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Clay–Polymer Nanocomposites: An Efficient Adsorbent for Wastewater Treatment

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Abstract

Despite the abundance of water sources, the globe today lacks potable water because to pollution. Pollutants can be removed from water using a variety of technologies, but adsorption is considered the most simple, effective, economical, and ecologically beneficial method. The class of adsorbents known as clay–polymer nanocomposite (CPN) adsorbents is one that is now gaining popularity. By adsorbing and flocculating inorganic and organic micropollutants from water, CPNs efficiently cleanse water. Compared to clean clay, CPNs are far simpler to retrieved from aqueous conditions. In comparison to clay or polymer adsorbents, they also show much longer treatment periods. When compared to clay alone, they have a greater potential for adsorption and superior life cycles. Thus, CPNs exhibit great promise as extremely effective agents for the treatment of waste and water. The extremely high temperatures and pressures that usually arise in a fixed bed system are well suited for CPNs since they possess higher levels of mechanical and thermal strength than polymer resins. Thus, it is reasonable to anticipate significantly less CPN deterioration when using CPNs on an industrial scale, at least over an extended period of time. This article explores a variety of CPNs that have recently been developed and applied as adsorbents to remove inorganic, organic, and biological micropollutants from aqueous solutions. The levels of micropollutants in water are brought down to a safe level by the CPNs.

Keywords: CPN, Wastewater, Adsorbents, Clay minerals, Coagulation, Flocculation

INTRODUCTION

The correct operation of the earth's ecosystems depends heavily on water, which is a significant and fundamental component of the cosmos (1). large-scale wastewater releases into the environment as a consequence of harmful human activity, intensive agricultural practices, and rapid industrialization have made clean water a critical concern on a global scale, despite the existence of extensive water bodies. Toxic contaminants like pesticides, phenols and metalloids, etc. are all present in these wastewaters. The supply of clean water for irrigation and drinking has thus grown to be a global concern. Wastewater must be treated in order to meet the basic needs of industry and human existence for high-quality water. Water that is pure enough to be used in many different sectors and industries, including agriculture, can be produced by eliminating microorganisms and hazardous chemicals. Numerous cutting-edge methods for treating wastewater have been covered in earlier research, including "reverse osmosis, complexation, membrane filtration, photo-and electro-catalysis, precipitation, and electrodialysis". among the most effective and affordable techniques for cleaning wastewater is adsorption (2, 3).

The primary variables influencing the selection of adsorbents are the benefit-cost ratio, adsorption efficiency, and specificity for a particular hazardous chemical. A variety of adsorbents, including both organic and inorganic materials, have demonstrated effective decontamination of wastewater. Because of their simple availability

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and financial advantages, naturally occurring clay minerals are widely employed (4,5). Nevertheless, the limited surface area of natural clay minerals and the absence of a clear process for recovery and regeneration in aqueous systems limit their utility and poor ability to remove micro-pollutants (6,7).

Conversely, polymeric resins have proven to be able to get around the drawbacks of the natural clay minerals. However, due to their high cost, sensitivity to particle size, dependence on pH, and poor water wettability, resins have not been widely used in industries or water treatment facilities (6). In an effort to get over their individual limitations, researchers have focused a great deal of emphasis on the development of clay–polymer nanocomposites (CPNs), which, in a single adsorbent, combine the beneficial qualities of clay minerals and polymers. Additionally, CPNs contain filler in modest amounts (1-2 vol.%), which gives pure polymers or resin their intrinsic properties and stability (8). Due to their greater availability and lower cost compared to activated carbon, zeolites, and membranes, clays and their modified forms have drawn a lot of interest for their application as adsorbents of metal ions from aqueous media. Bhattacharyya and Gupta (2008) as well as de Paiva et al. (2008) (9,10) have conducted extensive studies on the adsorption of organic micropollutants and heavy metals from aqueous solution. These studies focused on clay minerals and organoclay minerals. A comprehensive review of the most current advancements in CPNs, their application in wastewater treatment, and their long-term financial sustainability is provided by this critical examination. Discussing the route that this field of study will take going forward is another goal of this review, as it requires a lot more investigation in the near future. By examining extremely promising but as of yet underutilized or undiscovered CPNs, this review aims to provide a future-oriented perspective on CPNs as adsorbents for wastewater treatment.

TYPES AND TEXTURES OF CLAY MINERALS

The layers that make up the crystalline structures of clay particles are primarily made up of octahedral $[AlO_3(OH)_3]$6-and tetrahedral $[SiO_4]$4-sheets. The minerals that make up clay belong to seven groups: (i) "kaolinite group where tetrahedral $[SiO_4]$4− and octahedral $[AlO_3(OH)_3]$6-sheets are present in a 1:1 ratio (e.g., kaolinite, halloysite, serpentine) (11), (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) (12)".

