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Nanomedicine & Nanotechnology Open Access
ISSN: 2574-187X

Insights of Montmorillonite Clay Nanocomposites for Adsorption of Toxic Colorant and Metals Ions from Wastewater: A Mini Review

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Mini Review
Volume 8 Issue 4
Received Date: October 04, 2023
Published Date: November 14, 2023
DOI: 10.23880/nnoa-16000269

Abstract

The development of lowcost adsorbents is triggered often by not utilizing the costly starting material that pave the path for synthesizing cost comparative adsorbents for purpose of sequestration of toxic pollutants from water. Clay minerals are alternatives that are low-cost to activated charcoal due to their abundance presence, excellent textural properties, high specific surface area, strong chemical, and mechanical stability Pollution, in recent years has become an increasingly serious problem, leading to health issues in human and deteriorating environmental condition. Various remediation technologies are introduced so far, but adsorption regarded as important industrial technique for separation and purification of effluent media. This review paper showcases the importance of montmorillonite nanocomposites for the remediation of toxic contaminants from water. The preferred method of remediation is adsorption. It also emphasizes the recent development in the field of montmorillonite nanocomposites in sequestering different types of dyes and various heavy metals from water. Hence, this brief review authorises the various montmorillonite adsorbents conceivability towards water treatment.

Keywords: Nanocomposite; Montmorillonite; Adsorption; Dyes; Heavy Metals

Introduction

In recent years, environmental concerns have triggered an environmental alert for care of the environment. This leads to the optimization and lessen the resources utilization in industrial process for purpose of textile dyeing. This has led to look for recover or reuse options for colorant in wastewater [1]. Their high solubility results in greater dissemination into the environment, thus making it detrimental to crops as well as life [2]. Similarly, the industrial growth and human activities such as fluidised bed bioreactor, petrochemicals, metal smelting, electrolysis applications, and paper manufacturing has also led to the increased presence of heavy metals in wastewater. The metal ion laden wastewater makes its way to environment threatening life. The non-biodegradable and carcinogenic nature of them [3-7] leading to critical health issues in living beings. Adsorption regarded as important industrial technique for separation and purification of effluent media. A mass transfer operation via a solid material can sequester selectively the dissolved components from aqueous media by allowing the dissolved solute to attract its surface. This technique of separation encounters ample applications in remediation of pollutants from aqueous solutions. Specifically, adsorption finds in industries where water recovery is essential. To attain and sustain recovery of water quality efficient, a good selection of adsorbent deserves a paramount attention [8,9]. The primary determination of adsorbent price and its regeneration process ultimately decides the cost of adsorption process. Activated carbon due to the elevated specific surface area, good porous configuration, commendable adsorption capacity and enhanced surface reactivity opines it as frequent use adsorbent for pollutant sequestration from wastewater. Nonetheless, high processing cost, and intricate isolation and recovery techniques constraint their extended usage. This resulted in development of copious low-cost adsorbents to supplant activated carbon. Clay minerals (sepiolite, zeolite, perlite, alunite, and bentonite) are alternatives that are low-cost to activated charcoal due to their abundance presence, excellent textural properties, high specific surface area, strong chemical and mechanical stability [10]. Clays possess exchangeable cations and anions at the surface and that desired worldwide scientist to focus on employing natural or modified clay minerals as adsorbents for water treatment [11]. Being negatively charged most of the clay minerals are effective and extensive in adsorbing metal cations from solutions fairly. This is attributed to their high cation exchange capacity, surface area and pore volume. The uptake mechanism involves series of complex adsorption phenomena such as metal cations direct bonding on to clay mineral surface, ion exchange, surface complexation etc [12]. Generally, clay particles in nano range are referred to as nano clays. Montmorillonite among all natural substances used widely owing to inexpensive and nontoxic nature qualifies as option for various environmental applications [13]. The nano-composite materials definition has extended over the years significantly to varieties of system such viz amorphous and 1,2 and 3 dimensional material ,fabricated by two dissimilar materials at the scale of nanometre. Thus, the nanocomposite is advanced material that possess property of (1 billion of meter) fillers detached from different variety of matrix. The stage may be like organic-organic, inorganic-inorganic, organic-inorganic [14]. The organic -inorganic combination of materials is a developing area of new as well as advanced research that can be apprehended. The goal of this review is to provide a specific and elaborative information regarding montmorillonite clay and its excellent adsorption capacities for various toxic pollutants especially dyes and heavy metals. This review paper showcases the importance of montmorillonite nanocomposites for the remediation of toxic contaminants especially dyes and toxic heavy metals from water. It also at the same time depicts the adsorption capacity or % removal of the various montmorillonite based nanocomposite adsorbents representing their efficiency in remediation of pollutants.

