materials containing abundant functional groups. They are sustainable, highly

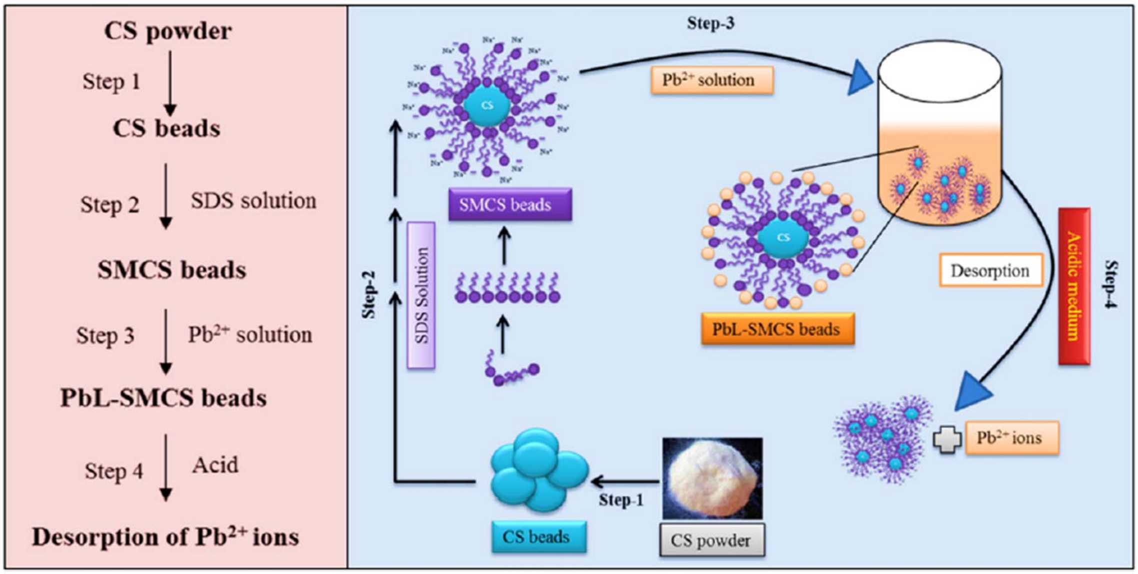

Fig. 1 Schematic showing the process of formation of a bilayer over CS beads and its subsequent use for the adsorption of metal ions.[4]

efficient materials often explored for adsorption and catalytic degradation of pollutants.[26–28] Chitosan, alginate, and carrageenan are some of the commonly used biopolymers for wastewater treatment. Besides, some gum biopolymers, such as locust bean gum, tragacanth gum, xanthan gum, *etc.*, have also been reported in recent years for pollutant eradication purposes.[14,29,30] Notably, biopolymer composites are often deployed in bead form. In one of our recent studies, cationic surfactant (*e.g.* CPC) modified hydrogel biopolymer composites of alginate and xanthan gum were applied for the uptake of both cationic dye MB and anionic dye MO from water media, followed by selective extraction of MO.[14] The composite was synthesized by following a standard protocol. Firstly, a homogeneous suspension of alginate powder and xanthan gum was prepared in Millipore water. Later on, this mixture was injected dropwise into a previously prepared calcium chloride solution. Hydrogel alginate–xanthan bead formation started instantaneously. The beads were kept immersed in water overnight in order to develop higher strength. After that, these hydrogel beads were dipped in CPC solution (initial concentration = 600 mg L^{-1}) to form CPC-loaded alginate–xanthan hydrogel beads. CPC bilayers on the bead surface were used to adsolubilize MO dye from water medium.

Like alginate beads, chitosan beads have also been prepared by crosslinking. Das and Pal prepared hydrogel chitosan beads and used them to adsorb the anionic surfactant SDS from water.[31] Later on, these SDS-modified chitosan beads were used for the removal of MG dye in high concentrations. Firstly, for the preparation of chitosan beads, chitosan powder was dissolved in acetic acid and kept for stirring overnight. After that, the solution was transferred dropwise into a mixture of water, methanol, and NaOH. The beads thus formed were subjected to SDS adsorption, and SDS-modified hydrogel chitosan beads were found to be promising biosorbents for trapping high concentrations of MG dye from water. In other studies, Pal and Pal utilized SDS-modified hydrogel chitosan beads for Pb(II) and Cd(II) removal purposes.[4,22] The schematic for bead synthesis and Pb(II) removal has been presented in Fig. 1.

Chatterjee *et al.* prepared non-ionic surfactant (TX-100), anionic surfactant (SDS), and cationic surfactant (CTAB) impregnated chitosan hydrogel beads for the removal of CR dye and naphthalene from water.[32–35] In the case of the non-ionic and cationic surfactant-impregnated chitosan hydrogel beads, firstly, TX-100 or CTAB was added to the chitosan acetic acid solution, followed by the dropwise addition of this mixture to alkaline methanol solution. However, in the case of SDS impregnation, chitosan powder was dissolved in the SDS acetic acid solution in order to prevent the formation of chitosan SDS aggregates.

Zang *et al.* immobilized a CTAB-modified *Auricularia auricula* spent substrate in the alginate biopolymer matrix for the removal of Cr(VI).[36] Firstly, the spent substrate was ground to a fine powder and placed in 1 L of CTAB solution having a concentration of 9.2×10^{-4} mol L^{-1} for modification purposes. After keeping for 24 h under agitation, the solid was taken out and dried, followed by mixing with a sodium alginate solution (2%) in a mass ratio of 1 : 15. The mixture was transferred into a 2.5% calcium chloride solution using a peristaltic pump. Beads of size 3–5 mm started to form by means of crosslinking. The *Auricularia auricula* spent substrate modified with CTAB was abbreviated as AASS, while the beads were termed MIAASS. The beads thus formed were dried at 60 °C and kept for further use.

2.2. Agrowaste-based materials

Agrowaste materials are often high in lignocellulosic content. Besides biopolymers, different agro-waste-based materials have been reported as promising adsorbents after surfactant modification. Various research groups reported the application of

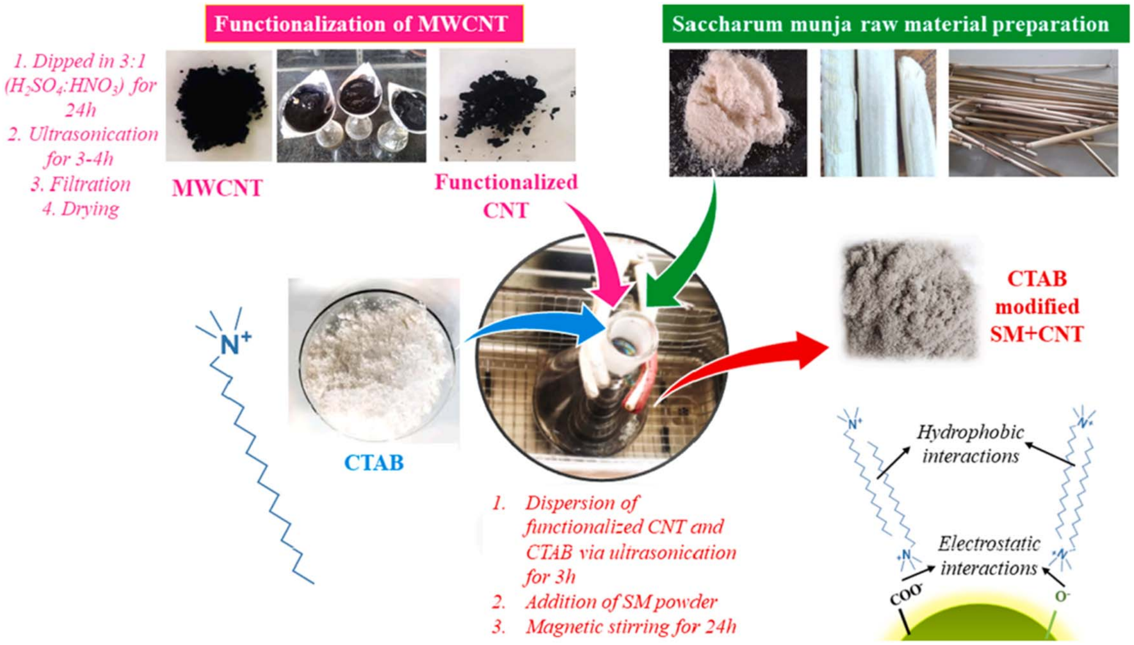

Fig. 2 Preparation of the CTAB modified SM + CNT bio-composite.[38]

surfactant-modified agro products for the removal of dyes, heavy metals, and other pollutants.

Rafatullah *et al.* explored the potential of surfactant-modified oil palm leaf powder to adsorb Cu(II) ions from aqueous media.[37] First, oil palm leaves were washed thoroughly with distilled water, dried, and ground to the appropriate size. Later on, the anionic surfactant SDBS was chosen for surface modification purposes. Next 10 g of oil palm leaf powder was mixed with 100 mL of 2% SDBS solution, and the setup was kept under agitation for 24 h. After that, the SDBS modified adsorbent was separated from the water medium and dried for 24 h in a hot air oven at 50 °C to produce the final adsorbent.

Yadav *et al.* deployed a CTAB-modified *Saccharum munja* (SM) based biocomposite containing CNTs for the adsorptive removal of anionic dyes BB R-250, RR 35, and RO 107 from water solution in single as well as in multicomponent systems.[38] In order to prepare the adsorbent, an aqueous solution containing 0.01 g of functionalized multiwalled carbon nanotubes (MWCNTs) and varied amounts of CTAB in 100 mL solution was first prepared. To this solution, 1 g of SM powder was poured, and the resultant mixture was kept under magnetic stirring for 24 h. In the end, the CTAB modified SM + CNT composite was separated and dried in an oven at 50 °C for 24 h. The preparation, as well as the dye uptake mechanism, is shown in Fig. 2.

Tea and coffee wastes have also been modified with surfactants to take up other pollutants from wastewater. Lafi and Hafiane used cationic surfactant (*e.g.* CTAB and CPC) modified coffee waste powder to remove MO dye.[39] Firstly, the waste material was collected from a coffee shop and washed with boiled distilled water to remove dirt and color. After that, it was ground and powdered to a size of 250–800 μm. In the next step, 12.5 g of coffee waste was chemically modified with 500 mL of 0.027 M surfactant solution to produce a cationic surfactant-modified coffee waste adsorbent. Foroughi-dahr *et al.* prepared a cationic surfactant-modified tea waste adsorbent for CR removal in a similar fashion. CTAB and CPB were used as cationic surfactants for modification.[40] First, the tea waste was collected and subjected to boiling several times till a clear filtrate was obtained. Then, it was oven-dried for 48 h at 70 °C, followed by grinding to a suitable sieve size of 125–250 μm. After that, 10 g of the tea waste powder was taken in 1 L of distilled water, and the cationic surfactant was slowly added to it. The whole setup was agitated mechanically for 40 °C for 48 h to produce a surfactant-modified tea waste adsorbent.

3. Application of SMBs for the adsorption of different categories of pollutants

3.1. Adsorption of dyes

Dyes are one of the most common classes of pollutants often found in water bodies. The textile, tanning, and food industries often discharge a huge quantity of dye into natural streams.[41] Many of the discharged dyes are severely toxic, while some may be less toxic. However, due to the aesthetic problem, the dyes are not at all tolerable, even at a trace level. Owing to the possession of different stable aromatic functional groups, these molecules are not degradable under natural ambient conditions.[7] They often block the passage of natural sunlight, and the photosynthesis process is often hampered.[42] The reaction of several dyes with microorganisms may lead to the formation of toxic, carcinogenic compounds in the gastrointestinal tract.[43] Hence, dye removal from wastewater streams is an important task for environmental scientists and engineers.