Organoclays are the byproducts of modifying clay minerals like palygorskite and MMT with organic compounds. Because the manufacture of organoclays is frequently the initial stage in the synthesis of CPNs, organoclays are relevant in the topic of CPNs. Hydrophilic clay minerals are found in nature. When clay minerals are saturated with cations like Na^+ or Li^+, their hydrophilicity increases even more. These clay minerals that are hydrophilic only react favorably with hydrophilic polymers, such as PVA and polyethylene oxide; non-polar polymers react adversely with them. Thus, the original purpose of organoclays was to render "hydrophilic clay minerals compatible with hydrophobic polymers" and non-polar molecules (12–17). Clay minerals can be modified with non-polar polymers by substituting hydrated cations with positively charged organic molecules, using ion-exchange procedures. This process results in clays that are hydrophobic (18–20).

NANOCOMPOSITES OF CLAY AND POLYMERS

Layered composites made of clay and polymer fall into three categories: Three types of nanocomposites can be distinguished: phase-separated, intercalated, and exfoliated (13,21). When a polymer fails to integrate into the layers of silicate, phase-separated composites are created. The composites' measurements and characteristics, however, are unchanged from those of conventional micro composites. Polymer chains that rip crystalline silicate layers are what produce incorporated nanocomposites, regardless of the ratio of polymer to clay. In exfoliated nanocomposites, individual clay layers, about one nanometer thick, are removed from the polymer matrix (22). Nowadays, a variety of polymers are utilized to create CPN, including polyesters, epoxies, polyurethanes, polypropylene, polystyrene, and chitosan (CTS).

CPN IN THE TREATMENT OF WASTEWATER

Removal of Inorganics

The capacity of CPNs to eliminate inorganic micropollutants from aqueous solutions has been the subject of the most investigation. Using a clay-poly methoxy ethyl acrylamide (PMEA) nanocomposite, it possesses a remarkably high capacity for adsorption, Pb (II) was extracted from an aqueous solution by Sölener et al. (2008)(23). Pb (II) adsorption on the CPN is endothermic and occurs through physisorption. In the pH range of 4.0–6.0, the material's adsorption capability remains unchanged. This adsorbent has excellent Pb (II) adsorption capacity even at extremely low pH levels of approximately 3.0. “Cu (II), Zn (II), and Co (II)” can be successfully removed from aqueous solutions using “humic acid immobilized-amine-modified bentonite–polyacrylamide (HA-Am–Bent–PAA) nanocomposite”, as demonstrated by Anirudhan and Suchithra (2010a) (24). They found that 5.0, 9.0, and 8.0 are the ideal pHs for employing this CPN to take these metal ions out of water. After the metal ions were adsorbed for 30 minutes, 73% of them were removed from the solution, and equilibrium was reached after 120 minutes. According to reports, the “HA-Am-Bent-PAA nanocomposite” outperformed a number of other previously employed adsorbents, such as multiwalled carbon nanotubes, in its ability to adsorb the aforementioned metal ions. According to Unuabonah et al. (25), “Pb (II) and Cd (II)” may be successfully removed from aqueous solution using a CPN made of “kaolinite and polyvinyl alcohol (Kaol–PVA)”. In 2013, “Dlamini et al.”(26) synthesized a “cloisite C20A-polycaprolactone (C20A-PCL) nanocomposite” using dry Na_2SO_4. The polymer's thermoplastic properties and the cloisite C20A's hydrophobic properties did not prevent this CPN from extracting 87% of Pb (II) from water.

Iron oxide nanoparticles, methyl methacrylate monomer, bentonite clay, and in situ polymerization were utilized by Sundaram and Dharmalingam (2018) (27) to create magnetized-CPN recently. The scientists used it to adsorb Cr (VI) in an aqueous solution, and it absorbed 113 mg of Cr (VI)/g of the adsorbent. Using the intraparticle diffusion equation to fit the data, Sundaram and Dharmalingam (2018) (27) demonstrated that film-diffusion was the primary adsorption mechanism. According to Wang et al. (2016), a “CTS–Al-pillared MMT nanocomposite” was able to eliminate 15.67 mg/g of Cr (VI) before. Similar adsorbents with a CTS-to-clay ratio of 0.45:1 was used to adsorb “Cu (II) and Pb (II)”. The adsorbents showed good regeneration capability with 0.1M HNO_3 and removed the metals at rates of 96.0 and 99.5%, respectively, through chemisorption at a pH of 6.5 (28). In order to remove arsenic (As), a water-soluble CPN composed of organically modified MMT clay particles and "N-methyl-D-glucamine-based monomer" was recently used by Urbano et al. (2012) (29). The resin's ability to remove 55 mg of As/g was demonstrated by a Langmuir adsorption isotherm analysis, demonstrating that the solution's final As concentration was within the allowable limits set by the World Health Organization.

