

Clay–polymer nanocomposites: Progress and challenges for use in sustainable water treatment

Raj Mukhopadhyay^{a,1}, Debarati Bhaduri^{b,1}, Binoy Sarkar^{c,*}, Ruhaida Rusmin^d, Deyi Hou^e, Rubina Khanam^b, Subhas Sarkar^f, Jayanta Kumar Biswas^g, Meththika Vithanage^h, Amit Bhatnagarⁱ, Yong Sik Ok^{j,*}

^a Division of Irrigation and Drainage Engineering, ICAR-Central Soil Salinity Research Institute, Karnal, Haryana, India

^b ICAR-National Rice Research Institute, Cuttack, Odisha, India

^c Department of Animal and Plant Sciences, The University of Sheffield, Western Bank, Sheffield, S10 2TN, UK

^d Faculty of Applied Sciences, Universiti Teknologi MARA, Negeri Sembilan Branch, Kuala Pilah Campus, Kuala Pilah, Negeri Sembilan, Malaysia

^e School of Environment, Tsinghua University, Beijing, 100084, China

^f ICAR-Central Institute of Freshwater Aquaculture, Bhubaneswar, Odisha, India

^g International Centre for Ecological Engineering, Department of Ecological Studies, University of Kalyani, Kalyani, Nadia, West Bengal, India

^h Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

ⁱ Department of Environmental and Biological Sciences, University of Eastern Finland, P.O. Box 1627, FI-70211, Kuopio, Finland

^j Korea Biochar Research Centre & Division of Environmental Science and Ecological Engineering, Korea University, Seoul, Republic of Korea

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ABSTRACT

Contaminant removal from water involves various technologies among which adsorption is considered to be simple, effective, economical, and sustainable. In recent years, nanocomposites prepared by combining clay minerals and polymers have emerged as a novel technology for cleaning contaminated water. Here, we provide an overview of various types of clay–polymer nanocomposites focusing on their synthesis processes, characteristics, and possible applications in water treatment. By evaluating various mechanisms and factors involved in the decontamination processes, we demonstrate that the nanocomposites can overcome the limitations of individual polymer and clay components such as poor specificity, pH dependence, particle size sensitivity, and low water wettability. We also discuss different regeneration and wastewater treatment options (e.g., membrane, coagulant, and barrier/columns) using clay–polymer nanocomposites. Finally, we provide an economic analysis of the use of these adsorbents and suggest future research directions.

1. Introduction

In recent years, clean water has emerged as a critical issue globally because of rapid industrialization, intensive agricultural practices, and various harmful anthropogenic activities that have led to the release of large amounts of wastewater in the environment. These wastewaters are contaminated with various toxic pollutants such as heavy metals and metalloids, pesticides, phenols, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and polybrominated diphenyl ethers. As a result, the availability of clean water for drinking and irrigation purposes has become a global challenge.

The treatment of wastewater is necessary to satisfy the basic demands of good-quality water for human life and industrial use. Removal of various toxic pollutants and microbes can generate clean water that

can be used for different sectors such as agriculture and industry. Previous studies have discussed various novel approaches for wastewater treatment such as precipitation, complexation, membrane filtration, photo- and electro-catalysis, reverse osmosis, and electrodialysis (Fu and Wang, 2011; Barakat, 2011; Zhu et al., 2016; Szczepanik, 2017). Several of these techniques have disadvantages such as high costs, unproven performance in large-scale implementation, sludge formation, and the risk of secondary pollution. For example, photocatalytic degradation using semiconductor photocatalysts such as ZnO and TiO₂ has been demonstrated to be competitive as these oxides can remove a wide variety of contaminants; oxygen is used as the oxidative agent, and degradation of contaminants up to the parts-per-billion level is possible. However, the main disadvantage of this technology is that metal oxides and sulfides such as TiO₂ and CdS, if used as

photocatalysts without any supporting materials (e.g., clays, zeolites), may have low adsorption capacity, less surface area, and may release toxic metals into the environment (Asahi et al., 2001). Similarly, most of the above-cited methods suffer from low removal efficiency, high cost, and the generation of toxic chemicals and large quantities of sludge. Adsorption is considered to be one of the most efficient and cost-effective technologies for wastewater purification (Raval et al., 2016; Singh et al., 2018). The selection of adsorbents primarily depends on the specificity for a particular toxic agent, the adsorption efficiency, and the benefit–cost ratio. Different types of adsorbents (organic and inorganic materials) have exhibited satisfactory results for the decontamination of wastewater. These adsorbents include zeolites (activated and natural) (Singh et al., 2018; Bosso and Enzweiler, 2002; Inglezakis et al., 2003; Syafalni et al., 2014), natural clay minerals (Singh et al., 2018; Fan et al., 2009; Nishikiori et al., 2009), modified clay minerals (Rusmin et al., 2015; Olu-Owolabi et al., 2017; Mukhopadhyay et al., 2017; Kumararaja et al., 2018; Yadav et al., 2019; Han et al., 2019), activated carbons (Singh et al., 2018; Mirmohseni, 2012; Nethaji et al., 2013; Ahmed, 2017), agricultural waste (Anastopoulos and Kyzas, 2014; Bhatnagar et al., 2015; Shakoor et al., 2018; Ahmad and Danish, 2018), biochar (Mohan et al., 2014; Xie et al., 2015; Shaheen et al., 2018; Palansooriya et al., 2019; Premarathna et al., 2019), industrial waste and sludge materials (Bhatnagar and Sillanpää, 2010; Zhao et al., 2016; Anastopoulos et al., 2017), and polymeric resins (Singh et al., 2018; Rivas and Muñoz, 2009; Gandhi et al., 2010). Naturally occurring clay minerals are intensively used because of their easy availability and economic benefits (Mukhopadhyay et al., 2017; Sarkar et al., 2012a, 2013). However, the use of natural clay minerals is limited because of their low surface area, lack of standard protocol for regeneration and recovery in aqueous systems (Unuabonah et al., 2018), and limited potential for the removal of micro-pollutants (Bhattacharyya and Gupta, 2008; de Paiva et al., 2008; Unuabonah and Taubert, 2014; Sarkar et al., 2019). In contrast, polymeric resins have shown the potential to overcome the drawbacks of natural clay minerals, but their characteristics such as pH dependence, high cost, poor water wettability, and particle size sensitivity have limited the use of resins for widespread applications in industries and water treatment plants (Unuabonah and Taubert, 2014).

Researchers have paid significant attention to the development of clay–polymer nanocomposites (CPNs) with the aim of combining the beneficial characteristics of both clay minerals and polymers in a single adsorbent to overcome their respective limitations. The synthesis of CPNs is becoming popular because of their multiple applications and large-scale advantages for numerous industries including water decontamination. During CPN synthesis, polymers (thermoplastics, thermosets, or elastomers) are incorporated in minute quantities (< 5% by weight) into the supporting materials such as nano-sized particles of clay or other nanoparticles (< 100 nm in any dimension) with high aspect ratios ($L/H > 300$) (Denault and Labrecque, 2004). However, reinforcement is in the order of micrometers in the case of traditional composites, whereas CPNs are in the order of a few nanometers. CPNs also contain filler (1–5 vol. %) in small quantities and thus impart inherent characteristics and stability to pure polymer or resin (Wagner and Vaia, 2004). This critical review provides an overview of the recent advances of CPNs and their application in wastewater treatment along with their economic sustainability on a long-term basis. The other purpose of this review is to discuss the future direction in this area of research, which needs extensive exploration in the near future.

2. Clay mineral types and structures

Clay particles are crystalline structures and consist of layers mainly composed of tetrahedral $[\text{SiO}_4]^{4-}$ and octahedral $[\text{AlO}_3(\text{OH})_3]^{6-}$ sheets. There are seven groups of clay minerals, namely: (i) kaolinite group where tetrahedral $[\text{SiO}_4]^{4-}$ and octahedral $[\text{AlO}_3(\text{OH})_3]^{6-}$ sheets are present in a 1:1 ratio (e.g., kaolinite, halloysite, serpentine) (Miranda-

Trevino and Coles, 2003), (ii) 2:1 non-expanding group (e.g., mica and illite) where the tetrahedral and octahedral sheets are present in a 2:1 ratio, (iii) 2:1 limited expanding group (e.g., vermiculite), (iv) 2:1 strongly expanding group (e.g., montmorillonite (MMT)), (v) uncharged 2:1 group (e.g., pyrophyllite and talc), (vi) 2:1:1 group (e.g., chlorites) with an extra brucite octahedral layer sandwiched to a 2:1 mineral, and (vii) fibrous-layered silicates (e.g., palygorskite and sepiolite) (Lee and Tiwari, 2012). The layers of clay minerals forge stacks forming an ‘interlayer’ through weak van der Waals forces (Lee and Tiwari, 2012). Isomorphous substitution in the tetrahedral and octahedral layers along with pH of the medium normally generate negative and positive surface charges on these clay minerals. The 2:1-type layer silicates such as MMT, hectorite, and saponite along with fibrous palygorskite, commonly provide the support and matrix for CPNs (Sinha Ray and Okamoto, 2003). The above-cited clay minerals fall under the category of nano-scale materials in at least one dimension (either thickness of layer or diameter of fiber) and mainly depends upon the origin and type of clay mineral (Sinha Ray and Okamoto, 2003).

When clay minerals such as palygorskite and MMT are modified with organic molecules, the products are called organoclays. Organoclays are pertinent in the discussion of CPNs because the preparation of organoclays is often the first step (pre-treatment) of synthesizing CPNs. Naturally occurring clay minerals are hydrophilic. The hydrophilicity of clay minerals increases further following their saturation with cations such as Na^+ or Li^+ . These hydrophilic clay minerals are only compatible with hydrophilic polymers such as polyethylene oxide and polyvinyl alcohol (PVA) but are incompatible with non-polar polymers. Hence, organoclays are prepared as a preliminary step to make hydrophilic clay minerals compatible with hydrophobic polymers and non-polar molecules (Lee and Tiwari, 2012; Alexandre and Dubois, 2000; Manias et al., 2001; Zanetti et al., 2000; Dutta and Singh, 2015; Shayesteh et al., 2016). Conventionally, organoclays are prepared by combining clay minerals with quaternary ammonium, phosphonium, or sulfonium cations (Sarkar et al., 2012a; de Paiva et al., 2008; He et al., 2014). Positively charged organic molecules such as surfactant cations (hexadecyl trimethylammonium) can replace the hydrated cations (e.g., Na^+ , Ca^{2+}) in clay minerals via ion-exchange reactions giving the resulting clays a hydrophobic property and thus preparing them for modification with non-polar polymers. Organoclays are also known to enhance the contaminant adsorption capacity of natural clay minerals by their polar–nonpolar partition mechanisms, increased surface positive charge, and interlayer packing of contaminants (Sarkar et al., 2010a,b; Sarkar et al., 2012a,b,c).