Undoubtedly, surfactant-mediated biosorption is a sustainable and green technique for dye wastewater treatment. CTAB-

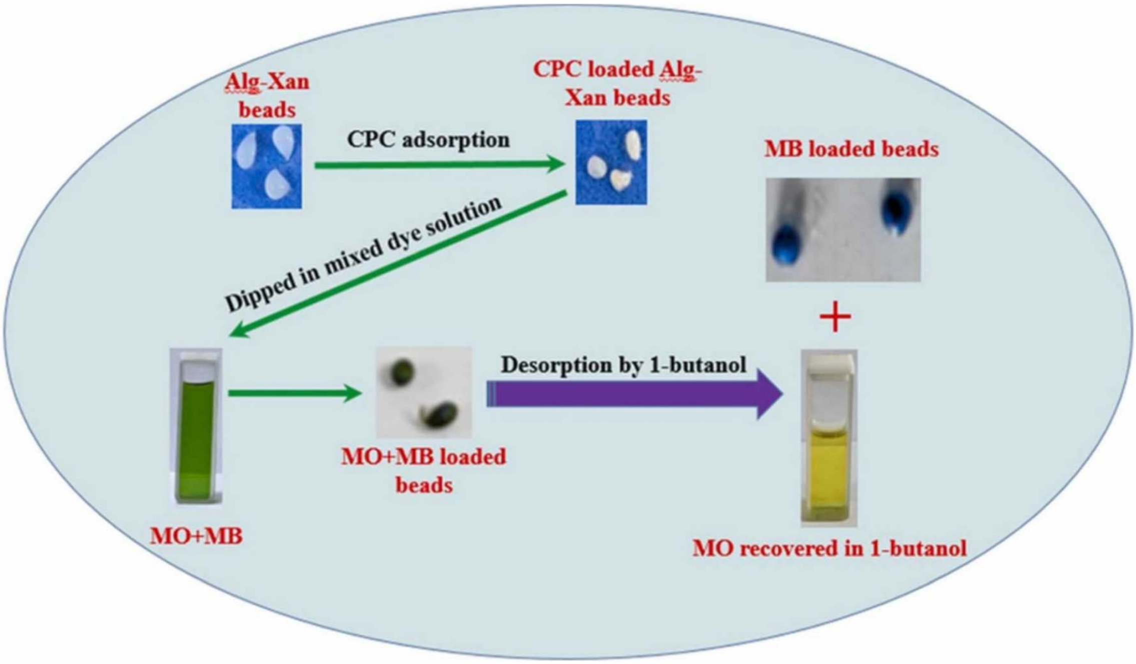

Fig. 3 Schematic showing the selective recovery of MO from a mixture of MO and MB by application of CPC-loaded alginate–xanthan hydrogel beads.[14]

modified spent mushroom waste was explored by Alhujaily *et al.* for the removal of toxic dyes such as DR 5B, DB 71, and RB.[44] High adsorption capacity (249.57–338.67 mg g^{-1}) was achieved. The solution pH showed a significant influence on the dye adsorption. The pH_{ZPC} of the surfactant-modified adsorbent was 7.2, and the maximum uptake was obtained in the solution pH range of 3–5. In this pH range, the surface of the adsorbent remained positively charged, which facilitated the removal of anionic dyes. The adsorption phenomenon followed the mechanism of chemisorption, and from the thermodynamic study, it was revealed that the adsorption process was endothermic and spontaneous in nature.

Karaman *et al.* prepared biomass-derived carbon from waste orange peels and activated it with $ZnCl_2$.[45] Activated carbon thus produced was further modified with CTAB and explored for the removal of CR dye from wastewater. Within a time period of 35 min, the adsorption process was completed. The effect of pH on the removal efficiency was quite interesting. The initial pH of the dye solution was varied from 2 to 10, keeping the dose of adsorbent at 1 g L^{-1} and the initial concentration of CR at 100 mg L^{-1}. Maximum removal (~90%) was obtained at a pH of ~6. At a lower pH, less removal was observed as the $-NH_2$ and $-SO_3$ groups of the dye become protonated, and at alkaline pH, there is competition between the OH group and the anionic dye, which ultimately hampers adsorption capacity. Ranjbar *et al.* synthesized cationic a surfactant-modified cellulose nanocrystal as a novel adsorbent for the elimination of CR from aqueous media.[46] Various amounts of CTAB were used for the modification of cellulose nanocrystals, and it was found that at a weight ratio of CTAB : cellulose nanocrystals of 0.24, maximum adsorption capacity (220 mg g^{-1}) was attained. Arumugan *et al.* reported the removal of MG dye by applying a composite made of coconut coir pith, chitosan, and SDS.[1] The adsorption process was found to be highly pH-dependent. At pH ~4, the maximum adsorption took place (83%). On the other hand, at high pH (~10), the removal efficiency decreased to 65%.

In contemporary times, we reported the application of a cationic surfactant (*e.g.* CPC) modified alginate biopolymer-based system, which is useful in the selective recovery of anionic dyes from a mixture of cationic and anionic dyes.[14] Firstly, an alginate–xanthan biopolymer hydrogel composite was synthesized through cross-linking. In the next step, CPC adsorption on the surface of the hydrogel beads was carried out under static conditions. The concentration of CPC was kept above the critical micelle concentration (CMC) of CPC in order to form the bilayer structure. CPC-modified alginate–xanthan composite hydrogel beads were inserted in the mixture containing MO and MB dye. It was quite interesting to observe that both dyes attached to the bead surface. However, the mechanism for the two dyes was different. MO was trapped in the CPC bilayer by the adsolubilization phenomenon, while MB stuck to the bead surface by electrostatic attraction. After the uptake of both dyes, the MO MB-loaded beads were dipped in 1-butanol for desorption. Interestingly, MO was detached from the bead surface while MB remained attached. The relatively loose bond between MO and CPC was weakened by the solvent, while it could not affect the strong electrostatic bond between MB and the anionic polymeric beads *viz.*, alginate and xanthan. The schematic is shown in Fig. 3.

Kasperiski *et al.* applied CTAB functionalized aqai stalk for the removal of DB 15 and DR 23 dyes from wastewater.[47] The contact time required for DB 15 was 180 min, while for DR 23, it was 30 min. A significant difference between the contact times was due to the difference in the size of the molecules and polar surface area. The initial concentration of both the dyes was varied in the range of 180–1500 mg L^{-1}, while the solution pH was maintained in the range of 2–9. The removal efficiency was found to be low at acidic pH, and it was higher (>90%) in a solution pH range of 5–9. Detailed investigations showed that the kinetic data for both dyes followed the Avrami fractional model.

Cationic surfactant (CTAB) modified corn stalk was explored by Soldatkina and Zavrichko for the adsorptive removal of anionic dyes from wastewater.[48] Chemisorption and ion exchange have been identified as the predominant mechanisms behind dye uptake. Wong *et al.* utilized cationic surfactant-modified spent tea leaves for the adsorption of anionic dyes from a water medium.[49] The maximum adsorption capacity for RB5 and MO was found to be 71.9 mg g^{-1} and 62.11 mg g^{-1}, respectively. Zhang *et al.* reported the removal of AR 18 by deploying cationic surfactant-modified wheat bran.[50] The adsorption capacity of the surfactant-modified biosorbent (wheat bran) was significantly higher in comparison to the raw wheat bran. A thermodynamic study reveals that the process was exothermic and spontaneous in nature.

Yadav *et al.* deployed CTAB-modified biocomposite containing SM biomass and 1% CNT for the adsorption of multiple anionic dyes, including BB R-250, RR 35, *etc.*[38] The molecular structure of the dyes as well as the solution pH played an important role in the adsorption process. Various mechanisms such as electrostatic interaction, π–π interaction, and H bonding played crucial roles in the dye uptake. The overall mechanism is shown in Fig. 4.

A list of surfactant-modified biosorbents prepared and tested for dye removal purposes is shown in Table 1 with the most suitable experimental conditions and their maximum adsorption capacities:

3.2. Adsorption of heavy metals

Heavy metals constitute one of the most common classes of non-biodegradable water pollutants. They are discharged as waste from various industrial units such as electroplating, mining, smelting, metal surface finishing, *etc.* Heavy metals are highly toxic to plants and animals, even at low concentrations. Some latest studies have established the fact that surfactant assisted biosorption can often be considered as one of the sustainable solutions for decontaminating heavy metal-laden wastewater.

Most of the heavy metal ions exist as cations in wastewater. Hence, modification with an anionic surfactant often enhances the adsorption capacity of biosorbents. SDS bilayers anchored on chitosan hydrogel beads have been explored by our group for the removal of heavy metals such as Pb(II), Cd(II), and Ni(II).[3,4,21,22] In the case of Ni(II) adsorption, the formation of a SDS bilayer on the chitosan hydrogel bead surface enhanced the maximum adsorption capacity up to 76.92 mg g^{-1}.[3] The uptake proceeded following a pseudo-second-order kinetic model. However, the detailed experimental investigation revealed that both physisorption and chemisorption governed the adsorption process. The schematic of Ni(II) removal by SDS-modified chitosan hydrogel beads is shown in Fig. 5. In the case

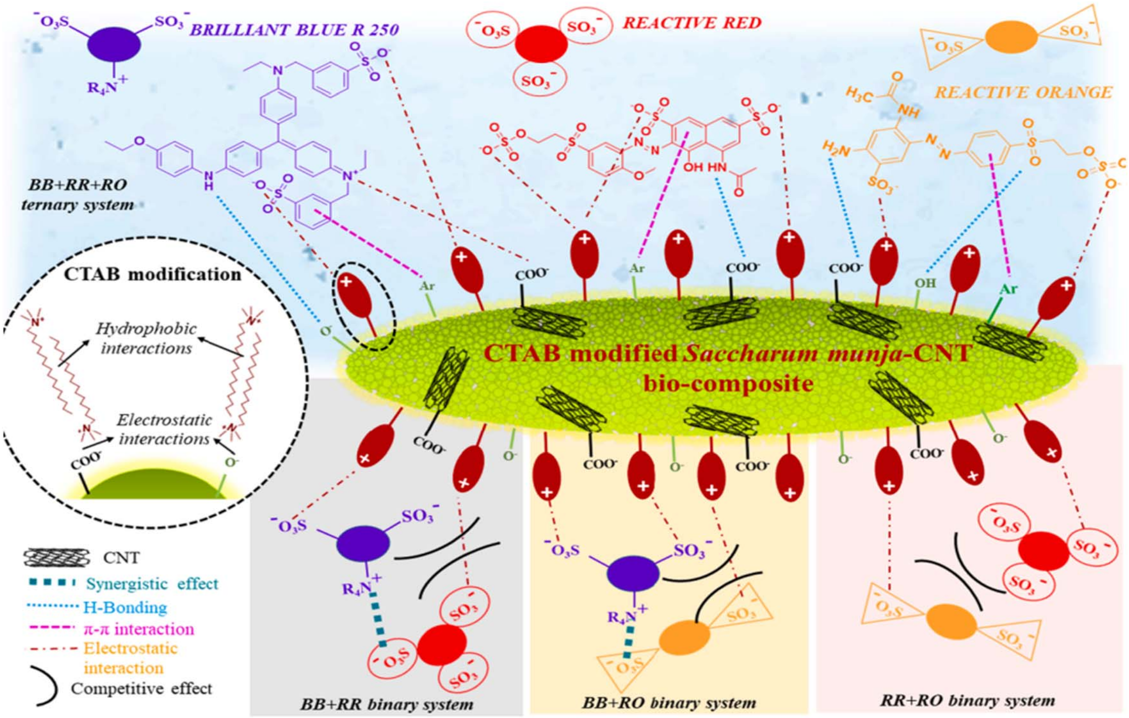

Fig. 4 Proposed adsorption mechanism involved in the removal of BB, RR, and RO dyes using CTAB-modified SM + CNT.[38]