Removal of Organics

CPNs have been used to treat organic micropollutants in water in addition to the traditional removal of inorganics. When an organic component, such a polymer molecule, is present in the adsorbent, it becomes more hydrophobic and can thus collect organic micropollutants from water more efficiently. Atrazine, a major endocrine disruptor, was removed from water by Zadaka et al. (2009 (30) using a CPN of “montmorillonite and poly-4-vinylpyridine-co-styrene (90%) (Mt–PVP-co-S90%)” as an adsorbent. It took 20 to 40 minutes to eliminate 90–99% of the atrazine (0.5–28 ppm). The 800 ppb of atrazine in a fixed bed trial was removed by granular activated carbon filters only 75–93% of the time, but 93–96% of it was removed by the same CPN. Ganigar et al. (2010) (31) employed nanocomposite materials consisting of “montmorillonite–poly-4-vinylpyridine–co-styrene (Mt–PVPcoS) and montmorillonite–poly diallydiamethyl ammonium (Mt–PDADMAC)” to eliminate TCP and TNP from water. Due to partial PDADMAC desorption into solution, the "Mt–PvPcoS nanocomposite" adsorbent demonstrated superior adsorption ability for these contaminants than the "Mt–PDADMAC nanocomposite." 99.5% of the trinitrophenol (TNP) was eliminated from the "Mt–PvPcoS nanocomposite", whereas 40–60% of the original amount in solution was effectively eliminated when TCP was removed. The primary explanation for how these organic micropollutants were adsorbed onto the “Mt–PVPcoS nanocomposite” was given by the adsorption isotherms of the pollutants' adsorption, but electrostatic interactions also contributed in the case of TNP. According to Ganigar et al. (2010) (31), van der Waals interactions were the primary force for the binding of both contaminants onto the nanocomposite.

Recently, a thin coating of CPN has been used to address problems with adsorbents whether they are used as pills, powder, or in other forms and recycled for environmental remediation (32). Thus, recycling of thin-layer clay-polymer composites with good adsorption capacity that have already been employed is encouraged by regeneration methods. The metanil blue (MB) concentration (152.2 mg/g) was 99.99% removed by Xu et al. (2018) (33) chitin-clay composites. Within the pH range of 5.0–8.0, the authors found that the maximal removal efficaciousness of CV, MB, and malachite green dyes were, respectively, 94, 97, and 98%. Bee et al.(34) employed magnetic chitosan/clay (CTS/clay) beads in a different investigation to eliminate MB in a pH range of 3–12 and a clay-to-CTS weight ratio>0.5.

Its adsorption maxima were found to be 82.0 mg/g, with a quicker removal efficiency of 50% in only 13 minutes. A 446.42 mg/g dye adsorption potential was obtained by “Vanamudan and Pamidimukkala (2015)”(35) using a CTS–clay nanocomposite for “Rhodamin-6 G” removal. Purification of wastewater tainted with pesticides like atrazine and 2, 4-dichlorophenol has been attempted, with CPNs serving as adsorbents. In order to remove atrazine, MMT was modified with 90% poly-4-vinylpyridine-co-styrene. This modification allowed for the rapid (20–40 min) removal of 90–99% of atrazine (30). Gamiz et al. (2015)(36) reports the application of the hexadimethrine–MMT nanocomposite as an adsorbent for pesticides. Water phenolic chemicals pose a hazard to living things as well. An alginate polymer matrix was treated with surfactant (hexadecyl trimethyl ammonium) to eradicate phenols as well as 4-chlorophenol. For 4-chlorophenol and phenols, they showed adsorption of 0.334 and 0.118 mg/g, respectively (37). Tannic acid is a poisonous organic chemical that is produced when organic matter breaks down. It is a polyphenolic component that harms living things. These substances are typically found in surface water and soil. It is therefore crucial to remove it from an aquatic environment.

Tannic acid elimination with CPNs has been the subject of very few investigations. Tannic acid was extracted from an aqueous solution using a new CTS-coated attapulgite adsorbent, which was created by Deng et al. (2012)(38). This new adsorbent eliminated 95.2 mg/g of tannic acid, according to the study.

Removal of Biological Contaminants

Microbes like Salmonella typhi and Salmonella para typhi are recognized to be the cause of water-borne illnesses. Diarrhea can be caused by Campylobacter, Vibrio cholerae, Escherichia coli, and Giardia. Chlorination is a decades-old method of eliminating microorganisms from drinking water. However, when water contains soluble organic materials, this approach is losing ground quickly due to the development of hazardous by-products as chlorophenols (39).