3. Clay–polymer nanocomposites

Clay–polymer layered composites can be categorized into three broad groups: (i) phase-separated microcomposites, (ii) intercalated nanocomposites, and (iii) exfoliated nanocomposites (Sinha Ray and Okamoto, 2003; Alexandre and Dubois, 2000; Wypych and Satyanarayana, 2005; Mukhopadhyay and De, 2014). The phase-separated composites are formed when a polymer fails to intercalate into the silicate layers. However, the dimensions and properties of the composites remain the same as those of traditional microcomposites. The intercalated nanocomposites are formed when polymer chains enter into the crystalline silicate layers (in the nano range) irrespective of the clay–polymer ratio. In exfoliated nanocomposites (Bergaya et al., 2006), individual approximately 1-nm-thick clay layers are separated into the polymer matrix. In this novel class of composites, characteristics such as high modulus, tensile strength, flexural properties, heat distortion, self-extinguishing behavior, and biodegradability are observed as opposed to those of traditional composites. Various polymers such as poly vinyl chloride (PVC), epoxies, polyurethanes, polyesters, polypropylene, polystyrene, and chitosan (CTS) are currently used for CPN synthesis.

3.1. Polyurethane–clay nanocomposites

Polyols become intercalated into organoclays (modified with onium ions) through the solvation process. The intercalation is strongly influenced by the length and structure of the onium ions. Studies have revealed that the in situ polymerization reaction between a polyol-isocyanate precursor and organoclay generates nanocomposites with 50-Å basal-spaced intercalated clay phases embedded in the cross-linked polyurethane network (Wang and Pinnavaia, 1998a). The produced nanocomposites exhibit more strength and toughness than that of a pristine polymer (Wang and Pinnavaia, 1998a).

3.2. Epoxy–clay nanocomposites

This type of novel nanocomposite is obtained by diffusing highly expanded onium-modified clay minerals into the epoxide (Wang and Pinnavaia, 1998b) to improve the thermal stability and solvent resistance properties. Aliphatic amine, aromatic amine, anhydride, and catalytic curing agents are used to form an epoxy matrix with broad glass-transition temperatures (Wang and Pinnavaia, 1998b).

3.3. Polyimide–clay hybrid

The polymerization reaction between 4, 4'-diaminodiphenyl ether and pyromellitic dianhydride in dimethylacetamide (DMAC) solvent in the presence of organoclay matrix forms a polyimide–clay nanocomposite film under suitable heating conditions (Yano et al., 1997). MMT showed high exfoliation during composite formation, and the thermal expansion coefficient decreased with an increase in aspect ratio of the clay mineral (Yano et al., 1997).

3.4. Organoclay–polymer blends

Poly-ethylene oxide–clay blend, poly(ϵ -caprolactone)–clay blend, and poly(*l*-lactide) are normally used as a polymer blend with organoclay (Ogata et al., 1997). For example, poly(*l*-lactide) pellets were mixed with distearyl dimethylammonium-modified MMT and blended together in hot chloroform. After vaporization of the chloroform, 100- μ m-thick films remained. Poly(*l*-lactide) showed no intercalation into the modified MMT, and tactoids of unmodified MMT were observed to be parallel-aligned on the film surface (Ogata et al., 1997).

3.5. Polystyrene–clay nanocomposite

Vinyl-exchanged organoclay with styrene was used to form a polystyrene–clay nanocomposite (Akelah and Moet, 1996). An interlayer expansion of 24.5 Å suggested intercalation of styrene that might be the result of the use of acetonitrile (proven to be the most effective solvent) (Akelah and Moet, 1996). However, the most effective and efficient technique for intercalation was the melt intercalation of the polymer into an organoclay containing quaternary alkylammonium-exchanged ions (Vaia and Giannelis, 1997).

3.6. Polysiloxane–clay nanocomposite

Normally, organoclay provides the base support for preparing a silicate-reinforced polysiloxane nanocomposite with the addition of a small amount of water. Organo-MMT (dimethyl ditallowammonium, a mixture of C₁₂, C₁₄, C₁₆, and C₁₈ alkyl chains) was mixed with silanol-terminated poly(dimethylsiloxane) and cross-linked with tetraethylorthosilicate in the presence of a catalyst to form a silicate-reinforced polysiloxane nanocomposite (Burnside and Giannelis, 1995).

3.7. Poly(acrylic acid-co-acrylamide) nanoclay–polymer composite

Acrylic acid and acrylamide were used to prepare a nanoclay

(bentonite) polymer composite (Saurabh et al., 2018). The first step of the preparation involved the conversion of acrylic acid to acrylamide in the presence of alkali followed by the addition of clay and cross-linking reactions using N,N'-methylenebisacrylamide. The reactions were carried out in an N₂ atmosphere. Following the addition of ammonium persulphate initiator, the polymerization process occurred at a slightly elevated temperature (65–70 °C). The produced poly(acrylic acid-co-acrylamide) nanoclay–polymer composite was found to be super-absorbent of water (137.5 g/g) (Saurabh et al., 2018).

3.8. Clay–biopolymer nanocomposites

Natural and synthesized biopolymers such as proteins, polysaccharides, polypeptides, nucleotides, and polynucleotides are generated from their respective primary structures of specific monomers (Walton and Blackwell, 1973; Ruiz-Hitzky et al., 2005). These biopolymers are known to be biocompatible in nature and considered as green materials compared to synthetic polymers. Biopolymers can be used for clay–nanocomposite preparation to enhance their reactivity and functionality toward various applications such as electrochemical sensing, controlled pesticide and drug delivery, tissue engineering, and packaging materials (Ruiz-Hitzky et al., 2005; Darder et al., 2003; Viseras et al., 2008; Aranda et al., 2006). CTS is one such biopolymer (a copolymer composed of glucosamine and N-acetylglucosamine units extracted from crustacean seafood wastes (Darder et al., 2003) that is used extensively for the preparation of clay–biopolymer nanocomposites for the removal of contaminants from water (Rusmin et al., 2015; Kumararaja et al., 2018; Abdel et al., 2012; Azzam et al., 2016) (see Section 4.1.2).

3.9. Magnetic clay–polymer nanocomposites

To improve the functionality of CPNs, magnetic nanoparticles can be introduced into the polymer matrix. Recently, a palygorskite–magnetic-iron-oxide nanocomposite was prepared by a co-precipitation method (Rusmin et al., 2017) to achieve an environmentally safe and more economical synthesis process. This nanocomposite removed Pb(II) from wastewater by avoiding the aggregation issue of iron nanoparticles (Rusmin et al., 2017). The magnetic susceptibility of palygorskite–iron-oxide nanocomposite was intact after three cycles of use (Rusmin et al., 2017). Similarly, nanocomposite films were prepared by casting a mixture of clay (laponite), poly(butyl acrylate) emulsion, and oleic-acid-coated nanoparticles resulting in magnetically coated nanoparticles (MNP) (Liu et al., 2012). Although these MNP/clay/polymer nanocomposites had a low content of oleic-acid-coated magnetic nanoparticles (OA-MNP), the nanocomposite showed a higher saturation magnetization compared to that of pure OA-MNP (Liu et al., 2012). The preparation of the magnetic nanocomposites involved three steps (Liu et al., 2012). First, a well-mixed polymer and clay dispersion was converted into a gel. At the early stage of drying of the gel, polymer particles and OA-MNP were fixed separately in a house-of-card structure of clay platelets. Finally, all polymer particles coalesced in a macroscopic bulk film. Thus, the clay platelets and OA-MNP were fixed in the polymer substrate providing a unique nanostructure network in the nanocomposite (Liu et al., 2012).

4. Removal of contaminants by clay–polymer nanocomposites

4.1. Removal of inorganic contaminants

4.1.1. Removal of heavy metals and metalloids

Inefficient management of heavy metals and metalloids in an aqueous system may cause harmful effects to the environment and human beings on a long-term basis. These inorganic contaminants are not degradable and are likely to accumulate in living organisms through biomagnification, causing serious toxicity because of the carcinogenic

Table 1
Adsorption capacities of CPNs for the removal of various heavy metals from water.

Adsorbate	Adsorbent	Maximum adsorption capacity (mg/g) or percent removal (%)	pH	Temperature (°C)	Best-fitted kinetic model	Best-fitted isotherm model	Reference
Pb(II)	Polyacrylic acid/bentonite	1,666.67	-	-	Pseudo-second-order	Langmuir	(Bulut et al., 2009)
	Alginate-MMT nanocomposite	244.6	6.0	-	-	-	(Shawky, 2011)
	Attapulgite/poly(acrylic acid)	37	5.0	-	pseudo-second-order	Freundlich	(Liu et al., 2014)
	CTS-Al-pillared MMT nanocomposite	99.5%	6.5	25	Pseudo-second-order	Freundlich	(Duan et al., 2016)
	CTS-to-clay ratio of 0.45:1						
	Cloisite-polycaprolactone nanocomposite	87%	-	-	-	-	(Dlamini et al., 2013)
	CTS immobilized on bentonite	26.38	-	35	Pseudo-second-order	Freundlich	(Futalan et al., 2011)
	Xanthated-bentonite nanocomposite (as an inorganic polymer)	99.9%	5.0	25	Pseudo-second-order	Freundlich	(He et al., 2010)
	Polymethacrylic acid grafted CTS-bentonite nanocomposite	126.6	-	50	-	Langmuir	(Rijth et al., 2015)
	Bentonite/thiourea-formaldehyde composite	13.38	4.0	-	Pseudo-second-order	Langmuir	(El-Korashy et al., 2016)
	L-cysteine modified bentonite-cellulose nanocomposite	18.52	-	50	Pseudo-second-order	Langmuir	(Ahmad and Hasan, 2016)
	Ni(II)	Cystene-MMT nanocomposite	0.179-0.231	-	-	-	-
Polyacrylic acid/bentonite		270.27	-	-	Pseudo-second-order	Langmuir	(Bulut et al., 2009)
CTS/clinoptilolite		247.03	5.0	25	Pseudo-second-order	Langmuir	(Dinu and Dragan, 2010)
Alginate-MMT nanocomposite		~100%	6.0	-	-	-	(Shawky, 2011)
CTS immobilized on bentonite		15.82	-	35	Pseudo-second-order	Langmuir	(Futalan et al., 2011)
CTS grafted poly acrylic acid bentonite composites		48	7.0 & 8.0	25	-	Langmuir	(Kumararaja et al., 2018)
Polyetherimide/porous activated bentonite clay nanocomposite membrane		76.2%	-	-	-	-	(Hebbar et al., 2014)
Polyacrylic acid/bentonite		rejection	-	-	-	-	(Bulut et al., 2009)
CTS grafted poly acrylic acid bentonite composites		416.67	-	-	Pseudo-second-order	Langmuir	(Kumararaja et al., 2018)
L-cysteine modified bentonite-cellulose nanocomposite		51.5	6.0	25	-	Langmuir	(Ahmad and Hasan, 2016)
Polyetherimide/porous activated bentonite clay nanocomposite membrane		16.12	-	50	Pseudo-second-order	-	(Hebbar et al., 2014)
Cu(II)		Polyacrylic acid/bentonite	82.5%	-	-	-	-
	Humic acid-immobilized amine-modified polyacrylamide/bentonite nanocomposite	rejection	-	-	Pseudo-second-order	Langmuir	(Bulut et al., 2009)
	Cellulose-graft- polyacrylamide/hydroxyapatite	222.22	5.0	30	Pseudo-second-order	Langmuir	(Anirudhan and Suchithra, 2010a)
	CTS-Al-pillared MMT nanocomposite,	108.06	-	-	-	-	(Saber-Samandari et al., 2013)
	CTS-to-clay ratio of 0.45:1	175.0	7.0	-	Pseudo-second-order	-	(Duan et al., 2016)
	Poly(acrylic acid-co-acrylamide)/attapulgite	96%	6.5	25	Pseudo-second-order	Freundlich	
	CTS (polyacrylic acid)/attapulgite (10%)						
	Bentonite/humic acid	69.75	6.0	-	-	-	(Liu et al., 2015a)
	CTS immobilized on bentonite	303.03	5.5	30	Pseudo-second-order	Langmuir	(Wang et al., 2009)
	CTS immobilized on bentonite and ethylene glycol diglycidyl ether	22.40	6.5	30	-	-	(Jin et al., 2016)
	Chitosan grafted poly acrylic acid bentonite composites	21.55	-	35	Pseudo-second-order	Freundlich	(Futalan et al., 2011)
	L-cysteine modified bentonite-cellulose nanocomposite	10.52	4.0	-	Pseudo-second-order	Langmuir	(Grisdanurak et al., 2012)
Polyetherimide/porous activated bentonite clay nanocomposite membrane	88.5	6.0	25	-	Langmuir	(Kumararaja et al., 2018)	
Poly(methacrylic acid) grafted CTS/bentonitegraftedCTS/bentonite MMT and CTS	32.36	-	50	Pseudo-second-order	Langmuir	(Ahmad and Hasan, 2016)	
CTS/PVA/bentonite nanocomposite	69.3%	-	-	-	-	(Hebbar et al., 2014)	
Alginate-MMT nanocomposite	rejection	-	-	-	-	(Anirudhan et al., 2010)	
CTS grafted poly acrylic acid bentonite composites	110.5	5.0	30	Pseudo-second-order	Langmuir	(Bleiman and Mishael, 2010)	
Alginate-MMT nanocomposite	18.4	-	-	-	-	(Wang et al., 2014)	
CTS grafted poly acrylic acid bentonite composites	360.73	6.0	-	-	-	(Shawky, 2011)	
Alginate-MMT nanocomposite	~100%	7.0	25	-	Langmuir	(Kumararaja et al., 2018)	
CTS grafted poly acrylic acid bentonite composites	72.9	6.0	-	-	-	(Shawky, 2011)	
CTS/attapulgite	~100%	3.0	25, 35, 45	Intraparticle diffusion	Langmuir	(Zou et al., 2011)	
Alginate-MMT nanocomposite	36.76, 47.17, 62.50	6.0	-	-	-	(Zou et al., 2011)	
CTS/attapulgite	~100%	5.0	25, 35, 45	Intraparticle diffusion	Langmuir	(Zou et al., 2011)	
	27.03, 46.08, 65.36	-	-	-	-	(Zou et al., 2011)	