Table 1 Different SMBs reported for dye removal purposes

Surfactant-modified biosorbent	Target dye	Optimizing operating conditions for maximum removal	Maximum adsorption capacity	References
SDS-modified chitosan composite	MG	With the dose of adsorbent = 0.1 g L^{-1}, solution pH 4, contact period = 60 min, T = 320 K	4.4	1
Alkyl BDAC-modified biomass derived from *Pyracantha coccinea*	RR 45	At a solution pH of 2, T = 298 K, surfactant used for modification purposes = 0.125%, dose of adsorbent = 0.8 g L^{-1}	152.49 mg g^{-1}	11
Anionic surfactant (SDS) modified *Pyracantha coccinea* based biosorbent	MV	At a solution pH of 6, dose of adsorbent = 2.4 g L^{-1}, contact time = 30 min	254.88 mg g^{-1}	12
SDS-modified orange peel residue	BB 9	—	272.43 mg g^{-1}	19
CTAB functionalized walnut shells	CR	At T = 303 K, initial concentration of CR = 60 mg L^{-1}, dose of adsorbent = 1 g L^{-1}	104.4 mg g^{-1}	20
Surfactant-modified ostrich bone waste	MO	With a contact time of 50 min, at a solution pH of 6.5, a dose of adsorbent = 1 g L^{-1}	~140 mg g^{-1}	24
SDS anchored on hydrogel chitosan beads	MG	With the dose of adsorbent: 0.58 g L^{-1}, initial concentration of MG = 10 mg L^{-1}, pH ~7	360 mg g^{-1}	31
CTAB-modified chitosan beads	CR	At a solution pH of 4	433.12 mg g^{-1}	32
TX-100 and SDS-modified chitosan beads	CR	—	378.79 mg g^{-1} in the case of TX-100 modified beads 318.47 mg g^{-1} in the case of SDS-modified beads	33
SDS chelated chitosan beads	CR	—	208.3 mg g^{-1}	34
CTAB modified tea waste	CR	With adsorbent dose = 4 g L^{-1}, initial concentration of CR = 50 mg L^{-1}	106.4 mg g^{-1}	40
Biomass derived from waste orange peels, activated by $ZnCl_2$ and modified with CTAB	CR	At an adsorbent dose of 1 g L^{-1}, at a solution pH of 6, T = 298 K, contact time = 120 min with an initial concentration of CR = 25 mg L^{-1}	666.67 mg g^{-1}	45
CTAB-modified cellulose nanocrystals	CR	With the dose of adsorbent = 0.2 g L^{-1}, pH 7.5, T = 298 K	220 mg g^{-1}	46
CTAB functionalized aqai stalk	DB 15 and DR 23	At an adsorbent dose of 0.6 g L^{-1}, at a solution pH of 2, the contact time for direct blue 15 is 180 min, and for direct red 23 is 30 min	394.2 mg g^{-1} for DB 15 and 454.9 mg g^{-1} for DR 23	47
CPB modified cornstalks	AR and AO	With adsorbent dose = 10 g L^{-1}, initial concentration of dyes = 50 mg L^{-1}, solution pH 2–3, at a shaking speed of 150 rpm	30.77 mg g^{-1} for AR, 31.06 mg g^{-1} for AO	48
Polyethylenimine-modified spent tea leaves	RB 5, MO	At pH 3, optimised dosage of adsorbent = 0.1 g, at T = 298 K	71.9 mg g^{-1} for RB 5, 62.11 mg g^{-1} for MO	49
Quaternary ammonium salt modified wheat bran	AR 18	At pH 3, adsorbent dosage: 1 g L^{-1}, initial concentration of AR 18 = 50 mg L^{-1}, T = 303 K, contact time = 12 h	49.12 mg g^{-1}	50
Quaternary ammonium salt modified sugar beet pulp	AR 1	At a solution pH of 2, T = 323 K, dose of adsorbent = 1 g L^{-1}	98.32 mg g^{-1}	51
SDS modified sawdust	MB	With 1 g of adsorbent material in the column, at solution pH = 6, initial concentration of MB = 50 mg L^{-1}, flowrate of 3 mL min^{-1}	129.68 mg g^{-1}	52
CTAB modified fallen leaves of *Prunus dulcis* (almond)	AB 113	With an adsorbent dose of 3 g L^{-1}, contact time = 2.5 h, T = 293 K	97.09 mg g^{-1}	53

Table 1 *(Contd.)*

Surfactant-modified biosorbent	Target dye	Optimizing operating conditions for maximum removal	Maximum adsorption capacity	References
HDRTMA-modified pineapple leaf powder	MB and MO	With the dose of adsorbent = 10 g L^{-1}, initial concentration of dye	52.6 mg g^{-1} for MB and 47.6 mg g^{-1} for MO	54
CTAB-acid modified celery (*Apium graveolens*)	CR	With the dose of adsorbent = 1.5 g L^{-1}, contact time = 6 h, pH of the solution = 6.5, initial concentration of CR = 100 mg L^{-1}	526.32 mg g^{-1}	55
HDTMA-modified coconut coir pith	ABB and PO	For ABB: at a solution pH of 6.5, with contact time = 60 min, with the dose of adsorbent = 1 g L^{-1} For PO: at a solution pH of 5.5, with contact time = 80 min, with the dose of adsorbent = 1 g L^{-1}	159 mg g^{-1} for ABB and 89 mg g^{-1} for PO	56
CPC-modified barley straw	AB 40 and RB 5	For AB 40, at solution pH < 5, and for RB 5, at solution pH > 6 with an adsorbent dose of 2 g L^{-1} for both dyes	47.6 mg g^{-1} for AB 40 and 25.4 mol g^{-1} for RB 5	57
CPB-modified wheat straw	LG	—	70.01 ± 3.39 mg g^{-1}	58
CTAB modified flax shives	AO 7, AR 18, AB 1	At a solution pH of 2, with the dose of adsorbent = 1 g L^{-1}, t = 10 h	92.47 mg g^{-1} for AO 7, 78.12 mg g^{-1} for AR 18, 99.38 mg g^{-1} for AB 1	59
Cationic gemini surfactant modified flax shives	AO 7, AR 18, AB 1	Optimized conditions for removing AO 7: initial concentration of gemini surfactant = 2.5 mmol L^{-1}, solution pH = 2, initial concentration of AO 7 = 100 mg L^{-1} Optimized conditions for removing AR 18 Optimized conditions for removing AB 1	88.7 mg g^{-1} for AO 7, 89.5 mg g^{-1} for AR 18, 95.2 mg g^{-1} for AB 1	60
CTAB-modified wheat straw	CR	At a solution pH of 4–5, dose of adsorbent = 0.5 g L^{-1}, T = 303 K, equilibrium time = 300 min	665 mg g^{-1}	61
CTAB-modified wheat straw	CR	—	—	62
CPB-modified peanut husk	LG	At a solution pH of 2–4, contact time = 200 min	146.2 ± 2.4 mg g^{-1}	63
CPB-modified peanut husk	LG	—	60.5 mg g^{-1}	64
Anionic surfactant-modified chitosan beads	CR	—	1766.20 mg g^{-1}	65
Pb loaded SDS modified chitosan hydrogel beads	CV and TZ	With a dose of adsorbent of 0.9 g L^{-1}, initial concentration of both dyes = 20 mg L^{-1}, at a solution pH of 6 for CV and 3 for TZ	97.09 mg g^{-1} for CV, 30.03 mg g^{-1} for TZ	66
SDS-modified chitosan hydrogel beads	CV	With the dose of adsorbent = 0.5 g L^{-1}, initial concentration of SDS = 50 mg L^{-1}, initial concentration of CV = 10 mg L^{-1}	18.2 mg g^{-1}	67
CPC-modified biomass of *Penicillium* YW01	AB 25	In the presence of phosphoric–phosphate buffer, solution pH of 3, contact time of 90 min, a dose of adsorbent of 1 g L^{-1}	118.48 mg g^{-1}	68

of Pb(II) uptake, a maximum adsorption capacity of 100 mg g^{-1} was obtained with an adsorbent dose of 0.675 g L^{-1} and an initial concentration of lead of 50 mg L^{-1}.[4] Excellent Pb(II) uptake was due to the adsolubilization of the metal ions in the SDS bilayer. Thermodynamic studies showed that the adsorption was exothermic in nature. A Cd(II) removal study was carried out in distilled water as well as in a real wastewater matrix.[21,22] In distilled water containing Cd(II) ions, the Langmuir isotherm model was followed, and a maximum adsorption capacity of 125 mg g^{-1} was obtained. In the lower concentration range of Cd(II) (10–30 mg L^{-1}), almost complete removal took place, and in the higher concentration range (40–100 mg L^{-1}), nearly 50% removal was achieved. The pseudo-second-order kinetic model fitted the experimental data best. However, in the real wastewater, the initial concentration of Cd(II) was detected in the range of 10–11 mg L^{-1}, and the

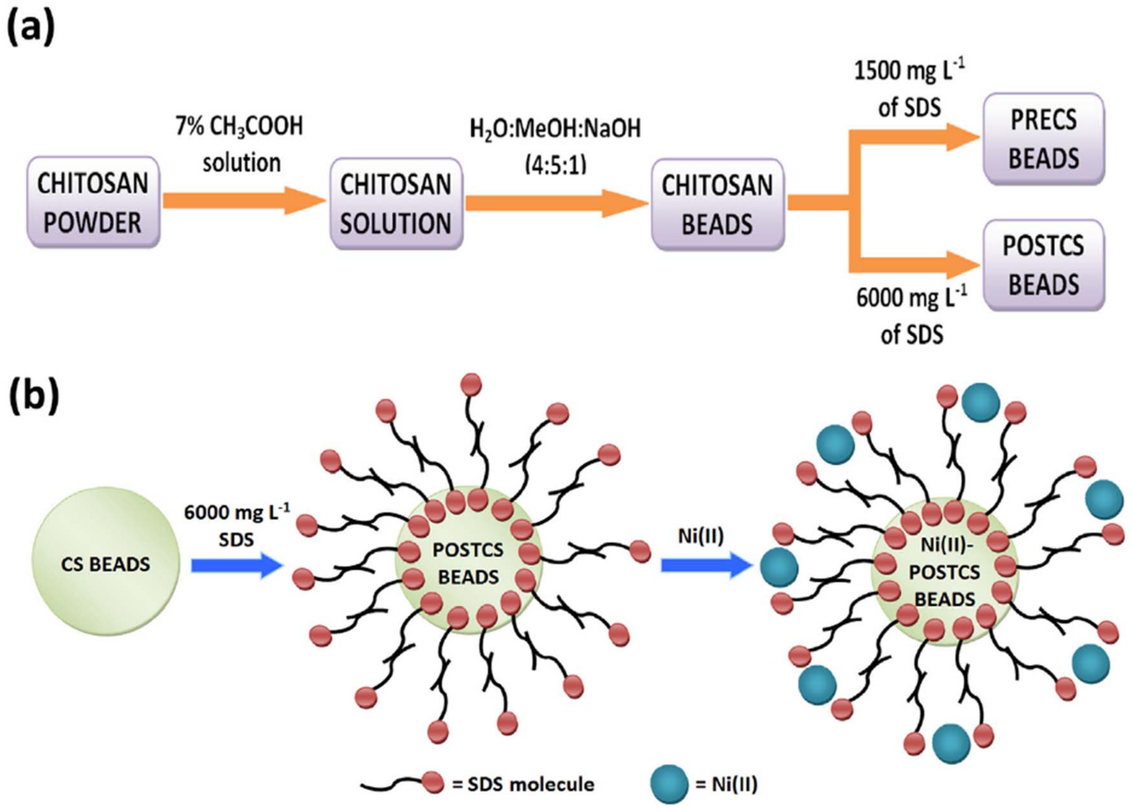

Fig. 5 Scheme of (a) SDS modified CS bead synthesis steps and (b) Ni(II) adsolubilization procedure.[3]

maximum adsorption capacity was found to be 18 mg g^{-1}. Unlike the distilled water matrix, in the real wastewater case, the Freundlich adsorption isotherm model showed a better correlation with the experimental results.