CPNs having antibacterial properties have recently been created. A collection of pathogenic bacteria are totally eliminated by a “clay–polydimethyloxane–chitosan–silver (Clay–PDMS–Ct–Ag) nanocomposite”(40). In a CPN film made by embolism from solution, strong antibacterial activity against Staphylococcus aureus (S. aureus) and Escherichia coli was demonstrated (41). Utilizing chitosan (CS) and chitosan-based materials, such as chitosan nanocomposites that demonstrate antibacterial action, is the focus of another class of CPNs (42, 43). Because CS has a faster death rate, a wider spectrum of activity, less toxicity to mammalian cells, and stronger antibacterial activity than other disinfectants, it has a number of advantages over other disinfectants.

The antibacterial activity of the "montmorillonite–chitosan (Mt–CS) nanocomposite" against S. aureus and E. coli is therefore noticeably greater when compared to pure chitosan and Na–montmorillonite alone (44). Furthermore, a new CPN derived from rectorite that was modified with cetyl trimethyl ammonium bromide (CTAB) and HTCC demonstrated strong antibacterial activity in an aqueous media with a weak acidic and basic concentration against a variety of microorganisms, including gram-positive and gram-negative bacteria and fungi, according to Wang et al. (2009) (45). Extensive in vitro antimicrobial tests demonstrate that 90% of S. aureus and 80% of E. coli are eliminated by the CPN in less than 30 minutes, and all other bacteria under investigation are eliminated in 3.0 hours. A CPN of Mt-CS treated with silver shown significant antibacterial activity against both gram-positive and gram-negative bacteria, according to Shameli et al. (2011) (46).

CPN to Aid in Wastewater Coagulation and Flocculation

Large volumes of organic and scattered debris can be found in agricultural effluents from soy or coffee bean industries, vineyards, piggeries, olive mills, and other industries. Typically known as the total amount of suspended solids, or TSS, these scattered solids are difficult for traditional adsorbents to extract from water when trying to remove both organic and inorganic micropollutants. The main reason for this is that they mostly exist in the colloidal condition, which can create filter clogging and make filtration challenging (47).

Certain pre-treatment methods have been effectively used to reduce or remove TSS entirely from water. Three processes are usually needed to reduce total suspended solids (TSS) in wastewater: flocculation, which aggregates the colloids into bigger aggregates, coagulation, which neutralizes the colloids, and separation by filtration or decanting. A pre-treatment method that decreases total suspended solids (TSS) in winery effluents by 85% was developed by Anastasiou et al. (2009) (48). Screening, passing the wastewater through a bioreactor, flocculation, and coagulation are all steps in the process. According to Rizzo et al. (2010) (49), the process was not improved by the introduction of chitosan. Reverse osmosis and nanofiltration, two pricey methods, processed a smaller volume of wastewater but were able to reduce TSS to 95% (50). The same paper (50) also shown how effectively and in a single step, a CPN made of sepiolite and polydiallyl dimethylammonium chloride (PDADMAC) lowers TSS and COD in wastewater. Moreover, Rytwo (50) proposed that the attaching particles should possess the following characteristics for effective coagoflocculation.

In order to have a large specific surface area, the particles must: (i) be less than 0.5 μm in at least one dimension; (ii) be able to adsorb cationic polymers through strong interactions; and (iii) have a bulk density greater than the effluent density. For this reason, smectites including montmorillonite, hectorite, laponite, and saponite as well as clay minerals like sepiolite and palygorskite are suggested anchoring particles (Rytwo, 2012)(50).

CONCLUDING REMARKS AND FUTURE DIRECTIONS

When utilized as a membrane, filter, catalytic agent, or coagulant, CPN-based adsorbents provide enormous potential for treating wastewater by eliminating hazardous microorganisms and organic and inorganic contaminants. Research has demonstrated that adding clay to aqueous systems at the right amounts, together with a variety of inorganic and nanoscale biopolymers, or creating nanocomposites with nanoclay, can enhance the effectiveness of CPNs in removing pollutants. To enhance the developed CPNs' safety and environmental sustainability, future considerations should be made of the following:

- Ti and Ag, which are hazardous to aquatic life, should be replaced with metal-doped CPNs that contain less hazardous metals like Cu, Zn, and Fe for water treatment purposes.
- Innovative CPN preparation should be encouraged utilizing affordable, sustainable resources and industrial waste products.
- The development of visible light photocatalytic polymer–clay nanocomposites is a promising avenue for more economically and ecologically benign removal of harmful microbes from water.
- The study of adsorbent regeneration that is employed in wastewater treatment needs more attention.
- Publicly available research that provide high-quality, verified information should be used to raise awareness of CPN-based water treatment.

- In order to employ CPNs at the rural level, field-scale applications must be investigated.

Above all, by incorporating experts and policymakers in the identification of the variables influencing the marketability of CPNs, the government should develop and carry out appropriate policies at the national and international levels.

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