(continued on next page)

Table 1 (continued)

Adsorbate	Adsorbent	Maximum adsorption capacity (mg/g) or percent removal (%)	pH	Temperature (°C)	Best-fitted kinetic model	Best-fitted isotherm model	Reference
Cr(VI)	CTS-Al-pillared MMT nanocomposite	15.67	5.37	25	Pseudo-second-order	Langmuir	(Wang et al., 2016)
	Na-MMT/cellulose	22.2	3.8-5.5	-	Pseudo-second-order	Langmuir	(Kumar et al., 2012)
	CTS-coated MMT	41.67, 40.65, 38.61	4.0	25, 35, 45	Pseudo-second-order	Langmuir	(Fan et al., 2006)
	CTS and nanoclay (Cloisite 10 A)	357.14	-	-	Pseudo-second-order	Langmuir	(Pandey and Mishra, 2011)
Mn(II)	Chitin/bentonite nanocomposite	443.71	4.0	-	-	Freundlich	(Saravanan et al., 2013)
	Bentonite/thiourea-formaldehyde composite	4.20	7.0	-	Pseudo-second-order	Langmuir	(El-Korashy et al., 2016)
	Alginate-MMT nanocomposite	~100%	6.0	-	-	-	(Shawky, 2011)
Mn(VII)	Bentonite/thiourea-formaldehyde composite	14.81	4.0	-	Pseudo-second-order	Langmuir	(El-Korashy et al., 2016)
U(VI)	Polyamine modified bentonite	14.1	6.5	20	Pseudo-second-order	Langmuir	(Liu et al., 2017)

nature of many heavy metals and metalloids (Fu and Wang, 2011). Various toxic cationic and anionic heavy metals and metalloids such as Cu, Pb, Ni, Cd, Cr, Sb, Se, U, and As constitute the major pollutants in water. These metals are exposed to the environment during rapid industrialization, intensive fertilizer application, and urbanization. Therefore, the removal of these metals and metalloids from effluent water is crucial in attaining environmental sustainability from a water management perspective. In this regard, CPNs have shown immense potential for wastewater treatment.

Recently, magnetized-CPN was prepared by Sundaram and Dharmalingam (2018) using bentonite clay, iron oxide nanoparticles, and monomer methyl methacrylate via in situ polymerization. The authors used it for Cr(VI) adsorption in an aqueous system and found that it adsorbed 113 mg Cr (VI)/g of the adsorbent. The main mechanism of adsorption was film-diffusion, which was confirmed by fitting the data to the intraparticle diffusion equation (Sundaram and Dharmalingam, 2018). Earlier, 15.67 mg/g of Cr (VI) was removed by a CTS-Al-pillared MMT nanocomposite (Wang et al., 2016). A similar type of adsorbent was used for the adsorption of Cu (II) and Pb(II) with a CTS-to-clay ratio of 0.45:1 that removed Cu (II) and Pb(II) at rates of 96.0 and 99.5%, respectively, at a pH of 6.5 through chemisorption (Table 1) and exhibited a good regeneration capacity with 0.1 M HNO₃ (Duan et al., 2016).

Similarly, organo-bentonite and polyacrylonitrile composites were synthesized through an in situ intercalation polymerization technique for heavy metal removal in an aqueous system (Anirudhan and Ramachandran, 2008). The synthesized composite adsorbed 52.6, 65.4, and 77.4 mg/g of Cd(II), Zn(II), and Cu(II) with a maximum removal efficiencies of 97.4, 98.9, and 99.8%, respectively, at pH 6.0 via ion exchange and metal chelation (with amidoxime) mechanisms (Anirudhan and Ramachandran, 2008). The authors reported that only 80% of the metals could be removed from the system after four cycles of regeneration (Anirudhan and Ramachandran, 2008).

In another study, Pb(II) was removed using nanocomposites composed of CTS with methyl cellulose and kaolin clay (Kanchana et al., 2012). Nano-CTS/methyl cellulose (NC + MC) and nano-CTS/kaolin clay (NC + KC) composites were separately prepared to obtain a more effective removal of Pb(II) by NC + KC than NC + MC at an optimum dose (7–8 g), and nearly 85 and 70% of Pb(II) was removed by NC + KC and NC + MC, respectively, at the optimum pH (6.0) (Kanchana et al., 2012). The pH was the most significant factor for adsorption because, with an increase in pH, the adsorption of Pb(II) decreased because of the formation of hydroxide complexes (Kanchana et al., 2012). Sölenner et al. (Sölenner et al., 2008) also prepared a clay-polymethoxy ethyl acrylamide nanocomposite to remove Pb(II) ions from an aqueous solution, and the adsorbent adsorbed ca. 81.02 mg Pb(II)/g at an optimum pH range of 4 to 6. This mechanism was followed by physical adsorption. The authors also found only a 6% decrease in adsorption after five cycles of regeneration with 0.01 M HNO₃ (Sölenner et al., 2008).

An ion-imprinted polymer/MMT-clay nanocomposite was also employed to remove Pb(II) in large quantities (Msaadi et al., 2017). The clay was exchanged with dimethyl aminobenzenediazonium (DMA), and the composite was prepared by a photo-polymerization process using exchanged clay, acrylamide, and bisacrylamide (Msaadi et al., 2017). The amount of Pb(II) adsorbed was 301 mg/g, demonstrating a specificity for Pb(II) removal. Aryldiazonium salt with photo-polymerization was employed for the first time in this study to synthesize clay/ion-imprinted nanocomposites (Msaadi et al., 2017).

Apart from smectite and kaolinite clay minerals, fibrous clay minerals such as palygorskite were also used with CTS for the successful preparation of CPNs. Rusmin et al. (2015) prepared palygorskite (P)-CTS CPNs in different mass ratios of CTS to P (1:1 = CTSP1, 1:2 = CTSP2, and 2:1 = CTS2P) to immobilize Pb(II) in water systems. The results suggested that CTSP1 was the most efficient adsorbent to remove Pb(II) (201.47 mg/g). Researchers pointed out that the

availability of reactive sites from both CTS and P, solute transport, porosity, and other structural characteristics may have contributed to the high Pb(II) adsorption capacity of the composite (Rusmin et al., 2015).

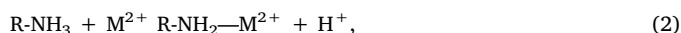
A study on the adsorption of Pb(II) considering the amount of clay with respect to polystyrene polymer in a composite revealed that increasing the clay content up to 10% increased the Pb(II) adsorption by several fold in aqueous systems (Asewailem and Aljlil, 2013). Unuabonah et al. (2008a) used a PVA-modified kaolinite adsorbent for Cu(II) removal, where PVA was used as a water-soluble polymer to modify kaolinite. Their results showed that the adsorbent adsorbed Pb (II) (56.18 mg/g) and Cd(II) (41.67 mg/g) ions from aqueous solutions through the formation of inner-sphere complexes. It was also observed that 99% of these metals became desorbed during regeneration with 0.1 M HCl (Unuabonah et al., 2008b). Further optimization of the results in a fixed-bed system showed that 4 kg of this adsorbent removed 95% Pb(II) within 30 min (Unuabonah et al., 2009). During the fixed-bed experiment with this composite, the authors concluded that 20 g of PVA-modified kaolinite composite was needed to purify ca. 1180 mL and 1243 mL of Cd(II) and Pb(II) contaminated waters, respectively (Unuabonah et al., 2010, 2012). However, the volume of water reduced to 927 mL and 1020 mL after regeneration of the adsorbent (Unuabonah et al., 2010, 2012).

Recently, Urbano et al. (2012) synthesized an ion-exchange resin with a water-soluble CPN composed of N-methyl-D-glucamine-based monomer and organically modified MMT clay particles via an in situ radical polymerization reaction and applied it to arsenic (As) removal. A Langmuir adsorption isotherm study indicated that the resin was capable of removing 55 mg As/g, which suggested that the final As concentration of the solution was below the permissible limits of the World Health Organization (Urbano et al., 2012).