Among all heavy metals, hexavalent chromium (Cr(VI)) occupies a significant position, and unlike most other heavy metals, it exists in nature as oxyanions. Various researchers explored surfactant-modified biomaterials for Cr(VI) eradication from wastewater. Karnjanakom and Maneechakr utilized cationic surfactant (*e.g.* HDTMA and DDAB) modified carbonized carbon for chromium adsorption purposes.[69] Due to surfactant modification, adsorption capacity towards Cr(VI) was enhanced significantly. Experimental data showed a good correlation with the Langmuir model as well as with the Dubinin–Radushkevich (DR) isotherm model. From the DR isotherm model, the free energy of adsorption was found to be <8 kJ mol^{-1}. It indicated that the adsorption was mainly governed by physical forces. In another study, Li *et al.* modified *Auricularia auricula* dreg biochar with a cationic surfactant and explored the same for the adsorptive removal of Cr(VI) from wastewater.[70] At an initial concentration of Cr(VI) of 20 mg L^{-1} and an adsorbent dose of 3 g L^{-1}, adsorption took place at a contact time of 120 min. Due to CTAB modification, the adsorption quantity was enhanced by 8%. In another study, Dong *et al.* explored the effects of coexisting cations and anions on Cr(VI) removal using a CTAB-modified *Auricularia auricula* spent substrate.[71] Experimental results revealed that in the presence of Pb^{2+} ions, the removal efficiency was reduced by 21.79%, while phosphate anions (PO_4^{3-}) caused 12.43% reduction in efficiency. These coexisting cations and anions competed with Cr(VI) for hydroxyl and amino groups contained in the adsorbent matrix. Moreover, it was quite interesting to observe that in the absence of any competing ions, the adsorption of hexavalent chromium was best fitted to the Langmuir isotherm model, while in the presence of ionic interference, it showed the best trend with the Freundlich model. Sarfraz *et al.* carried out adsorption experiments for the removal of Cr(VI) by applying anionic and cationic surfactant-modified wheat bran.[72] Cationic surfactant modification was more effective for Cr(VI) removal than anionic surfactant modification. The adsorption process was facilitated at a lower pH.

Vanadium removal by application of CTAB-modified palm fruit husk was reported by Thamilarasi *et al.*[73] The pH_{ZPC} of the raw palm fruit husk was found to be 6.2, while due to CTAB modification, the pH_{ZPC} increased to 7.4. The effect of the presence of other coexisting ions on Cr(VI) removal was also studied. It was found that the molybdate interfered with the adsorption process and hampered the uptake process at all concentrations. On the other hand, sulphate and thiocyanate started interfering at a concentration greater than 50 mg L^{-1} and chloride adversely affected the removal process at a concentration beyond 100 mg L^{-1}. Other anions, such as nitrate and phosphate, showed no significant interference. A

Table 2 Different SMBs reported for heavy metal removal purposes

SMBs	Target heavy metals	Optimized reaction conditions for maximum removal	Maximum adsorption capacity	References
HDTMA-modified coconut coir pith	Cr(VI)	At a solution pH of 2	76.3 mg g^{-1}	2
SDS-modified chitosan hydrogel beads	Ni(II)	At a solution pH of 6.5, dose of adsorbent of 1.75 g L^{-1}, concentration of Ni(II) = 10 mg L^{-1}	76.92 mg g^{-1}	3
SDS-modified chitosan hydrogel beads	Pb(II)	At a solution pH of 5, with the dose of adsorbent = 0.675 g L^{-1}, initial concentration of Pb(II) = 30 mg L^{-1}, contact time = 480 min	100 mg g^{-1}	4
SDS-modified *Punicagranatum* peel	Cesium (Cs) and europium (Eu)	At a solution pH of 6 for Cs, 5 for Eu	133.09 mg g^{-1} for Cs, 202.01 mg g^{-1} for Eu	18
SDS-modified chitosan hydrogel beads	Cd(II)	With the dose of adsorbent = 0.45 g L^{-1}, in the initial concentration of 10–30 mg L^{-1}, contact time = 10 h	125 mg g^{-1}	21
CTAB-modified *Auricularia auricula* spent substrate immobilized on alginate beads	Cr(VI)	With an adsorbent dose of 2 g L^{-1}, pH < 6	27.25 mg g^{-1}	36
SDBS-modified oil palm leaf powder	Cu(II)	At a solution pH of 6, with a dose of adsorbent 10 g L^{-1}, with an initial concentration of 200 mg L^{-1}	75.98 mg g^{-1}	37
HDTMA and DDAB modified activated carbon prepared from carbonized carbon of *Leucaena leucocephala*	Cr(VI)	With the dose of adsorbent being 4 g L^{-1}, initial concentration of $Cr_2O_7^{2-}$ of 10 mg L^{-1}	3.46 mg g^{-1}	69
CTAB modified *Auricularia auricula* dreg biochar	Cr(VI)	With the dose of adsorbent being 3 g L^{-1}, solution pH of 2, initial concentration of Cr(VI) = 20 mg L^{-1}, contact time = 120 min, T = 298 K	24.90 mg g^{-1}	70
CTAB-modified *Auricularia auricula* spent substrate	Cr(VI)	At a pH of 3, the dose of adsorbent = 2 g L^{-1}	9.327 mg g^{-1}	71
CTAB-modified wheat bran	Cr(VI)	With a contact time of 240 min, initial concentration of Cr(VI) = 5 mg L^{-1}, a dose of adsorbent = 50 g L^{-1}, pH = 2	—	72
CTAB-modified palm fruit husk	V(V)	At a solution pH of 4, the dose of adsorbent is kept at 4 g L^{-1}, initial concentration of vanadium = 20 mg L^{-1}	14.03 mg g^{-1}	73
DDBAB modified spent mushroom	Cr(VI)	At a solution pH of 3.39, the dose of adsorbent = 5 g L^{-1}, initial concentration of Cr(VI) = 10 mg L^{-1}	43.86 mg g^{-1}	74
CTAB, SDS, and TX-100 modified activated carbon prepared from husk and pods of *Moringa oleifera*	Cd(II)	With the dose of adsorbent = 1 g L^{-1}, solution pH of 8, contact time = 120 min	279.5 mg g^{-1}	75
SDS-modified jackfruit peel	Cr(III), Ni(II)	With the dose of adsorbent = 8 g L^{-1}, optimum pH for Ni(II) removal is ∼5–6, for Cu(II) removal ∼4–5	26.25 mg g^{-1} for Cr(III) and 20.88 mg g^{-1} for Ni(II)	76
N-Lauroylsarcosine sodium salt modified bamboo sawdust	Zn(II)	—	111.12 mg g^{-1}	77
SDS-impregnated chitosan beads	Cu(II), Ni(II), Zn(II)	At a solution pH of 5.4 for Cu(II), 7.3 for Ni(II), 6.5 for Zn(II)	221.46 mg g^{-1} for Cu(II), 226.50 mg g^{-1} for Ni(II), 230.70 mg g^{-1} for Zn(II)	78
CTAB modified lichen	Cr(VI)	At a solution pH of 2, with an initial concentration of Cr(VI) < 30 mg L^{-1}	—	79
CTAB-modified activated carbon prepared from *Enteromorpha prolifera*	Ni(II)	At a solution pH of 5	49.8 mg g^{-1}	80

list of SMBs prepared and tested for heavy metal removal purposes is shown in Table 2, which also includes the most suitable experimental conditions and their maximum adsorption capacities.

3.3. Adsorption of emerging pollutants

Emerging pollutants constitute a group of organic compounds that are relatively new and have already attracted the attention of scientists worldwide. These chemicals are extremely dangerous, and the concern regarding the effects of these compounds is continuously rising. Endocrine-disrupting chemicals such as BPA, pesticides (such as endosulfan), phenolic compounds, various phthalates, and xylenes are active members of this class. Pharmaceutical compounds such as ibuprofen, tetracycline, diclofenac, *etc.*, and personal care products also fall into this group. Due to their toxic characteristics and persistent nature, they are of special importance to environmental scientists and engineers. A list of emerging pollutants with their toxicity levels and sources in the environment is presented in Table 3. Biosorption often offers a sustainable solution for the eradication of these recalcitrant compounds from aqueous media. Moreover, in recent times, various research groups have explored several biomaterials modified with surfactants for adsorbing pharmaceuticals, pesticides, and phenolic compounds from water bodies.

Bandforuzi and Hadjmohammadi synthesized SDS-modified magnetic chitosan nanoparticles for the extraction of organophosphorus pesticides such as diazinon, phosalone, and chlorpyrifos from water bodies.[87] The formation of SDS hemimicelles on the solid support helped in the solubilization of organic pollutants by means of hydrophobic as well as electrostatic interaction. Adsorption data fitted well to the Langmuir isotherm model.