4.1.2. Use of biopolymer chitosan-modified clay for metal removal

Many studies have been conducted for heavy metal removal in aqueous systems using CTS and clay as the polymer and supporting agent, respectively. A CTS-and-kaolin-based ceramic membrane was prepared using PVA as the chelating agent to remove As and Hg in an aqueous system in which 100% removal of these metal ions was achieved (Jana et al., 2011). CTS immobilized on bentonite also showed good adsorption capacity for heavy metals such as Pb(II), Cu(II), and Ni (II). Studies have revealed that the maximum adsorption capacity of the adsorbent was 26.38, 21.55, and 15.82 mg/g for Pb(II), Cu(II), and Ni (II), respectively, and the percent removal of these metals was 75.41, 45.10, and 36.23%, respectively, at 35 °C (Futalan et al., 2011). Thermodynamic studies for metal removal showed an exothermic adsorption reaction with a decreasing trend in entropy (Futalan et al., 2011). In addition, the reaction of Pb(II) adsorption was spontaneous, whereas that of Ni(II) was non-spontaneous at 25–55 °C, and Cu(II) adsorption was only spontaneous at 25 °C (Futalan et al., 2011). The main controlling factor of the adsorption process was considered to be the pH. When an initial pH 4.0 is maintained, amine groups of CTS become protonated, and metal ions compete with H⁺ ions for adsorption sites via an ion-exchange mechanism (Eq. 1 and Eq. 2) (Futalan et al., 2011).

At pH 4.0,



where M²⁺ indicates divalent metal ions (e.g., Cu, Pb, and Ni).

CTS immobilized on bentonite using ethylene glycol diglycidyl ether as a cross-linking agent was found to be most suitable for aquatic Cu(II) removal via the chemisorption mechanism (Grisdanurak et al., 2012). In a desorption study, more than 92% of Cu(II) was recovered from composite beads using an HCl solution (pH = 1) agitated for 2 h (Grisdanurak et al., 2012).

CTS grafted poly acrylic acid bentonite composites were used to

remove Cu(II), Zn(II), Cd(II), and Ni(II) in aqueous systems (Kumararaja et al., 2018). Researchers have shown that maximum Cu (II) and Cd(II) adsorption occurs at pH 6.0, while maximum Zn(II) and Ni(II) adsorption occurs at pH 7.0 and 8.0, respectively. A high pH might generate a greater negative surface charge on an adsorbent which consequently helps to adsorb cationic heavy metals (Kumararaja et al., 2018). Previously, CTS/attapulgite composites were prepared for Cr(III) and Fe(III) removal in water. With an increase in temperature, the adsorption capacity of an adsorbent increases (Table 1), and covalent bonding (sharing of electrons between the adsorbate and adsorbent) is the fundamental mechanism for adsorption (Zou et al., 2011).

The poly-methacrylic acid grafted CTS–bentonite composite proved to be an efficient removal agent of Hg(II), Pb(II), and Cd(II) with a removal efficiencies of 94, 89, and 78%, respectively, and high pH was favorable for metal ion adsorption (Abdel et al., 2012). In another study, CTS grafted (polyacrylic acid acrylamide)/attapulgite composites showed faster bulk Cu(II) removal with a decrease in the concentration of the clay mineral from 50 to 10%, resulting in a maximum of 90% Cu(II) removal within 15 min of the initial adsorption (Wang et al., 2009). A pH of 5.50 was suitable for a faster removal of Cu(II). Cu (OH)₂ precipitation occurred above this pH value, and at a low pH, Cu (II) might compete with H⁺ ions, and electrostatic repulsion of Cu(II) ions with NH₃⁺ might occur (Wang et al., 2009).

A CTS–silver nanoparticle clay composite was used to remove Cu (II) in an aqueous system by Azzam et al. (2016). The composite adsorbed a maximum of 181.5 mg Cu (II)/g of adsorbent at pH 7.0. The formation of Cu(OH)₂ at a high pH (> 7.0) resulted in little adsorption of Cu(II), whereas chelate formation between Cu(II) ions and the surface functional groups of CTS at pH 7.0 made the adsorbent suitable for Cu(II) retention (Azzam et al., 2016).

4.1.3. Removal of gaseous metals and toxic gases

The gaseous form of metals (Hg⁰) and toxic gases such as NH₃ can be adsorbed by CPNs. Zhang et al. (2009) carried out an adsorption study to remove gaseous mercury (Hg⁰) using a CTS–bentonite composite as an adsorbent. They observed that the small surface area of the composite as compared to raw bentonite (owing to micropore blockage in clay because of modification) caused low gaseous Hg⁰ removal (Zhang et al., 2009). The removal of Hg was highly dependent on the phase in which the target element existed (Zhang et al., 2009). Similarly, NH₃, a toxic gas, was adsorbed in bulk amount from contaminated air by clay–polymer composites prepared from natural palygorskite and acid-activated bentonite through the polymerization reaction between acrylic acid and N,N'-methylenebisacrylamide as a cross-linker (Liu et al., 2016). The NH₃ adsorption ability of these composites increased multifold after binding with Cu(II) ions through Lewis acid–base interaction (Liu et al., 2016). A composite with 75% palygorskite exhibited the highest adsorption capacity (65.8 mg/g) among all the palygorskite/acrylic acid polymer composites. In contrast, the composite with 66% of acid-treated bentonite showed the maximum adsorption (80.0 mg/g) among all acid-treated bentonite/acrylic acid polymer composites (Liu et al., 2016). This difference in adsorption performance between palygorskite and acid-treated bentonite/acrylic acid polymer composites can be explained by the presence of mesopores in the Cu-complexed acid-treated bentonite that enabled a high amount of NH₃ to be attached to the reactive sites of the polymer (Liu et al., 2016). Researchers also found that NH₃ desorption occurs at 180 °C and concluded that these polymer composites are useful for application as air filters. However, there are possibilities of heavy-metal contamination of water by metal-containing CPNs that need to be evaluated in detail. A list of the removal performances of various CPNs for inorganic contaminants is presented in Table 1.

4.2. Removal of organic contaminants

Wastewater also contains various organic pollutants such as dyes,

pesticides, phenols, and harmful organic acids that are toxic to environmental receptors even when present in low concentrations and not readily biodegradable. Recently, adsorption techniques using CPNs have drawn attention for the purification of wastewater contaminated with various organic pollutants. The presence of hydrophobic polymeric molecules in CPNs renders them efficient adsorbents of organic pollutants. Furthermore, a regeneration study provides a clear picture of the economic feasibility of the adsorbents as well as the mechanisms involved in the adsorption process. Recently, a thin coating of clay–polymer composite was utilized and recycled for environmental remediation to eliminate the problems of adsorbents when used as tablets, powder, or in other forms (Momina and Shahadat, 2018). Therefore, regeneration techniques promote the recycling of already-used thin-layer-coated clay–polymer composites with good adsorption capacity. The removal of different organic pollutants by CPNs along with the mechanisms, adsorption factors, and regeneration studies is discussed in the following sections.

4.2.1. Dye removal

Several studies have reported successful removal of dye compounds from aqueous media using CPNs. Wang and Wang (2007) removed aqueous Congo red, a secondary diazo dye, using an adsorbent based on an MMT and CTS biopolymer. The authors observed that the adsorption capacity of synthesized CPN (54.5 mg/g) was higher than the average of the adsorption capacity of CTS and MMT (46.9 mg/g), and more importantly, their molar ratio played the key role in Congo red adsorption (Wang and Wang, 2007). Furthermore, X-ray diffraction showed that the CTS polymer was uniformly distributed in the MMT interlayer of clay, which disrupted the clay structure and formed a nanocomposite. In this study, electrostatic interaction and chemisorption mechanisms controlled the adsorption process. The addition of H^+ ion to the NH_2 group in CTS at low pH led to an electrostatic interaction because of the development of positively charged sites, whereas above pH 7, the reduced adsorption of anionic dye was attributed to the competition of OH^- ions for active sites. The chemisorption process can explain the maximum adsorption at higher pH values (Wang and Wang, 2007). Wang et al. (2008) prepared CTS-g-poly(acrylic acid)–MMT nanocomposites and applied them to the removal of methylene blue (MB) from water. Their findings revealed that the weight ratio of acrylic acid to CTS of the CPN influenced the adsorption process and that incorporating a small quantity of MMT clay enhanced the adsorbent efficiency (Wang et al., 2008). The maximum adsorption potential of the composites was 1859 mg/g, which is very high. The adsorption data fitted well to the pseudo-second-order kinetic model and the Langmuir adsorption isotherm. Desorption studies have provided a suitable indication of the regeneration and recycling of CPN after MB adsorption (Wang et al., 2008). The use of CTS biopolymer for the synthesis of CPNs and their application for removal of organic pollutants have been investigated in several studies (Kumararaja et al., 2018; Wan Ngah et al., 2010a; Crini and Badot, 2008; Liu et al., 2015b). A cross-linked CTS/bentonite CPN was developed by Wan Ngah et al. (2010a) and used to remove tartrazine, an azo dye with detrimental effects on living organisms. Cross-linking with epichlorohydrin enhanced the adsorbent efficiency by making the CTS insoluble (Crini and Badot, 2008). According to Wan Ngah et al. (2010a), the pH of the dye was responsible for the adsorption. At $pH < pH_{zpc}$, tartrazine attached to the CPN because of the development of a positive charge, and with an increase in the pH, the surface charge became more negative, resulting in a reduced adsorption potential because of the repulsion between the dye and the adsorbent.

Xu et al. (2018) prepared chitin–clay composites that removed up to 99.99% of MB (152.2 mg/g) (Langmuir adsorption isotherm). They pointed out that pH was the fundamental factor affecting adsorption. Anirudhan et al. (2009) attempted to purify wastewaters laden with crystal violet (CV), MB, and malachite green dyes using a humic acid immobilized-amine modified bentonite–polyacrylamide nanocomposite. The

CPN adsorbent with a pH_{zpc} of 4.8 showed an adsorption maximum of 510, 648, and 657 $\mu\text{mol/g}$ for CV, MB, and malachite green, respectively, through intraparticle diffusion mechanism. The authors observed that the maximum removal efficiency of CV, MB, and malachite green dyes were 94, 97, and 98%, respectively, occurring in the pH range 5.0–8.0. In another study, Bee et al. (Bée et al., 2017) used magnetic CTS/clay beads to remove MB with a clay-to-CTS weight ratio > 0.5 and a pH range of 3–12. They found that its adsorption maxima were 82.0 mg/g with a faster removal efficiency of 50% within 13 min. They concluded that the electrostatic affinity among dye cations and the permanent negative charges of clay were the crucial mechanisms for the adsorption of MB in a wide pH range.