Different research groups have explored SMBs in recent times for the removal of various pharmaceutical compounds from water medium. Solution pH often plays a crucial role during the eradication of antibiotic compounds as they possess different structures under different solution pH conditions. In one of such research articles, Lafi *et al.* prepared surfactant-modified esparto grass using different cationic surfactants such as DTAB, CTAB, and BDHAC for the adsorptive removal of DC from wastewater.[88] At acidic pH, the adsorption was found to be better in comparison to that obtained at alkaline pH. DC remains in cationic form at a lower solution pH (pK_a of DC is 4.15). Better adsorption at acidic pH resulted from the hydrogen bonding between the protonated DC and nitrogen atom of the cationic surfactant. Similar results have also been reported by Abadian *et al.* while removing DC using cationic surfactant-modified agricultural waste (*Cuminum cyminum*).[5] It was observed that when the initial solution pH was increased from 3

Table 3 List of some emerging contaminants with their toxicity effects, utility, and sources in the environment

Emerging contaminant	Toxicity effect	Utility and source in the environment	References
BTEX	96 h LC50 values of benzene, toluene, xylene, and ethylbenzene were obtained as 61.04 mg L^{-1}, 59.36 mg L^{-1}, 44.09 mg L^{-1}, and 36.87 mg L^{-1}	Raw materials in the production of pesticides	81
BPA	BPA is an endocrine disrupting compound that can cause various adverse health effects, including carnal abnormality, infertility, alteration of the immune response, increase in prostate cancer risk	BPA is widely used for the preparation of epoxy resins and polycarbonate-based plastics	82
Chlorophenols	Classified as a priority pollutant by the US EPA, designated as a group 2B carcinogen by the International Agency for Research on Cancer	Industrial production of paper wood, microbial degradation of pesticides	83
Phthalate esters	Phthalate esters cause chronic toxicity, such as mutagenicity and carcinogenicity. Further testicular effects and reduction in sperm production are also noticed due to the exposure to phthalate esters. USEPA listed six phthalate esters as priority pollutants	Plasticizers for polyvinyl chloride products. They are also used in the preparation of toys, packaging materials, medical devices, *etc.*	84
Antibiotic compounds	Generation of antibiotic-resistant genes	Wastewater from pharmaceutical industries, municipal wastewater containing unmetabolized fragments of drug compounds	85
Nitrophenol	Enlisted as a criteria pollutant by USEPA	Used in the production of dyes, drugs, pesticides	86

Table 4 Different SMBs reported for emerging pollutant removal purposes

Surfactant-modified biosorbent	Target pollutant	Optimized reaction conditions for maximum removal	Maximum adsorption capacity	References
TTAB modified *Cuminum cyminum* agri-waste	DC	With the dose of adsorbent = 2 g L^{-1}, contact time = 150 min, at a solution pH of 3	93.65 mg g^{-1}	5
CTAB-modified ostrich bone waste	BTEX	With the dose of adsorbent = 10 g L^{-1}, at a pH of 7	85.9 mg g^{-1} for benzene, 119.5 mg g^{-1} for toluene, 144.1 mg g^{-1} for ethylbenzene, 137.7 mg g^{-1} for *p*-xylene	23
Surfactant (CTAB, SDS, TX-100) impregnated chitosan beads	Naphthalene	—	12.77 mg g^{-1}	35
HDTMA modified waste hazelnut shells	TC and CPX	For TC: a solution pH of 8.66, initial concentration of TC = 9.4 mg L^{-1}, contact time = 146.47 min, $T = 298.96$ K For CPX: a solution pH of 8.31, initial concentration of CPX = 29.26 mg L^{-1}, contact time = 100.71 min, $T = 309.53$ K	6.97 mg g^{-1} for TC and 47.77 mg g^{-1} for CPX	96
Rarasaponin-modified nanocrystalline cellulose	TC	—	18.11 mg g^{-1}	97
CPC modified phoenix tree leaves	2,4-DCP	At a solution pH of 2.41	188.8 mg g^{-1}	89
CPC-modified barley straw	Emulsified food and mineral oil	At neutral pH	613.3 mg g^{-1} for emulsified food and 584.2 mg g^{-1} for mineral oil	95
HDTMA-modified coconut coir pith	Thiocyanate	At a solution pH of 2	8.6 mg g^{-1}	98
CPC-modified magnetic chitosan beads	*p*-Nitrophenol	—	140 mg g^{-1}	91
HTAB modified fibric peat	BPA	—	31.4 mg g^{-1}	99
Quaternary ammonium surfactant-modified peat	Phenanthrene	At a solution pH of 2.5, equilibrium time = 45 min	1228 μg g^{-1}	100
Tween 80 modified coconut bagasse	Microplastic	—	80% removal	101

to 12, the uptake capacity decreased, with the highest adsorption capacity achieved at pH 3 (44.69 mg g^{-1}).

Phenolic compounds and their derivatives are also found in wastewater streams in considerably high concentration ranges. USEPA has classified chlorophenols as priority pollutants due to their carcinogenic and mutagenic nature, and the International Agency for Research on Cancer designates them as class 2B carcinogens. Some of the studies in recent times revealed that novel SMBs possess the potential to eradicate such compounds from water bodies with excellent efficiencies. Ren *et al.* utilized CPC-modified phoenix tree leaf powder for the adsorptive eradication of 2,4-DCP from aqueous media.[89] After CPC modification, the N content increased significantly, as evidenced by elemental analysis. Like pharmaceutical products, in this case, the solution pH also played a major role in the adsorption process. At pH < 6, 2,4-DCP existed as a neutral molecule, and at pH > 9, it existed as a phenolate anion. On the other hand, the pH_{ZPC} of the adsorbent was found to be 5.1. Considering the above phenomenon, a solution pH of 6.3 was chosen as the optimum where maximum adsorption capacity reached up to 188.8 mg g^{-1}. Further, experimental studies concluded that the adsorption data were in accordance with the pseudo-second-order kinetic model, implying that the removal process followed the chemisorption mechanism. Hamidon *et al.* explored CTAC-modified nanocrystal/alginate hydrogel beads for 4-CP removal from wastewater.[90] To get more insight into the adsorption mechanism, the kinetic data were fitted to the intraparticle diffusion model. Interestingly, from the detailed investigation, it was revealed that the kinetic plot was multistep in nature, having three different slopes. The first region indicated the transfer of 4-CP molecules from the solution to the solid surface, followed by the next two stages. As the rate of diffusion in three different regions was found not to be the same and the linearized plots did not pass through the origin, it was concluded that the intraparticle diffusion was not the rate-limiting step. Obeid *et al.*, in one of their studies, demonstrated the performance efficiency of magnetic alginate beads towards PNP removal in the presence and absence of the cationic surfactant CPC.[91] In the presence of CPC, the removal was enhanced because the PNP molecules were adsolubilised in the micellar domain of CPC. Below the pK_a of PNP, *i.e.*, 7.2, the adsorption only occurred through the hydrophobic interaction between the neutral PNP molecule and the carbon chain of CPC. However, above 7.2, the electrostatic attraction facilitated the process due to the existence of a phenolate ion.

BPA is another phenolic derivative that is of high concern to environmentalists. Dovi *et al.* applied CTAB modified walnut shells for the adsorptive elimination of BPA from wastewater.[20] Experimental data fitted well with the Langmuir isotherm model. The maximum monolayer adsorption capacity reached 38.5 mg g^{-1}. The pseudo-second order kinetic model showed good correlation with the experimental data. Meneses *et al.* studied the effect of CTAB-modified carboxymethyl cellulose/sugarcane bagasse cryogels for the removal of BPA, MB, and Cr(VI) in batch and column modes.[92] BPA was adsorbed to the hydrophobic core of the CTAB micelles. The removal process was not hampered significantly in the presence of the other two pollutants, MB and Cr(VI).

Wang *et al.*, in one of their current studies, reported the successful application of CPC-modified pine sawdust powder for the adsorption of DCP and BPA from wastewater.[93] In comparison to the raw pine sawdust, after CPC modification, the adsorption capacity increased drastically (98% for BPA and 122% for DCP). The enhanced removal occurred due to solubilization in the surfactant hemi micelles, π–π stacking between the benzene ring structures, and the effect of hydrogen bonding between the adsorbent and the adsorbate.

Water bodies are often reported to be extremely polluted due to the discharge of wastes from the petroleum and crude oil industries. BTEX is one of the representatives of such wastes. Shakeri *et al.*, in their novel work, reported the successful modification of ostrich bone waste with a cationic surfactant and its application for the removal of BTEX from wastewater.[23] The adsorption data fitted well with the pseudo-second order model, and the distinct feature of the adsorbent was that its capacity was not reduced significantly even after 12 cycles of usage. Bilici *et al.* applied SDS-functionalized calcium alginate beads to remove oil from wastewater.[94] SDS functionalization was done using polyethyleneimine as the binder. It was interesting to note that 95% of the oil was adsorbed by the anionic surfactant-modified beads when the initial concentration of the oil was 30 g L^{-1}. In another study, Ibrahim *et al.* showed the promising efficiency of CPC-modified barley straw for the adsorptive eradication of standard mineral oil and canola oil from wastewater.[95] The maximum adsorption capacity was achieved as 613.3 mg g^{-1} for canola oil and 584.2 mg g^{-1} for standard mineral oil. A list of SMBs explored by various researchers for the removal of emerging pollutants is presented in Table 4.

4. Optimization of biosorption using surfactant-modified materials

Multiparameter optimization procedures using statistical techniques are commonly used by researchers to obtain optimal biosorption efficiency. From a set of initial experiments, an idea regarding the range of removal efficiency, adsorbent dose, working concentration of pollutant, the effect of solution pH, *etc.*, is obtained. Based on that, a number of experiments are designed using statistical models to perform the optimization study. RSM and ANN are some of the statistical methods used for the optimization purpose. Apart from predicting the optimized experimental conditions, these techniques also give a clear picture regarding the interdependency of several operating parameters in pollutant removal. As three or more operating parameters are simultaneously considered in these models, they are more useful compared to the single-parameter optimization method. In the study of MV dye removal using anionic surfactant-modified *Pyracantha coccinea* biomass, Akar *et al.* performed an optimization study using BBD and RSM models.[12] Three operating parameters, *viz.*, solution pH (lower limit: 3 and upper limit: 9), biosorbent dose (lower limit: 0.4 g L^{-1} and upper limit: 4 g L^{-1}), and contact time (lower limit: 5 min and upper limit: 60 min), were chosen as the input variables and the percentage removal of MV was set as the response. Seventeen experiments were run and the experimentally obtained values showed good correlation with the predicted values. Through RSM, the optimum values for pH, biosorbent amount, and contact time were found to be 6, 0.055 g, and 30 min, respectively. In another study, Yadav *et al.* selected solution pH, the dose of adsorbent (CTAB modified *Saccharum munja*-based biocomposite containing 1% CNT) and the initial concentration of the anionic dye as the input variables for an optimization study using the BBD model.[38] The quadratic model obtained after running 17 trials for each dye was found to be the best fit with a coefficient of variation for RR, RO, and BB of 5.21%, 11.26% and 6.88%, respectively. From the three-dimensional response plots, it was revealed that with the increase in the dose of the adsorbent, the removal efficiency increased. On the other hand, a decrease in the solution pH improved the removal efficiency, while the removal efficiency decreased with the increase in pH.

In the study of TC and CPX removal using HDTMA-modified waste hazelnut shells, Guler and Solmaz[96] chose four parameters, *viz.*, initial solution pH, initial concentration of the pollutants, contact time, and temperature as the input variables for the RSM model. Based on the results of the initial experimental study, the lower and upper limits of solution pH, initial pollutant concentration, contact time, and temperature were set as (3 and 9), (5 and 100 mg L^{-1}), (5 and 180 min), and (20 and 50 °C). From the BBD model of RSM design, it was found that the optimal conditions for TC removal (37.34%) were as follows: initial concentration of TC = 9.4 mg L^{-1}, solution pH = 8.66, temperature = 25.96 °C and contact time = 146.47 min. On the other hand, at an initial concentration of 29.26 mg L^{-1}, solution pH = 8.31, contact time = 100.71 min, and temperature = 36.53 °C, the maximum CPX removal achieved was 83.07%.