Vanamudan and Pamidimukkala (2015) used a CTS–clay nanocomposite for Rhodamin-6 G removal and observed a 446.42 mg/g of dye adsorption potential. The kinetic data followed a pseudo-second-order model, and the negative potential of the adsorbent at a high pH facilitated the adsorption of this cationic dye. Kang et al. (2009) studied the removal of anionic dyes (e.g., reactive violet K-3R, eosin Y, and direct fast scarlet) from dye mixtures using a poly(epichlorohydrin dimethylamine)–bentonite composite. Furthermore, Wang et al. (2010) showed that cetyltrimethyl ammonium bromide-modified bentonite could be intercalated with polyacrylamide, and the resultant CPN could be applied for the removal of phenol and nitrobenzene. A CTS modified nano-organoclay (Cloisite 30B) biocomposite was used for the removal of reactive blue-21 and reactive red-141 by Vanaamudan and Sudhakar (2015). The maximum adsorption of reactive blue-21 and reactive red-141 was 476 and 439 mg/g, respectively. Kinetic experiments revealed that approximately 60–62% removal occurred within 50 min, and the data fitted well to a pseudo-second-order model. A fibrous palygorskite–clay composite after surface grafting with CTS showed a huge improvement in reactive dye adsorption (Yellow 3 RS) similar to that of heavy-metal removal (Peng et al., 2013). The maximum adsorption was 71.38 mg/g in the CTS-grafted clay composite, whereas it was only 6.3 mg/g for the unmodified clay. At a low pH (4.0), the adsorption mechanism was simple electrostatic attraction owing to the development of a positive surface charge on the NH_2 group of CTS as the adsorption decreased, while an increase in the pH led to repulsion because of deprotonation. Similarly, Li et al. (2011) prepared a nanocomposite of bentonite with poly(epichlorohydrin-dimethylamine) that they utilized for dye removal (e.g., disperse yellow-brown S-2RFL and reactive yellow K-4 G). The CPN showed adsorption maxima of 30.8 and 12.4 mg/g of adsorption capacity for K-4 G and S-2RFL, respectively. They later optimized doses of polymers for the complete removal of dyes.

4.2.2. Pesticide, tannic acid, and phenol removal

Attempts have been made to purify wastewater contaminated with pesticides such as atrazine and 2, 4-dichlorophenol using CPNs as adsorbents. Modification of MMT with poly-4-vinylpyridine-co-styrene (90%) was useful for atrazine removal, and 90–99% atrazine removal efficiency was achieved very quickly (20–40 min) (Zadaka et al., 2009). A fixed-bed experiment with the above adsorbent revealed highly efficient atrazine removal (93–96%), but the competition from soluble organic substances slightly decreased the adsorption efficiency. Furthermore, the authors showed that the nanocomposite was effective in reducing the atrazine concentration in a solution to 3 $\mu\text{g/L}$. Later, nanocomposite membranes comprising polyethersulfone and organo-MMT were synthesized by solution dispersion and wet-phase inversion methods and used for the removal of dinitrophenols (Ghaemi et al., 2011). The study revealed that the removal was improved by the addition of up to 4% of organo-MMT. At pH 4.5, the strong attraction of H-bonding between nitrophenols and the surface membrane was the primary cause for the rejection of dinitrophenols. Recently, the hexadimethrine–MMT nanocomposite has been used as a pesticide adsorbent (Gámiz et al., 2015), exhibiting high attraction for anionic pesticides such as clopyralid and mecoprop ($> 70\%$ removal capacity),

Table 2
Adsorption capacities of CPNs for the removal of various organic pollutants from water.

Adsorbate	Adsorbent	Maximum adsorption capacity (mg/g) or percent removal (%)	pH	Temp (°C)	Best-fitted kinetic model	Best-fitted isotherm model	Reference
Malachite green	Amine-modified polyacrylamide-bentonite nanocomposite	656.5	6.0	30	Pseudo-second-order	Freundlich	(Amirudhan et al., 2009)
Methylene blue	CTS/bentonite	435.0	6.0	37	Pseudo-second-order	Langmuir	(Wan Ngah et al., 2010b)
	CTS-g-poly (acrylic acid)/MMT	1859	6.5	-	Pseudo-second-order	Langmuir	(Wang et al., 2008)
	Kappa-carrageenan-g-poly(acrylamide)/MMT nanocomposite hydrogels	322.0	-	-	Pseudo-second-order	Langmuir	(Mahdavinia et al., 2014)
	MMT/layer double hydroxide Alginate-clay quasi-cryogel beads	74% 181.8	-	40	Pseudo-second-order	Langmuir	(Zhou et al., 2014) (Uyar et al., 2016)
Crystal violet	Poly(acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid)/MMT (0.5% by wt) Kappa-carrageenan-g-poly(acrylamide)/sepiolite nanocomposite hydrogels	215 47.0	10.0	25 Ambient temp.	Pseudo-second-order Pseudo-second-order	Redlich-Peterson Langmuir	(Hosseinzadeh and Khoshnood, 2016) (Mahdavinia and Asgari, 2013)
Tartrazine	CTS/bentonite	294.1	2.5	47	Pseudo-second-order	Langmuir	(Wan Ngah et al., 2010a)
Amido Black 10B (Azo dye)	CTS/bentonite	323.6	2.0	20	Pseudo-second-order	Langmuir	(Liu et al., 2015b)
Methyl orange Congo red	MMT/layer double hydroxide	88%	-	-	-	-	(Zhou et al., 2014)
	CTS/MMT	54.52	4	30	Pseudo-second-order	Langmuir	(Wang and Wang, 2007)
2,4-dichlorophenol Tannic acid	Humic acid-modified bentonite	14.23	6.5	30	-	-	(Jin et al., 2016)
	CTS-coated attapulgite	95.2	5.5	-	Pseudo-second-order	Freundlich	(Deng et al., 2012)
Safranin-T and brilliant cresyl blue	Protonated palygorskite/CTS resin microspheres	455.0	8.0	-	order	Langmuir	(Wu and Chen, 2013)
	Acrylamide (AAm)-2-acrylamide-2-methylpropanesulfonic acid sodium salt (AMPSNa) hydrogel and AAm-AMPSNa/clay hydrogel nanocomposite	484.2 and 494.2	-	25	order	Langmuir	(Kasgöz and Durmus, 2008)
Brilliant Green (BG) and Acid Red 1 (ARI)	Zwitterionic adsorbent-based composite coating (mixture of bentonite, acrylic polymer, and polyethylene-diamine)	255.99 (BG), 70.09 (ARI)	-	27 ± 2	-	-	(Azha et al., 2018)

which suggested that electrostatic attraction was involved in pesticide adsorption onto the positively charged NH_4^+ of the adsorbent.

Phenolic compounds in water are also a threat to living organisms. Surfactant (hexadecyl trimethyl ammonium)-modified clay was incorporated in an alginate polymer matrix to remove phenols and 4-chlorophenol. They exhibited adsorption of 0.334 and 0.118 mg/g for 4-chlorophenol and phenols, respectively (Hernández-Hernández et al., 2018). A few years ago, Ganigar et al. (2010) prepared a novel nanomaterial composite using poly-4-vinylpyridine-co-styrene to remove trinitrophenol and trichlorophenol from aqueous systems. It was observed that the nanocomposite removed approximately 99.5% of trinitrophenol and 40–60% of trichlorophenol through weak van der Waals forces. However, Zhu et al. (2011) used MMT modified with cetyltrimethylammonium poly(diallyldimethylammonium) as an adsorbent for phenolic compounds, but the surfactant was not intercalated properly in the interlayer position of the MMT. According to the report, despite the improper intercalation, the phenol removal capacity of the adsorbent was improved.

Tannic acid, a polyphenolic compound generated from the decomposition of organic matter, is a toxic organic substance that affects living organisms. These compounds are usually present in soil and surface water. Thus, its removal from an aquatic environment is essential. Very few studies have been conducted on the removal of tannic acid using CPNs. Deng et al. (2012) synthesized a novel CTS-coated attapulgite adsorbent for removing tannic acid from an aqueous solution. The study revealed that 95.2 mg/g of tannic acid was removed by this novel adsorbent. The main mechanisms of this adsorption were electrostatic attraction, hydrogen bonding, and van der Waals forces. Later, resin microspheres prepared by CTS with 20% weight of protonated palygorskite as a supporting agent adsorbed a high amount of tannic acid (455.0 mg/g) (Wu and Chen, 2013). After three cycles of the adsorption-desorption process, the sorption capacity of protonated palygorskite decreased by 57 mg/g, whereas the desorption ratio of tannic acid decreased by 9.4% from the first to the third cycle. The study also indicated that the adsorbent was recyclable when 0.1 M HCl was used as an eluent. A critical analysis of the various CPNs used to remove organic pollutants from wastewater is presented in Table 2.

4.3. Removal of biological contaminants

Harmful microbes cause water-borne diseases such as typhoid, dysentery, and diarrhea through the consumption of drinking water contaminated with harmful microbes such as *Salmonella typhi*, *Shigella* sp., and *Entamoeba histolytica*. The disinfection process is very important for the utilization of microbial-contaminated water (Undabeytia et al., 2014). Chlorination, a well-proven traditional technology that significantly minimizes the pathogen population, has now become less popular because of the formation of toxic substances such as trihalomethanes, haloacetic acids, and chlorophenols in the presence of soluble organics (Undabeytia et al., 2014; Nikolaou and Lekkas, 2001). Previously, chloramination and slow-sand filtering were proposed, but their practical utility is limited because of the formation of nitrosamines owing to chloramination (Charrois et al., 2007), clogging, and high filter maintenance expenses. Alternatively, clay-polymer composites can be employed for antimicrobial activity of a polymer, although the polymer should be soluble (Madkour et al., 2009). Bruna et al. (2012) synthesized a copper-doped MMT low-density polyethylene nanocomposite and tested its antimicrobial efficiency against *E. coli* 0157:H7 n/t. Results suggested that presence of MMT-Cu(II) (at a rate of 4%) in the synthesized CPN had antimicrobial activity (94%) that led to the death of 99.99% of *E. coli* by rupturing cells. Lejon et al. (2010) suggested that the interaction of Cu(II) with protein and nucleic acids of microbial cells causes cell death.

However, different novel CPNs have been used for antimicrobial activity. A nanocomposite based on clay-polydimethylsiloxane-CTS-silver and MMT-polydimethylsiloxane-chlorhexidine acetate had the bacteriostasis

property to kill bacteria (e.g., *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albicans*, and *Escherichia coli*) (Unuabonah and Taubert, 2014; Zhou et al., 2007; Meng et al., 2009). Undabeytia et al. (2014) synthesized starch-grafted quaternary ammonium ethers to modify a bentonite composite for *E. coli* removal. The cationic monomer of the quaternary ammonium ether loaded on the clay surface was responsible for the *E. coli* removal. A high monomer concentration increased the positive charge of the composite surface. A strong electrostatic attraction was thus formed between the positively charged composite surface and the negatively charged cell membrane phospholipids, which promoted disruption of the cell bilayer and caused cell lysis (Undabeytia et al., 2014). Hence, a clay-polymer composite is more suitable than a polymer alone. Moreover, the bacteria removal capacity of raw clays and organoclays (surfactant modified) is also known (Unuabonah et al., 2018).

CTS alone and CTS-based nanocomposites, both biopolymer-based materials, also exhibit antimicrobial activity. Han et al. (2010) prepared an MMT-CTS nanocomposite with a stronger tendency to kill *E. coli* and *S. aureus* than that of the individual components of the nanocomposite (e.g., MMT and CTS). Motshekga et al. (2015) also demonstrated the antibacterial activity of the above-mentioned composite made of bentonite supported with silver and zinc oxide nanoparticles. Regarding the mechanism of bacteria removal in water, they proposed that adsorbents probably use both killing and adhesion mechanisms. Similarly, a rectorite modified with sodium-dodecylsulfonate, CTS, and PVA (through intercalation) showed significantly higher activity (60%) against *E. coli* than each component of the nanocomposite (Unuabonah and Taubert, 2014; Deng et al., 2011). Moreover, studies on CTS-organoclay or CTS-MMT modified with silver nanocomposite also demonstrated high antimicrobial activity (Rhim et al., 2006; Shamel et al., 2011). However, CTS-based nanocomposites mostly displayed antibacterial activity only in the acidic pH range of the media (Unuabonah and Taubert, 2014), whereas N-(2-hydroxyl) propyl-3-trimethyl ammonium CTS chloride showed antibacterial activity irrespective of the pH range of the media (Chi et al., 2007).

Research on the regeneration aspect of these composites for the removal of harmful aquatic microbes is very important because of the limited number of published studies. Undabeytia et al. (2014) attempted to restore composites using HCl and NaClO for future use, while Unuabonah et al. (2017) used the steam regeneration method to regenerate hybrid clay adsorbents. Overall, the mechanisms of clay-based adsorbents to remove harmful microbes include adhesion, killing, bacteria and adsorbent hydrophobicity, flow condition, and surface charge (Unuabonah et al., 2018). Therefore, the antimicrobial activity of CPNs cannot only be harnessed for pharmaceutical and food packaging applications but can also be used to disinfect contaminated water (Unuabonah and Taubert, 2014).

5. Mechanisms involved in the removal of water contaminants by clay-polymer nanocomposites

The removal of contaminants from aqueous systems using CPNs mainly involves adsorption processes. The adsorption of contaminants such as heavy metals, metalloids, dyes, and other organic contaminants depends on: (1) the surface area, surface functional groups, and surface charge of the CPN adsorbents, and (2) the pH, temperature, ionic strength of the medium, initial concentration of the contaminants in question, and the concentrations of co-existing ions/compounds. Electron donor-acceptor interaction, electrostatic attraction, hydrogen bonding, chemisorption, ion-exchange, and pore-space filling by precipitation or complex formation are the main mechanisms during adsorption of inorganic, organic, and biological contaminants onto different CPN adsorbents (Fig. 1). For example, CTS-based biopolymer clay composites form an electron donor-acceptor interaction between CTS and metal cations at a low pH medium condition where the unshared pairs of electrons of nitrogen atoms of CTS serve as electron donors (Barakat, 2011). Similarly, CTS cross-linked MMT exhibits a

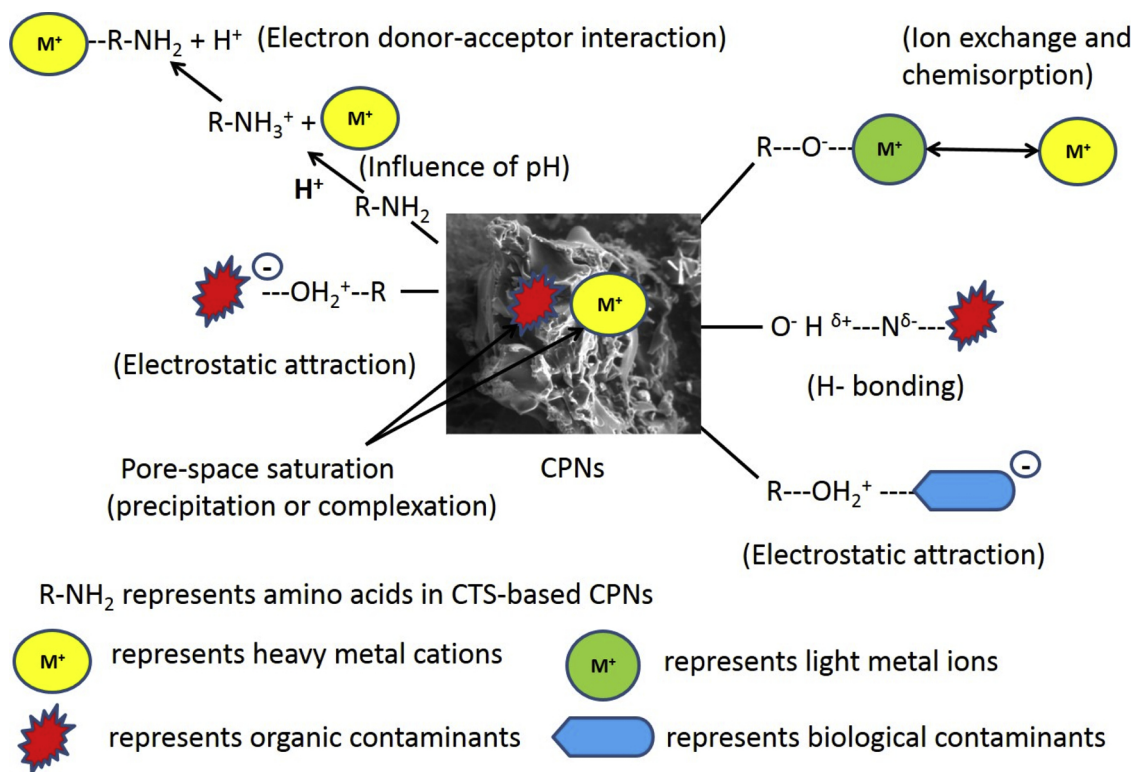


Fig. 1. Schematic representation of various mechanisms involved in removal of aquatic contaminants by CPNs.

chemisorption mechanism by sharing of electrons between the adsorbent and metal ions (Kumar et al., 2012). In the case of antimicrobial activity, a CTS-based bentonite composite supported with silver and zinc nanoparticles showed simple electrostatic attraction at low pH levels between the negatively charged bacteria and the protonated $-NH_2$ groups of CTS, which resulted in the death of bacterial cells (Yin and Deng, 2015). A CPN prepared using an N-methyl-D-glucamine-based monomer and organically modified MMT particles showed ion exchange mechanisms during the removal of As from water (Urbano et al., 2012). A zwitterionic adsorbent-based composite coating adsorbed Brilliant Green and Acid Red 1 dyes via hydrogen bonding with the $-NH_2$ groups of dyes that generated several $-OH$ groups (Azha et al., 2018). In addition, some CPNs formed complexes with the organic and inorganic contaminants and toxic gases such as NH_3 in their pore spaces to retain these contaminants (Liu et al., 2016). Therefore, a

careful assessment is needed to understand the underlying mechanisms of contaminant removal by CPNs because the affinity between a CPN adsorbent and a target contaminant may vary considerably according to the background environmental conditions and the mechanism involved in the adsorption process.

6. Water treatment options by clay-polymer nanocomposites

CPNs can be used as membranes, flocculation or coagulation agents, and in columns and barriers for decontaminating wastewater of harmful organic, inorganic, and biological pollutants (Fig. 2). The following sections provide a detailed discussion of the recent studies performed for different wastewater treatment options using CPNs.

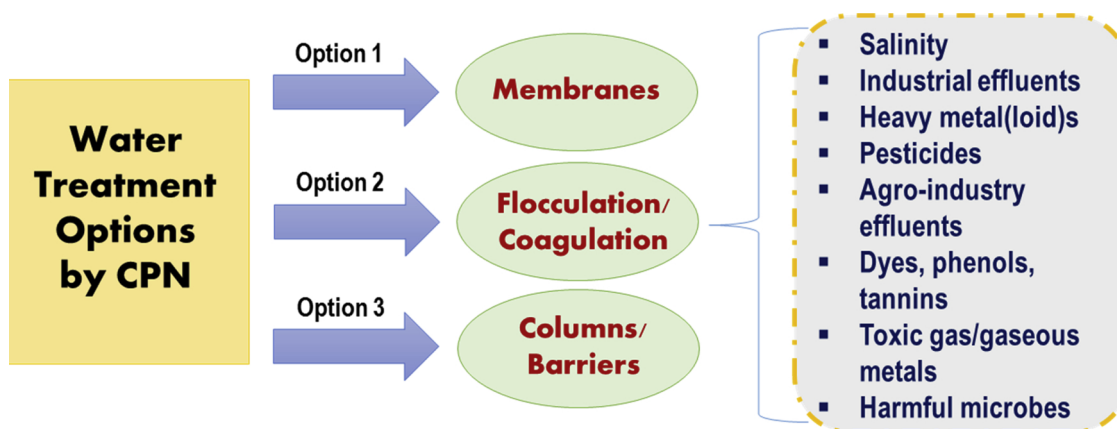


Fig. 2. Possible options for water remediation using CPNs.

Polymer nanocomposites are widely used for water purification, gas separation, and desalination because of their enhanced mechanical stability, flexibility, small footprint, and low preparation cost (Yin and Deng, 2015; Kononova et al., 2018). Recently, Ahmed et al. (Ahmad et al., 2018) prepared a bentonite–PVC membrane for the removal of oils in contaminated water. The maximum oil rejection rate was 98.6% with the optimum composition of the membrane (18.0-g PVC loading, 0.0-g bentonite loading, 250- μm membrane thickness, 5.1 pH, and 54.4-kPa trans membrane pressure). In contrast, the maximum permeation of the membrane occurred with a membrane composition of 15.01-g PVC loading, 1.37-g bentonite loading, 100- μm thickness, 9 pH, and 250-kPa trans membrane pressure. In another study, a thin-film nanocomposite membrane was prepared using MMT, PVC, and poly(4-styrenesulfonic acid-co-maleic acid) for the rejection of pharmaceutical solutes. The solute rejection percent was significantly higher (98.8%) after the incorporation of functionalized clay (Medhat Bojnourd and Pakizeh, 2018). A previously reported CTS-based ceramic ultrafiltration membrane composed of local kaolin clay with a PVC chelating agent resulted in a 100% removal of As and Hg (initial Hg and As concentrations were 500 and 1000 $\mu\text{g/L}$, respectively) (Jana et al., 2011). Apart from toxic metal removal, dyes are also removed using CPN membranes. A novel and efficient assembly was synthesized using Cloisite 15A and 30B/CTS clays coated on a microfiltration membrane made of poly(vinylidene fluoride) for the removal of aqueous MB (Unuabonah and Taubert, 2014; Daraei et al., 2013). However, the capability and cost of CPN-mediated membranes need to be improved so that they can be used at the grass-roots level or in rural areas on a small scale.