Karaman *et al.* explored the ANN technique for the optimization of CR dye removal from aqueous media using CTAB-modified biomass.[45] Different ANN models possessing distinct backpropagation algorithms and hidden layer topologies were experimented by the authors to determine which model had the highest prediction accuracy for CR removal. Four operating parameters, such as initial concentration of CR, initial pH of the dye solution, contact time, and reaction temperature, were chosen as the independent variables for training of the ANN model. Among the experimental data obtained, 70% were selected for training purposes, 15% were used for validation purposes, and the remaining 15% were deployed for training and assessing the model. Detailed mathematical analysis showed that the regulation backpropagation algorithm with the *tansig–purelin* transfer function containing a single hidden layer with 14 neurons was the best model for the purpose (MSE = 0.0002 and $R^2 = 0.9996$).

However, in modern times, machine learning algorithms are becoming more popular than the old statistical methods for optimization studies. They are found to be more efficient in solving complicated problems in relatively less time. Khalili *et al.* adopted the ML approach by deploying the GBRT and XGBoost models, for fitting the data of adsorptive removal of BB9 using NaOH modified, SDS modified, and Fe_3O_4 modified orange peels.[19] GBRT is an ML model, which is often used for prediction purposes, utilizes a group of decision trees to make accurate forecasts. Further, XGBoost is a specific implementation of GBRT developed by a group of researchers (Chen and Guestrin) to enhance the model efficiency.[102] The GBRT algorithm utilizes iteration of multiple decision trees to arrive at the final decision, and in this work, this model was explored to determine the removal efficiency of BB9 dye by using 8 different adsorbents. On the other hand, the XGBoost method was used to determine the removal efficiency offered by the optimal adsorbent. Both models provide good accuracy with respect to the output prediction, which is confirmed by the high R^2 value and low statistical error values. For the construction of the GBRT model, the importance of adsorption time has been found to be the highest (29%), while in the case of XGBoost, solution pH plays a crucial role (37.1%).

5. Application of surfactant-modified biomaterials for real wastewater treatment

Evaluating the efficiency of a particular adsorbent in a real wastewater matrix is essential from a practical point of view. Some studies have been reported in the literature regarding the application of surfactant-modified biomaterials for pollutant removal from real wastewater matrices. Shakeri *et al.* explored the efficiency of CTAB-modified ostrich bone waste towards BTEX spiked in the water of the Anzali lagoon as a real sample.[23]

Alhujaily *et al.* applied CTAB-modified mushroom waste for the treatment of dye-spiked real wastewater.[44] Seawater, lake water, industrial wastewater, and tap water were tested for this purpose. An attractive removal efficiency (>95%) was achieved in the case of seawater and tap water samples, while a slightly low removal (81–90%) was observed in the case of industrial wastewater.

Kasperiski *et al.* applied a CTAB-modified stalk adsorbent for the treatment of simulated dye wastewater.[47] The simulated wastewater was prepared by mixing various dyes such as DB 15, DR 23, RB 5, and acid green 25, and other compounds such as NaCl, Na_2CO_3, and KNO_3 in high concentrations. The CTAB-modified adsorbent showed excellent removal efficiencies (>90%), proving its capability to treat highly polluted industrial effluent.

Pal and Pal compared the efficiency of SDS-modified chitosan hydrogel beads for the removal of Cd(II) from synthetic and real wastewater.[22] In the case of distilled water, the initial concentration of Cd(II) was varied in the range of 10–100 mg L^{-1}, and the maximum adsorption capacity was obtained as 125 mg g^{-1}.[21] On the other hand, the concentration of cadmium in real wastewater was found to range from 10 to 11 mg L^{-1}, and the maximum adsorption capacity was obtained at 18 mg g^{-1}.[22] Detailed experimental investigation revealed that the pseudo-second order kinetic model fitted the data best for both distilled water and real wastewater. However, it was noted that, while the Langmuir isotherm model showed the best correlation with the experimental data obtained for distilled water, in the case of real wastewater, the Freundlich isotherm model best fitted the experimental values.

Real wastewater matrices often contain more than one pollutant at a time. So, it is very pertinent to justify the adsorption behaviour of an adsorbent towards a particular contaminant in the presence of other substances. Meneses *et al.* applied CTAB-modified carboxymethyl cellulose/bagasse cryogels to decontaminate a ternary mixture containing BPA, MB, and Cr(VI).[92] In comparison to the pure Cr(VI) solution, the removal efficiency increased by 3.5 times in the binary mixture with BPA or in the ternary mixture, and by 1.4 times in the presence of MB molecules. However, adsorption efficiency towards MB dye was reduced in the presence of the other two contaminants due to the screening effect. Dovi *et al.* reported the successful application of CTAB-modified walnut shells for the removal of both CR and BPA in the presence of others.[20] Thus, the incorporation of a surfactant into the biosorbent matrix to make it suitable for removing multiple pollutants is undoubtedly a great advancement in the field of biosorption.

Apart from testing the efficiencies of SMB against real wastewater, another important aspect is to check the viability of the newly developed adsorbents in continuous operation mode. Akar *et al.* explored an SDS-modified *Pyracantha coccinea* powder-based biosorbent for the removal of MV dye in both batch mode and column mode.[12] The effects of experimental parameters such as the flow rate, the internal diameter of the column, and the biosorbent dose were studied. The flow rate was varied in the range of 0.4–6 mL min^{-1}, while the internal diameter and amount of biosorbent were maintained in the ranges of 9–19 mm and 0.01–0.06 g. The optimized result was obtained at a flow rate of 1.3 mL min^{-1}, an internal diameter of 11 mm, and a mass of adsorbent 0.04 g. The initial concentration of MV was kept at 100 mg L^{-1}. Apart from the column study, the authors also performed an adsorption study on real wastewater samples. The sample was collected from the entry point of a wastewater treatment plant located at Eskisehir, Turkey. It was spiked with 100 mg L^{-1} MV dye, and the biosorption test was conducted in both batch mode and continuous mode. Nearly 87% removal efficiency was attained in the

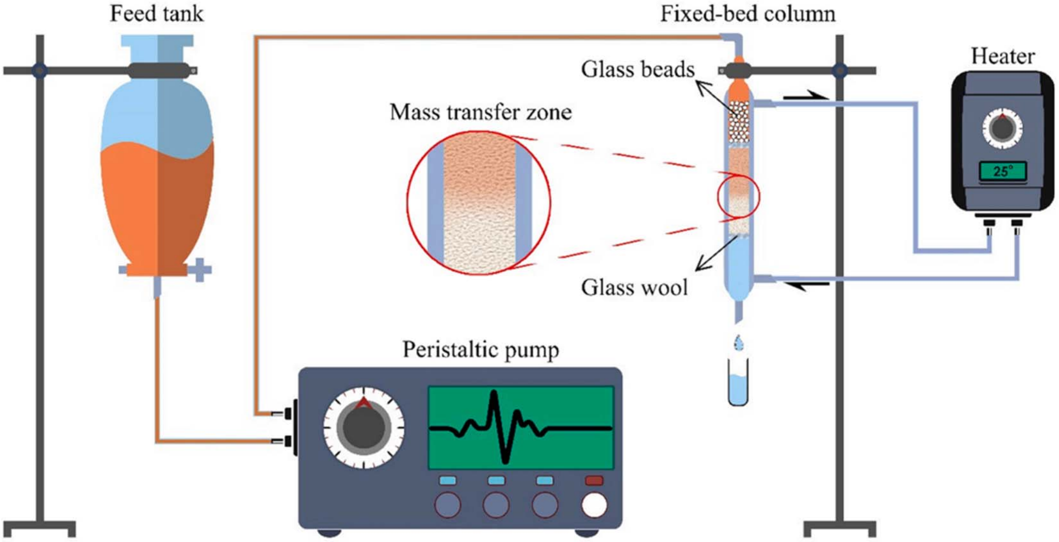

Fig. 6 Schematic diagram of the fixed-bed column apparatus.[103]

batch study, while nearly 95% removal efficiency was achieved in the case of column mode. In another study, the same group successfully applied a quaternary ammonium salt modified sugar beet pulp-based biosorbent for the removal of AR dye from wastewater in continuous mode.[51] Apart from the variation of the operating parameters, the authors also performed a breakthrough study, which is an important parameter for column designing. The breakthrough point was obtained at around 42 h, at which point nearly all of the dye was removed. However, saturation occurred at 56 h.

Babazadeh *et al.* investigated the adsorption efficiency of a surfactant-modified chitosan–clinoptilolite composite through column experiments.[103] 0.5 g, 0.6 g, and 0.7 g of adsorbent material were filled inside the column to get bed depths of 1, 1.2, and 1.4 cm, respectively. The column operation was carried out at three flow rates of 4.5, 6, and 7.5 mL min^{-1}, with an initial concentration of MO of 100 mg L^{-1} and a solution pH of 6.9. The schematic is shown in Fig. 6. It observed seen that with the increase in the mass of the adsorbent, the breakthrough time increased, and the empty bed contact time was also enhanced, indicating more active sites for adsorption to take place. On the other hand, with the increase in the flow rate, the removal efficiency decreased as enough contact time was not provided for the removal process to take place. The nature of the breakthrough curve obtained was attempted to be correlated with existing models such as the Adams–Bohart model, the Yoon–Nelson model, the Thomas model, and the BDST model. A detailed investigation proved that the BDST model was best suited to explain the experimental conditions.

6. Characterization techniques

6.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopic analysis is essential to explore the mechanism of adsorptive removal and to get an insight into the mechanism through the involvement of various functional groups. In the FTIR spectroscopy study of oil removal by CPC-modified barley straw, strong bands were observed in the region between 2922 and 2853 cm^{-1} in the spent adsorbent.[95]

Thamilarasi *et al.* carried out the FTIR analysis of unmodified and CTAB-modified palm fruit husks.[73] The peak at 1620 cm^{-1} indicates the presence of carboxylate ions, and the peaks at 1460 cm^{-1} and 1058 cm^{-1} represent the lactonic and phenolic groups of the lignin structure.

FTIR analysis of natural clinoptilolite, the composite with chitosan, and the composite after surfactant modification provided important information regarding MO uptake.[103] Strong bands in the spectrum at 2878 cm^{-1}, 1601 cm^{-1}, and 1382 cm^{-1} represent the –CH stretching vibration, –NH$_2$ vibration and C–N stretching vibration, respectively.

6.2. Electron microscopy

The morphological details of the adsorbents are determined by electron microscopic studies (Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), or both). With the help of an SEM study, Zang *et al.* found that mycelia were randomly dispersed over the surface of sawdust.[36] Hence, an irregularly shaped structure was revealed. However, after surfactant modification and immobilization on the alginate surface, the morphology looked more homogeneous in nature. At a lower magnification, a membrane-like structure appeared to wrap around the biosorbent surface. However, at a higher magnification, it was clearly observed that porosity existed, which ultimately indicated that CTAB modification did not hamper the porous structure of the adsorbent.

In many of the studies, a rough surface is visible after surfactant modification. Akar *et al.* observed that the rough surface of the sugar beet pulp transformed into a heterogeneous layered structure after surfactant modification.[51] However, after dye adsorption, the surface appeared to be smoother due to the presence of the dye layer.

Babazadeh *et al.* performed SEM analysis of natural clinoptilolite, chitosan clinoptilolite, surfactant (CTAB) modified chitosan–clinoptilolite and MO loaded CTAB modified chitosan–clinoptilolite composites, to gain a clear understanding of the morphological features of the adsorbent material.[103] The surface of the natural clinoptilolite exhibited a flake-like structure, while after forming a composite with chitosan, the surface of the clinoptilolite was found to be covered with a chitosan layer. On the other hand, after surfactant modification, it was found that the surfactant molecules intercalated into the interlayer region of the composite.