Effluents generated from various agro-industries such as wineries, piggeries, olive mills, or soy and coffee processing contain a significant quantity of organic matter and suspended particles. The total suspended solids (TSSs) remain in a dispersed condition and are difficult to remove with conventional adsorbents used for inorganic and organic micropollutant removal. Hence, these effluents are not suitable for direct discharge into standard sewage-treatment plants, and pre-treatment is necessary before its discharge. The reduction of TSSs for the pre-treatment of effluents involves three steps: coagulation of the colloidal particles, flocculation, and finally separation via filtration. Clay minerals have been applied widely in the pre-treatment of effluents, and the removal efficiency of colloidal organic particles increases when clay minerals are used in combination with organic compounds. Rytwo et al. (2011) modified sepiolite with crystal violet to bind the organic matter present in the effluents so that the larger particles settled and the amount of TSSs declined. The results suggested that 1.0 kg of organo-clay can remove the colloidal particles in 8000 L of effluent. Furthermore, Rytwo (2012) showed that a sepiolite CPN prepared with polydiallyl dimethyl ammonium chloride (PDADMAC) significantly reduced the chemical oxygen demand and TSS content in effluents. The study demonstrated that the TSSs from a winery effluent (1610 mg/L) was completely removed almost instantaneously (< 2 min) by using the CPN (0.1% sepiolite-PDADMAC nanocomposite), whereas using PDADMAC singly showed poor performance. Consequently, Rytwo et al. (2013) prepared various CPNs such as sepiolite–CTS, sepiolite–PDADMAC, and Volclay®–PDADMAC nanocomposites for winery effluent treatment that confirmed the fast treatment efficiency of the

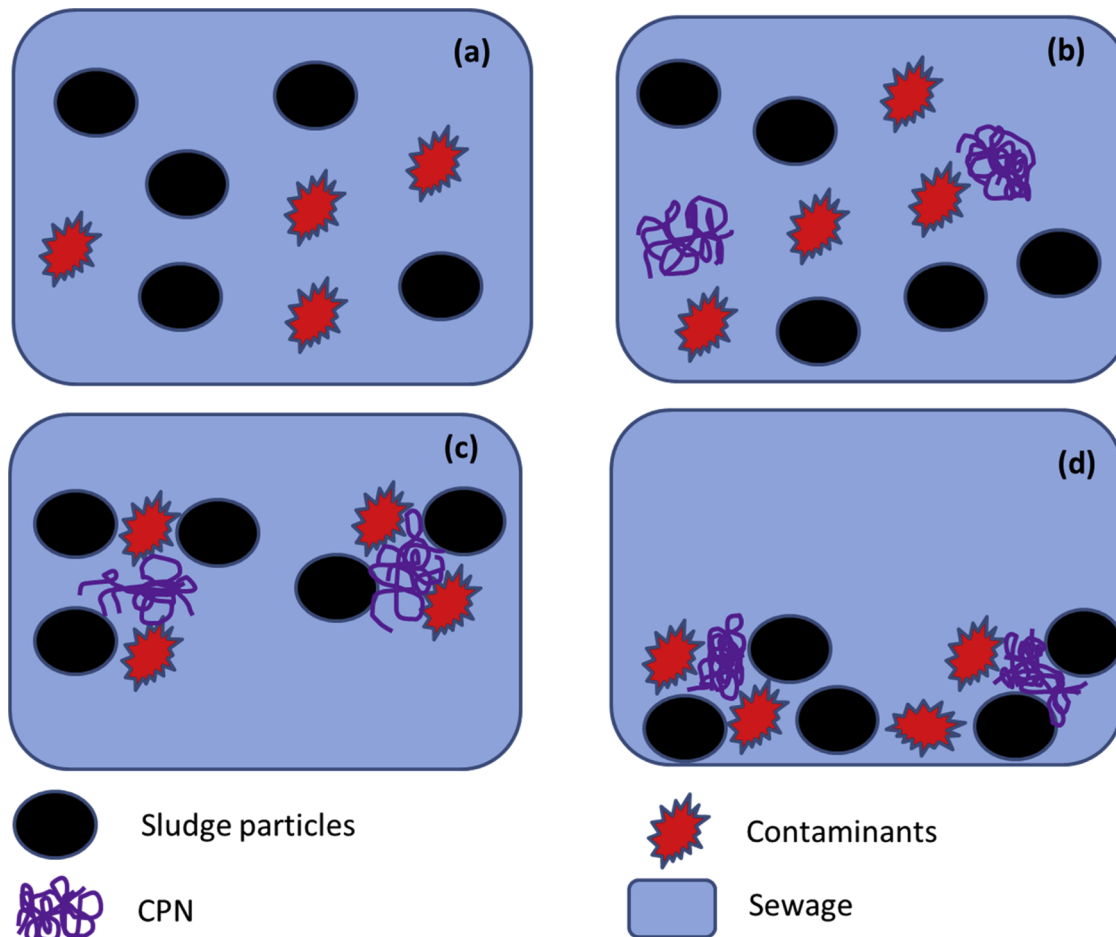


Fig. 3. Step-by-step mechanism of CPN for sedimentation of colloidal particles in effluent: (a) colloidal suspension, (b) CPNs in colloidal suspension, (c) coagulation and flocculation, and (d) sedimentation (Unuabonah and Taubert, 2014; Rytwo et al., 2013).

CPNs. The step-by-step mechanisms by which the CPNs make sediment in the effluents are shown in Fig. 3. The authors concluded that very fast coagulation is a significant advantage of the nanocomposites. According to the study, the best wastewater pre-treatment polymers are water-soluble polymers, bio-polymers such as CTS, aromatic polymers, and molecules such as quarternized hydroxyethyl cellulose ethoxylate. The potential of CPN-based coagulation–flocculation for treating agro-industrial wastewater needs to be further explored.

6.3. Columns/barriers

Use of a CPN as a column or barrier for water treatment is a promising area of research. Rytwo et al. (2007) used tetraphenylphosphonium ions on MMT as an organoclay to remove 2, 4, 5-trichlorophenol (TCP), a dangerous pollutant in water. The study revealed that 0.25 g of organoclay lowered the concentration of 1000 µM of TCP to below 3 µM concentration (bed breakthrough) by using column filter methods. Similarly, Undabeytia et al. (2008) prepared positively charged didodecyldimethylammonium bromide-modified MMT known as vesicle–clay complex for the removal of pesticides. They used it as a column agent (18 cm) (a mixture of vesicle clay, quartz, and sand). Results revealed that 94% of alachlor and 53.1% of atrazine were successfully removed from 1 L of water with an initial pesticide concentration of 10 ppm. Later, Zadaka et al. (2009) used poly(4-vinylpyridine-co-styrene)-MMT as a column filter (20 × 1.6 cm) to remove atrazine. Results showed the removal of 93–96% of atrazine from an 800 parts-per-billion initial concentration by mixing 2.0 g of composites with excess sand. Recently, Unuabonah et al. (2017) used Zn-doped bacteriostatic hybrid clay composites in a column composed of *Carica papaya* seeds, plantain peels (*Musa paradisiaca*), and ZnCl₂ as a water disinfectant. The study revealed that the *Carica papaya* composites successfully removed 1.5×10^6 cfu/mL of *S. typhi* and *V. cholera* within 400 and 700 min, respectively. Thus, CPN adsorbents prepared using organically modified clays may be used as a column filter to treat wastewater. However, more research attention should be paid to the use of CPNs as columns as a cost-effective technique for water treatment.

7. Clay–polymer nanocomposites as a remediation tool: going beyond the laboratory scale

Converting laboratory-based findings into real practice is difficult and requires many large-scale assessments. Although an increasing amount of research focusing on CPNs has been conducted over the past ten years, at this stage, the focus tends to be limited to the laboratory scale. Generally, experiments have been performed using synthetic polluted water (prepared by dissolving metal salts in deionized water) and tested under predetermined conditions (initial concentration, pH, temperature, and co-existing ions). The adsorption data have been collected, and the results interpreted according to well-known adsorption isotherm models (e.g., Freundlich, Langmuir, Temkin). So far, research findings under these controlled laboratory conditions have shown favorable results as previously discussed. Furthermore, laboratory-scale studies have provided fundamental knowledge to interpret the removal efficiencies, removal mechanisms, kinetics, and thermodynamics of the adsorption of contaminants.

However, practically speaking, a contaminated site (or water) is a complex system in which a diverse collection of biological and interference species and organic components can present themselves in great quantities. Several attempts have been made to evaluate the performance of prepared clay–polymer composites in treating real or simulated contaminated wastewater.

Kumar et al. (2012) investigated the removal of Cr(VI) from an industrial effluent using a clay–cellulose composite. The optimization of experimental parameters (e.g., pH, adsorbent loading, and time) was first investigated through a batch method and was followed by column

studies using synthetic Cr(VI) wastewater. The column studies were further extended to treat a chrome tannery leather effluent that consisted of basic chromium sulfate. The original effluent consisted of a variety of cations (e.g., Zn, Cu, and Fe) and a high concentration of chlorides and total dissolved solids (> 1000 mg/L) and organic components. The authors reported the highly successful removal of Cr(III) (> 95%) from the diluted eluent sample in which anionic and cationic interference was found to be insignificant.

A micro-scale adsorption experiment in simulated contaminated water was performed in a study involving the ability of a humic acid-immobilized amine-modified polyacrylamide–bentonite composite to remove heavy metals from an aqueous solution (Anirudhan and Suchithra, 2010a). Three types of effluents were tested for specific heavy metals: (i) simulated electroplating wastewater for Cu(II), (ii) industrial estate wastewater for Zn(II), and (iii) nuclear power plant coolant water for Co(II) (Anirudhan and Suchithra, 2010b). At an adsorbent dosage as low as 10 g/L, almost 100% removal of heavy metals was recorded in each respective simulated example of wastewater. The findings were in close agreement with the results obtained previously through a batch method. Hence, the humic acid-immobilized amine-modified polyacrylamide–bentonite composite demonstrated the capability to treat real industry effluent, although factors such as the effluent pH and the initial concentration of the heavy metals should be assessed in more detail.

In a recent study, Sallam et al. (2017) investigated polymer–clay composites prepared by natural zeolite (clinoptilolite) and local clay deposits obtained from the Shama Mountain to remove chromium from the alkaline wastewater of a tannery. The influence of adsorbent dosage and retention of interfering ions (e.g. Na⁺, Cl⁻, and SO₄²⁻) was studied and compared with that of pristine materials (zeolite and raw clays) and clay–polymer composites (zeolite–polymer and clay–polymer). The Cr(III) removal efficiencies in the tannery wastewater were recorded in the order of zeolite–polymer > zeolite > clay > clay–polymer composite within the adsorbent dosage range of 4 to 10 g/L. Nevertheless, the trend was reversed when the adsorbents were tested in synthetic contaminated water where clay–polymer composites demonstrated the highest removal efficiencies (90.1% at pH 2 and 55.3% at pH 10). The clay–polymer composite also showed excellent removal of Na⁺, Cl⁻, and SO₄²⁻ in the tannery wastewater compared to other adsorbents (Sallam et al., 2017).

A new regenerable dual-site composite comprised of polymerized β-cyclodextrin (pCD) modified with a cationic group (pCD⁺) and deposited to MMT known as pCD⁺–MMT composite was synthesized and tested for the removal of bisphenol A (Shabtai and Mishael, 2018). The composite was compared with activated carbon to treat arrays of micro-pollutants (concentrations ranged from 1 ng/L to 1600 ng/L) that existed in treated wastewater effluent. It was demonstrated that pCD–MMT showed greater removal efficiencies than that of the activated carbon. However, the bisphenol A removal could not be quantified because of recovery issues (Shabtai and Mishael, 2018).

Besides acting as a pollutant adsorbent, clay and its composites can also be used as a coagulation or flocculation agent in wastewater treatment. These roles are useful, especially when involving effluent with high turbidity. The treatment of olive and winery wastewater, for example, is extremely challenging and costly because of the huge amounts of dissolved organic species (especially phenols) and suspended matter present (Rytwo et al., 2013). Conventional sewage treatment is considered inefficient to solve to these issues, whereas the combination of removal technologies (e.g., filtration with reverse osmosis system) in treating olive and winery wastewater incurs a high maintenance cost. Hence, wastewater pre-treatment to reduce the suspended solid is a strategy to lower the cost and increase the efficiency of the treatment. The coagulant and flocculation agent can work together to alter the colloidal stability of particles in an aqueous solution to enhance the water clarity. In this approach, a clay–polymer composite made of polymer (poly(diallyldimethylammonium) chloride (poly-

DADMAC) and CTS) and clay minerals (bentonite and sepiolite) were prepared to enhance the solid sedimentation rate through a “coagulation-flocculation” mechanism (a combination of neutralization, aggregation, and increased density) (Rytwo et al., 2013). Polymer intercalation was observed in a bentonite-based nanocomposite, in contrast with a sepiolite-based composite. Nevertheless, all composites showed a rapid and high degree of clarification (90% light intensity) measured during dispersion analysis. Hence, clay composites exhibit significant potential as coagulating agents to assist in the pre-treatment of industry effluent as demonstrated in this study (Rytwo et al., 2013).

It is clear that more work needs to be done to bridge the knowledge gap in evaluating the efficiencies of CPNs in treating real wastewater effluent. To the best of our knowledge, a full-scale application of CPNs has not yet been demonstrated in any remediation site or water treatment. Nevertheless, just as with other remediation technologies, an in-depth understanding on the nano-architecture stability of CPNs together with their environmental impact and toxicity should first be obtained to demonstrate their practical utility. For example, although within the past 20 years of research zero-valent iron has been extensively studied at the laboratory scale and was successfully applied at a remediation site, there are still fundamental and technical limitations that arise such as reaction pathways, longevity, and the impact of zero-valent iron at a remediation site (Guan et al., 2015). In this context, with proper research design, clay-polymer composites may demonstrate properties comparable with zero-valent iron such as the availability of raw materials, less toxicity, stability, and a more environmentally benign synthesis route. Hence, clay minerals and their composites have a bright future in serving as material for remediating contaminated sites or in real wastewater treatment.

8. Economics and sustainable water treatment considerations

Economic analysis in terms of the benefit-cost ratio is one of the most important areas of research for applying CPNs to water treatment. The feasibility and sustainability of this type of special adsorbent highly depends on the cost of the preparation of adsorbents, energy inputs, and ecosystem safety. An economic analysis would be very helpful in determining whether these products are suitable for use at ground level for long durations. However, few studies have analyzed the economics of CPNs for sustainable water treatment. In this section, we discuss the cost of raw materials such as clay or polymers that can minimize the cost of production of a nanocomposite with a high contaminant removal capacity.

There is a huge difference in price between clay minerals such as normal bentonite, kaolin, MMT, and palygorskite and polymers such as

Table 3
Price of selected clays and polymers used for preparation of CPNs.

Clays and polymers	Price	References
Bentonite	\$43.59/ton	(Virta, 2001)
Nano Ca-bentonite	€4400–10,000/ton	(Roes et al., 2007)
MMT	\$40–120/ton	(Ahmaruzzaman, 2008)
Kaolin	\$106.91/ton	(Virta, 2001)
Palygorskite	\$200/ton	(Rusmin et al., 2017)
CTS	\$11,500/ton	(Roberts, 2008)
Polypropylene	€787–1,191/ton	(Roes et al., 2007)

CTS and polypropylene (Table 3). Many researchers have reported that the addition of clay minerals to a biopolymer such as CTS improved the adsorption capacity of the polymer-clay nanocomposite for organic and inorganic contaminants. In addition, incorporation of naturally available clay minerals into a polymer matrix may also minimize the cost of the product. Although only a few studies have addressed regeneration capacity, these low-cost minerals can effectively be used for the regeneration study of adsorbents. Regeneration capacities of clay-polymer-based adsorbents have the advantage of less generated waste and bulk amount contaminant removal within an entire cycle.

Some CPNs have been used as catalytic agents to study contaminant degradation. An MMT clay/TiO₂ nanocomposite was used for MB removal in an aqueous system (Szczepanik, 2017). It was prepared by a simple sol-gel process that was economically sound and showed high degradation capacity. However, green leaf extract has been used with clays to minimize the cost of production and maintain environmental sustainability. Similarly, metal-doped clay-polymer composites should also be prepared along with metals that are less toxic than elements such as Ti and Ag. At present, sepiolite, palygorskite, and halloysite (modified or raw) can also be utilized more effectively for the disinfection of water instead of kaolinite or MMT (Unuabonah et al., 2018). Overall, selection of low-cost suitable clay minerals, green leaf extract, and inexpensive raw materials as filler and polymers can be used for the economical preparation of low-cost efficient CPNs to maintain environmental sustainability.

9. Conclusions and way forward

All the CPN-based adsorbents discussed here have tremendous potential for wastewater treatment in removing organic and inorganic pollutants and harmful microbes when used as a coagulant, catalytic agent, membrane, or filter. Studies confirmed that proper inclusion of clay at optimal doses with several inorganic polymers and biopolymers in the nanometer range or nanoclay for the preparation of nanocomposites improved the efficiency of CPNs for pollutant removal in aqueous systems. At this stage, the scope of most studies demonstrated successful performance of CPNs at a laboratory scale, while only a few attempted to evaluate their practicality in real wastewater or contaminated sites. To maintain the economic viability and sustainability of CPNs for water treatment, a schematic representation of the scope of future research is shown in Fig. 4. Furthermore, to boost the environmental sustainability and safety of developed CPNs, the following points need to be considered in the future:

- 1 Metal-doped CPNs with less toxic metals such as Cu, Zn, and Fe should be promoted for water treatment in place of Ti and Ag, which are harmful and toxic to living organisms residing in water.
- 2 A valid standardized methodology must be developed to evaluate environmental safety and sustainability at an international level.
- 3 The preparation of innovative CPNs using economical and green materials such as agro-waste, green extract, and industrial by-products should be promoted.
- 4 To remove harmful microbes from water in a more economical and sustainable way, development of visible light photocatalytic polymer-clay nanocomposites should be initiated.
- 5 More focus should be given to the regeneration study of adsorbents used for wastewater treatment.
- 6 Awareness of CPN-based water remediation must be heightened

Water treatment by CPNs: A way forward to sustainability and environmental safety

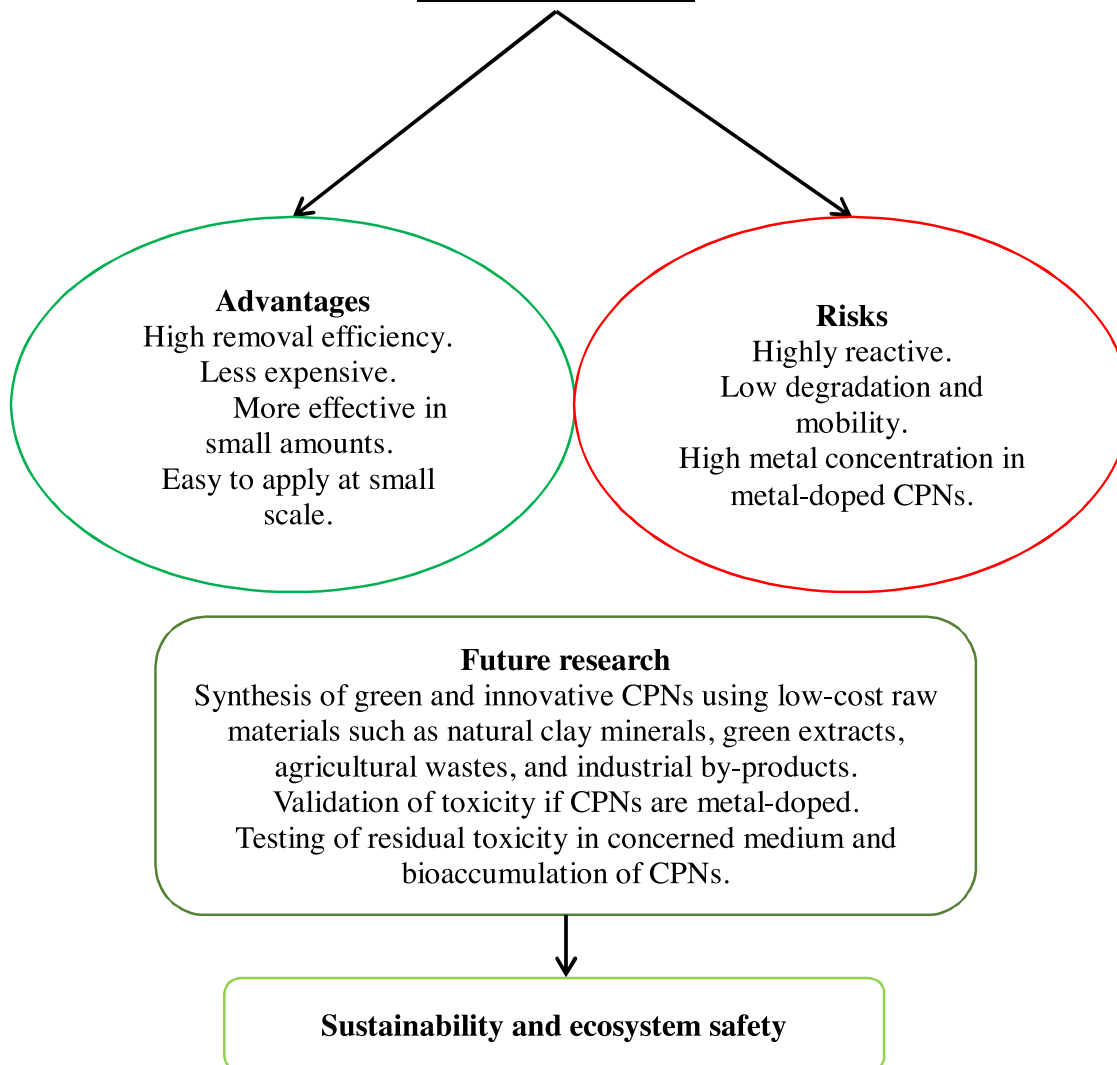


Fig. 4. Schematic representation of sustainable approaches for CPN-based water treatment.

through the high quality and validated information available in published studies.

- 7 Field-scale applications of CPNs need to be explored for use at the rural level.
- 8 Above all, the government should prepare and implement proper policies at national and global levels by involving policymakers and experts in the determination of the factors affecting the marketability of CPNs.

Contributions

Raj Mukhopadhyay, Debarati Bhaduri, and Binoy Sarkar prepared the outline and wrote the first draft. All authors subsequently added sections and improved the contents.

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