6.3. BET analysis

In adsorption studies, BET surface area analysis is important. Ren *et al.* reported that the BET surface area of natural and CPC-modified phoenix tree leaves obtained was 2.08 and 1.32 $m^2 g^{-1}$, respectively.[89] Due to CPC modification, the pore channels were constricted, which produced such results. Other researchers also reported similar results. Babazadeh *et al.* carried out N_2 adsorption–desorption experiments on natural clinoptilolite, a chitosan–clinoptilolite composite, and a cationic surfactant-modified chitosan–clinoptilolite composite.[103] The adsorption–desorption curves resemble type IV isotherms, indicating the presence of mesopores in the adsorbent material. The specific surface area of the natural clinoptilolite was found to be 21.8 $m^2 g^{-1}$, whereas the specific surface area of the chitosan–clinoptilolite composite and surfactant-modified chitosan–clinoptilolite was obtained as 13.6 $m^2 g^{-1}$ and 10.5 $m^2 g^{-1}$, respectively. Among the three, the surface area of the natural clinoptilolite was the highest. After forming a composite with chitosan, it was reduced due to the occupation of the void space by the chitosan layer. Further, after surfactant modification, the pores were blocked, leading to a further reduction in the specific surface area.

Jain and Gogate reported the results of the BET analysis of the dried powdered adsorbent of *Prunus dulcis*, as well as of a NaOH-modified and surfactant-modified adsorbent.[53] The specific surface area of the unmodified natural leaf powder was found to be 67.02 $m^2 g^{-1}$, while it was enhanced to 426.35 $m^2 g^{-1}$ after being modified with NaOH. However, upon being modified, the specific surface area was reduced to 243.64 $m^2 g^{-1}$. During the alkali treatment, some pores might have been created, which were blocked subsequently by the alkyl chain of the surfactant. Hence, this result has been obtained.

6.4. XRD analysis

XRD analysis is often used to determine the crystallinity of the SMBs applied for wastewater treatment. Alhujaily *et al.* performed the XRD analysis of spent mushroom waste and CTAB-modified spent mushroom waste in relation to the removal of dyes such as DR 5B, DB 71, and RB 5.[44] Similar types of peaks appeared in the XRD spectra of the biomass before and after surfactant modification. Peaks were noticed at 14° and 22° corresponding to lignocellulose. The peak at 22° looked sharper than the other peak at 14°. After CTAB modification, the intensity of the sharper peak was enhanced.

Zhao *et al.* performed an XRD analysis of peanut husk and CPB-modified peanut husk utilized for the adsorption of light green dye from wastewater.[63] In both cases, peaks appeared at 16° and 22° corresponding to the cellulose and polysaccharide structures.

6.5. XPS analysis

To determine the chemical composition of the SMBs and gain a deeper insight into the adsorption process, an XPS study is often carried out. Prior to CTAB modification, only C and O were the major elements present in walnut shells.[20] However, due to CTAB loading, prominent N 1s and Br 3d peaks were observed on the wide survey spectrum. Additionally, the visibility of the S 2p peak confirmed the attachment of CR dye to the CTAB-modified walnut shells during the adsorption process. Oraon *et al.* conducted an XPS analysis of microporous nitric acid-treated biochar before and after SDS modification to examine the functional group and bond formation during the dye (MB) uptake process.[104] In the core level spectra of C 1s of HNO_3-modified biochar both before and after SDS modification, four peaks were visible corresponding to C–C/C=C, –C–O, –C=O, and –O–C=O bonds. After SDS modification, a change in the binding energy was visible, indicating the successful incorporation of the anionic surfactant in the biochar matrix. Likewise, the core level spectra of O 1s also showed changes in peaks before and after SDS loading onto the biochar. Moreover, due to HNO_3 pre-treatment, the nitrogen peak was noticed in the XPS spectra.

6.6. pH_{ZPC} measurement

Surfactants are often incorporated into biomass to increase its selectivity towards environmental pollutants. In that regard, the knowledge of the pH_{ZPC} of the adsorbent material is very important to predict the working pH range. Especially for heavy metal adsorption, the solution pH plays a crucial role. In the study of Cu(II) uptake by surfactant (SDBS) modified oil palm leaf powder, Rafatullah *et al.* obtained the pH_{ZPC} value of the biosorbent as 5.9.[37] In the solution pH range of 2–5, the removal of Cu(II) was not good (<80%), because the surface charge of the adsorbent was positive resulting in repulsion with the copper ions. However, the best removal efficiency was attained at pH 6, after which it decreased due to precipitation.

Foroughi-dahr *et al.* reported the pH_{ZPC} of tea waste as 4.75.[40] Hence, surface modification of the waste material with a cationic surfactant was possible at a solution pH > 4.75. For CR adsorption, the solution pH was varied in the range of 3–13. In a wide range of pH (4–10), the adsorption percentage remained almost constant. However, at extremely lower and higher pH, the removal efficiency dropped.

6.7. Other analysis

Other important characterization studies often performed include TGA, XRF, and elemental composition analysis (CHNS). As a certain loss of mass with the rise in temperature is a frequent incident in the case of biomaterials, the TGA study is very significant in the case of SMBS. Babazadeh *et al.* reported

Table 5 Effect of different surfactant modifications towards the removal of a particular pollutant

Pollutant	Surfactant used for modification	$q_{\max}$ (mg g^{-1})	References
Cr(VI)	HDTMA-modified activated carbon	1.80	69
	DDAB modified activated carbon	1.86	
Cd(II)	CTAB-modified activated carbon	279.5	75
	SDS-modified activated carbon	263.2	
	TX-100 modified activated carbon	232.9	
Pb(II)	CTAB-modified ostrich bone waste	3.412	25
	Laundry detergent (anionic surfactant) modified ostrich bone waste	91.51	
Hg(II)	CTAB-modified ostrich bone waste	4.98	25
	Laundry detergent (anionic surfactant) modified ostrich bone waste	38.02	
DC	DTAB modified esparto grass	3.31	88
	CTAB modified esparto grass	6.45	
	BDAC modified esparto grass	10.30	

the results of TGA for natural clinoptilolite, a chitosan–clinoptilolite composite and a CTAB modified chitosan–clinoptilolite biosorbent in the temperature range of 30–800 °C.[103] For the natural clinoptilolite, weight loss in two stages was visible. The first one occurred in the range of room temperature to 335 °C due to the loss of the physically adsorbed and unbound water molecules. In the second stage (335–728 °C), the loss in weight occurred due to the degradation of the hydroxyl groups present in the silicate minerals.

Zhao *et al.* concluded, from XRF analysis, the presence of Si, K, Ca, Fe, Al, and Mg in peanut husk.[63] After CPB modification, bromine, in addition to the other elements, was found to be present. It indicated successful modification by CPB.

7. Comparative analysis for usage of different surfactants

Surfactants are used in most of the studies as surface modifiers. Hence, depending on the charge of the pollutant, a suitable surfactant is often selected for surface modification. Among the heavy metal ions, in nature Cr(VI) exists in an oxyanion form ($Cr_2O_7^{2-}$ or CrO_4^{2-}). Therefore, cationic surfactants are commonly explored to modify adsorbents for Cr(VI) removal from wastewater. Dong *et al.* explored a CTAB-modified *Auricularia auricula* spent substrate for the removal of Cr(VI) from wastewater.[71] Namasivayam and Sureshkumar reported the successful application of CTAB-modified coconut coir pith for Cr(VI) eradication.[2] Sarfraz *et al.* (2022) utilized both anionic surfactant (SDS) and cationic surfactant (CTAB) modified wheat bran to determine their efficiencies regarding Cr(VI) uptake from wastewater.[72] The percentage removal for raw wheat bran and SDS-modified wheat bran was found to be more or less the same (87.7% and 83.5%) in the case of Cr(VI). However, due to CTAB modification, the percentage removal of Cr(VI) was enhanced to 98.9%.

Apart from Cr(VI), other metal ions such as Cd(II), Pb(II), and Ni(II) exist as cations in nature. So, most of the studies involved the application of anionic surfactant-modified materials for the removal of these heavy metals from wastewater. However, in one study, Nadeem *et al.* utilized CTAB, SDS, and TX-100 modified activated carbon adsorbents for Cd(II) adsorption purposes. Interestingly, the CTAB-modified material yielded the best results.[75] In another study, Amiri *et al.* performed an adsorption study for the removal of Pb(II) and Hg(II) ions from water medium using pristine ostrich bone waste material. The same pristine material but after modification with cationic and anionic surfactants was also used for the same purpose.[25] It was interesting to observe that, while the cationic surfactant could not improve the adsorption capacity, the anionic surfactant was able to increase the adsorptive removal efficiency of the ostrich bone material drastically.

Pharmaceutical compounds often change their structure with a change in solution pH. Lafi *et al.* modified esparto grass with different cationic surfactants and applied the prepared SMBs for the adsorption of DC from wastewater.[88] The cationic surfactants DTAB, CTAB, and BDAC were used for the modification purpose, and the maximum adsorption capacities were obtained as 3.31 mg g^{-1}, 6.45 mg g^{-1}, and 10.30 mg g^{-1}, respectively. Hence, it is seen that with the increase in the number of carbon atoms, the adsorption capacity increases.

For comparison purposes, the applicability of different surfactants towards the removal of a particular pollutant is compiled in Table 5.

8. Regeneration and reusability of adsorbents

The regeneration and reusability of adsorbents often play a vital role in the adsorption process from commercial and industrial points of view. An adsorbent having good efficiency and recycling ability is undoubtedly economically more attractive. However, in most of the adsorption studies, the regeneration and reusability studies are left out. In some cases, the performance of the regenerated materials is not so good. The lower performance is due to the deactivation of the adsorbent during the desorption process. Zang *et al.* reported a significant decrease in the removal efficiency of spent *Auricularia auricula* for Cr(VI) removal after three cycles.[36]

However, some of the studies showed the promising regeneration of spent SMBs. Dovi *et al.* used NaOH, ethanol, HCl, and

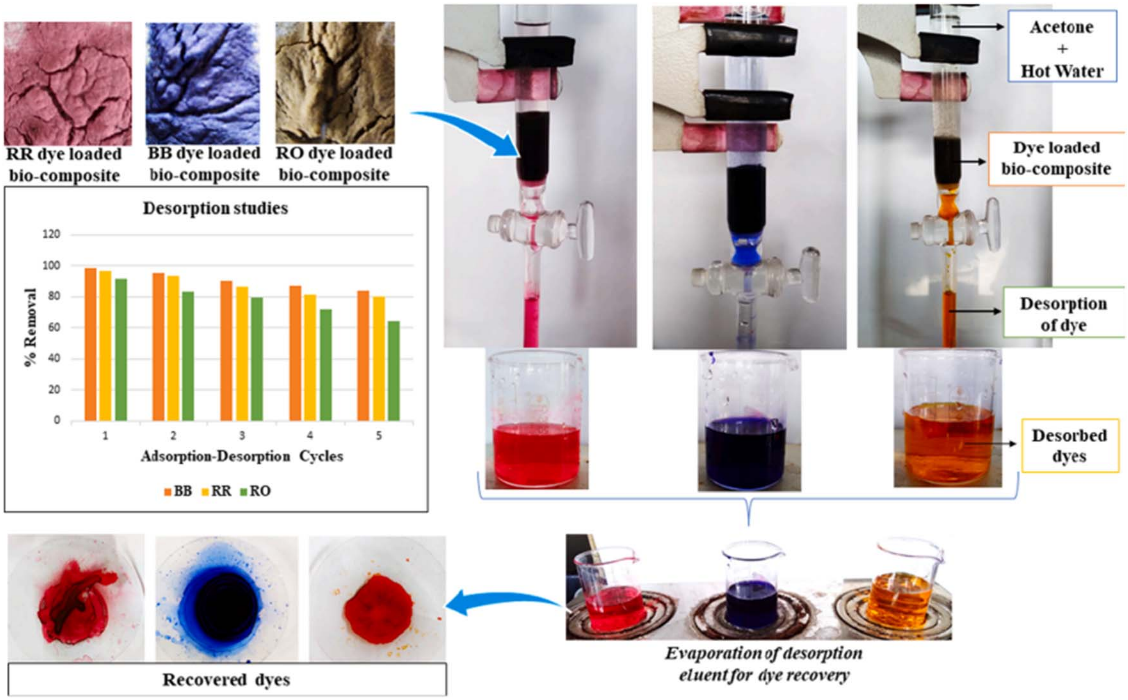

Fig. 7 Desorption studies of a dye-loaded bio-composite.[38]

NaCl for the desorption of BPA and CR from a CTAB-modified walnut shell biosorbent.[20] Among all the desorbing reagents, NaOH performed the best, and hence, it was deployed as the eluent solution. Yadav *et al.* explored a mixture of acetone and hot water for unloading anionic dyes from the surface of CTAB-modified CNTs.[38] The regenerated biosorbent performed well, even up to five cycles, without any loss of adsorption capacity. The results of the desorption study are shown in Fig. 7.

In our study, a reuse and regeneration study was performed to determine the suitability of CPC-modified alginate–xanthan beads for practical purposes.[14] It has already been explained in the previous section that after being dipped into 1-butanol, MO was detached from the bead surface while MB remained attached to it. However, with only MO desorbed, the beads were reinserted in the dye mixture (MO–MB) for the next cycle. Interestingly, adsorption–desorption continued for three more cycles without affecting the efficiency. Hence, it may be concluded that these CPC-loaded alginate–xanthan hydrogel beads may also be suitable for practical purposes to separate dyes from dye mixtures.

9. Surfactant-influenced biosorption in the light of UN SDGs

In modern times, it is very pertinent to justify the sustainability and impact of an environmental remediation technique. In 2015, in the UN General Assembly, 17 goals were adopted to develop strategies for the improvement of health and education, reduction in inequality, and boosting economic growth throughout the world by 2030. Many goals are based on environmental parameters, while some are dependent on socio-economic factors. The eradication of heavy metals, carcinogens, mutagens, and teratogens from environmental matrices obviously falls within the domain of the SDGs. Hence, any environmental clean-up action should satisfy the principles of different aims of these goals.

Environmental remediation through chemical adsorption is often rapid and suitable for highly contaminated sites. In contrast, biosorption is a slow process, achieving environmental purification by using environmentally benign materials. In this regard, surfactant-assisted biosorption is a wonderful remediation technique that offers both selectivity as well as sustainability. It can be considered as one of the most efficient uses of resource in modern times. It provides proper utilization of natural materials empowered by chemical modification for decontaminating polluted water. Hence, it properly fits with UNSDG 6 (clean water and sanitation) and UNSDG 7 (affordable and clean energy). Moreover, it also satisfies the criteria of UNSDG 3 (human health and well-being) and UNSDG 13 (climate action). It can also be fitted to UNSDG 9 (industry, innovation and infrastructure).

Many research articles in recent times justified the biosorption phenomenon in accordance with some UN SDGs. Dhaka *et al.* described the biosorptive removal of Pb(II) by *Aspergillus niger* in accordance with UNSDGs 6 and 9.[105] Gomez-Aguilar *et al.* utilized coffee pulp for the adsorption of Pb(II) from wastewater.[106] The authors justified that this treatment technology is as per the provisions of goals 3 and 6. As biosorption has been recognized by researchers as a sustainable option, surfactant modification is obviously a stronger version of this sustainable technology. For example, in our recent work, it was reported that Alg-Xan hydrogel beads were capable of removing only cationic dye MB from aqueous media. However, after CPC modification, it was interesting to observe that both anionic (MO) and cationic dye (MB) can be eliminated from wastewater. So, after surfactant modification, it is suitable for removing both types of dyes.

10. Conclusions and future perspectives

It is already highlighted in the previous sections that biomaterials are regarded as new-age attractive sorbents for wastewater remediation, and surfactant modification may further add extra advantages with respect to the applicability of these materials in pollution abatement with higher efficiency. The inclusion of surfactants helps to alter the surface chemistry of the original biosorbent. Rasheed *et al.*, in their recent review article, highlighted that surfactant modification provides an effective way of trapping different categories of pollutants from water media.[17] Micelles anchored on the solid surface provide a congenial core area for adsorbing hydrophobic pollutants and inorganic pollutants on the outer part. Palmer and Hatley, in their review article, discussed the roles of surfactants in enhancing the performance efficiency of traditional wastewater treatment processes.[107] The authors highlighted the exploration of surfactant-modified zeolites for eradicating different pollutants from water media. Moreover, the authors also emphasized the improvement in the ultrafiltration process for wastewater treatment in the presence of micelles.

Despite offering several advantages, the scientific community needs to address several aspects to make SMBs more widely accepted. Firstly, biosorption itself is a complicated process, often involving multiple mechanisms in capturing pollutants. In addition to it, surfactant inclusion makes the clean-up chemistry process more interesting. Hence, detailed analysis and clearer insight into surfactant-assisted biosorption are desirable for a better understanding of the process. Secondly, a myriad of synthetic surfactant-modified biomaterials are available in the literature to explore their promising pollutant-removing efficiencies. However, synthetic surfactants are petroleum derived products. On the other hand, biosurfactants are more sustainable options of the present era. However, to date, only a few studies describing the successful modification of biomass with biosurfactants for pollutant abatement purposes have been reported. More studies with biosurfactants are recommended to be carried out in order to satisfy various criteria of UNSDGs. Thirdly, most of the SMBs reported in the literature are often subjected to capture a specific pollutant. Very few studies have been involved in the exploration of SMBs for the cleaning of wastewater containing multiple pollutants. Hence, more such studies are recommended from a practical point of view. It is essential to understand the removal efficiency of SMBs when more than one pollutant is present in wastewater. It is also evidenced from our previous study that, sometimes, the presence of one pollutant increases the removal efficiency of the other due to the synergistic effect. However, many times, a decrease in the adsorption percentage of a particular adsorbate is noticed due to the interference of others. It has already been mentioned in Section 5 that adsorption in column or continuous mode is extremely necessary for practical purposes. It is true that some researchers conducted adsorption studies in continuous mode with different SMBs. However, the problem persists with biopolymer hydrogel beads. Therefore, researchers may attempt to use different reinforcing agents or pretreatment to address this issue.

Although the regeneration and recycling of the adsorbent are crucial from an economic standpoint, in most of the adsorption studies, regeneration and reusability studies are not carried out. In some cases, the performance of regeneration and the efficiency of the regenerated materials are not satisfactory. The lower performance is due to the deactivation of the adsorbent during the desorption process. So, more rigorous attention is desirable from researchers regarding the development of a novel reusable SMB.

Optimization is a very useful part of adsorption studies. A good number of research articles on multivariate statistical methods of optimization are already available. However, in recent times, AI-ML and AI-ML-based algorithms have been developed for model generation and optimization purposes. They are superior to traditional statistical methods in terms of complicated data handling. Khalili *et al.* reported one such study on NaOH, SDS, and Fe_3O_4-modified orange peel adsorbents regarding the uptake of BB9 from wastewater.[19] However, more studies are required in the upcoming days.

When an SMB is utilized for wastewater treatment, there is a chance of surfactant leaching from the solid surface, producing secondary pollutants. However, only a handful of studies have tested the leaching issue. Biosorbents are often generated from waste products. Hence, their life cycle analyses and material flow analyses are recommended to gain a clear understanding of their environmental impact. Lastly, cost–benefit analysis must be performed in order to get a comparative idea regarding the applicability of SMBs in real wastewater treatment. Waste biomass obtained from agricultural and forest residues is undoubtedly a low-cost adsorbent material.[99,100,104] Hence, the selection of such materials may make the process economical. Apart from that, the cost of surfactant modification is also justified in some reports. For example, Namasivayam *et al.*, in their studies of Cr(VI) and thiocyanate removal, compared the cost of surfactant modified coir pith with that of other materials.[2,98] As coconut coir pith is a discarded industrial waste, the only cost incurred is for its modification. The authors reported that the adsorbent preparation cost was around $8 per kg. In comparison to that, Filtrasorb 400, with lower adsorption capacity, was reported earlier to remove Cr(VI) at a cost of nearly $30 per kg. So, it indicates that there are various advantages to using SMBs. However, besides these positive aspects, the cost of collection and the seasonal availability of an abundant amount of agro-waste may be some challenging tasks. These issues need to be addressed and more studies involving economic analysis need to be performed in the near future.

List of abbreviations

ABB	acid brilliant blue
AB 1	acid black 1
AB 25	acid blue 25
AB 40	acid blue 40
AB 113	acid blue 113
ANN	artificial neural network
AO	acid orange
AO 7	acid orange 7
AR	acid red
AR 1	acid red 1
AR 18	acid red 18
BPA	bisphenol A
BB 9	basic blue 9
BB R-250	brilliant blue R-250
BDAC	benzyldimethyl ammonium chloride
BDHAC	benzyldimethyl hexadecyl ammonium chloride
CNT	carbon nanotube
CP	chlorophenol
CPB	cetylpyridinium bromide
CPC	cetylpyridinium chloride
CPX	cephalexin
CR	congo red
CTAB	cetyltrimethylammonium bromide
CTAC	cetyltrimethylammonium chloride
CV	crystal violet
DB 15	direct blue 15
DB 71	direct blue 71
DC	diclofenac
DCP	dichlorophenol
DDBAB	dodecyl dimethyl benzylammonium bromide
DR 5B	direct red 5B
DR 23	direct red 23
DR	Dubinin–Radushkevich
GBRT	gradient boosting regression tree
HDTMA	hexadecyltrimethylammonium bromide
LG	light green
MB	methylene blue
MG	malachite green
ML	machine learning
MO	methyl orange
MV	methyl violet
MWCNT	multiwalled carbon nanotubes
PNP	*para* nitrophenol
PO	procion orange
RB	reactive black
RB 5	reactive black 5
RO 107	reactive orange 107
RR 35	reactive red 35
RR 45	reactive red 45
RSM	response surface methodology
SDBS	sodium dodecyl benzene sulphonate
SDS	sodium dodecyl sulphate
SMB	surfactant-modified biosorbent
TC	tetracycline
TGA	thermogravimetric analysis
TTAB	tetradecyltrimethylammonium bromide
TZ	tartrazine
XGBoost	extreme gradient boosting
XRF	X-ray fluorescence

Data availability

This is a review article. All the data reported here can be found in the cited papers.

Conflicts of interest

There are no conflicts of interest to declare.

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