Montmorillonite Clay

Clay is the term applied to materials that possess particle size of less than 2 micro meter and also to minerals having similar chemical composition and same characteristics of crystal structure [15]. Montmorillonite is both used for group linked to clay mineral and for a specific member of that group [16]. Smectite is the name of mineral given to this group of Na, Fe, Mg, Ca and Li-A1 silicates. In smectite group commonly used mineral name are Na-montmorillonite,Fe-nontronite,Mg-saponite,Ca-montmorillonite,Li-hectorite [17]. Montmorillonite, a very delicate phyllosilicate mineral which forms in microscopic crystals, forming clay [18]. Layer, is the basic structural unit that consist of two tetrahedral sheets pointing inwards .These layers are in length and width direction continuous, bonds in between the layers are show excellent cleavage and are weak. This resulted in water and other molecules to go in between the layers leading in expansion in highest direction [19]. Also is a kind of swelling clay due to expandable lattice resulted by polar molecules. Additionally, there may be fluctuation in the intermolecular spacing due to change in cations between the silicate sheets [20]. Large surface area and expandable layered structure leads to excellent adsorption capacity. Hence, modified montmorillonite that has been utilised to get rid of various heavy metals in aqueous solutions [21].

Investigating the Adsorption Properties Montmorillonite Clay towards Dyes and Heavy Metal

Towards Heavy Metals Adsorption: Montmorillonite modified chemically to increase the surface area for synthesising highly porous composites. The chemically modified forms of MMT, treatment, and adsorption details have been investigated. Organically modified MMT clay was employed in polymer/clay nanocomposite to sequester Cu(II) as a function of pH, stirring time, concentration, eluent type, common ion effects and volume [22]. It exhibited good selectivity and removal efficiency (99.2 ± 0.9%)at pH-6 towards Cu(II) with a stirring time of 10 min [22] was applied successfully to recover Cu(II) from different samples. The recent work was conducted in advancement of organically modified MMT clay in which oregano-montmorillonite were modified by cationic and zwitterionic surfactant (Z16) [23] and was compared with raw montmorillonite towards Cu(II). The result of this work may provide information regarding development of new adsorbents effective for heavy metal. Almasri, et al. [24] synthesized hydroxy iron -modified montmorillonite for the arsenic removal. It was noticed that untreated montmorillonite nanoclay was incapable to remove arsenic. An increase in the adsorbent amount (1 to 4 g/L^{-1}) of treated montmorillonite enhanced the removal efficiency from20% to 90%. The change in contact time from 1 to 20 min results in increment in removal efficiency from 55 to 80%.The adsorption was dependant on pH, increasing pH 3 to 9 have improved removal efficiency to 90%. In another study, polyethyleneimine modified montmorillonite was reported for the removal of Co(II) and Ni (II) from aqueous solutions [25]. The Cobalt sorption noticed to be increased on the modified montmorillonite compared to natural one ascribed to cobalt binding with amine group attached to treated sorbent. It was concluded that utilization of such composite sorbent is promising for the wastewater purification with a pH at neutral. Other modified forms, chitosan-montmorillonite beads to remove Cu (II) [26] from aqueous solutions while synthetic iron-free montmorillonite was employed to uptake Fe (II) [27] from aqueous solution. Their promising results suggested that applied treatment on the adsorbent improved metal removal in wastewater streams. In another study humic acid modified Ca -montmorillonite and its performance was investigated towards Cu (II), Cd(II), and Cr(III) ions from aqueous solutions [28]. A shift in H-O-H band to lower the wave number showed by IR spectra indicated an interlayer increase in water that facilitated Cd(II) accumulation in interlayer space of montmorillonite. Akopomie, et al. [29] investigated removal of Ni (II) and Mn ((II) ions from solutions by alkaline modification of montmorillonite increasing specific surface are from 23.2 to 30.7m^2g^{-1} and due to modification there was increased porosity of material that leads to maximum capacity of removal of Mn(II) (111.95mgg^{-1}) and Ni (II) (125.95mgg^{-1})respectively.

Montmorillonite Nanocomposites	AIM	Heavy metal removed	References
Lignocellulose/ MontmorilloniteLnNC/ MMT	Prepared by chemical intercalation of LNC onto MMT. The ion adsorption was expected to be 94.86 mgg^{-1} at a pH of 6.8.	Ni (II)	[30]
Cellulose -Montmorillonite	Surfactant modified Na Montmorillonite with maximum adsorption capacity of 22.2mgg^{-1}	Cr (VI)	[31]
Hydrogel/Montmorillonite	synthesized an organomontmorillonite hydrogel nanocomposite for the reported a maximum removal capacity of 430 mgg^{-1}.	Pb(II)	[32]
Starch/sodium Montmorillonite (Starch-NaMMT)	Prepared by intercalation techniquein starch to nanoclay ratio of 5:1, 10:1 and 10:3 An adsorption of 97.1% at a pH of 4.5.	Ni (II)	[33]
Fe_3O_4/montmorillonite Fe_3O_4/MMT	Removal efficiency of 89.72%, 94.89%, and 76.15% Pb^{2+}, Cu^{2+} and Ni^{2+} ions	Pb^{2+}, Cu^{2+} and Ni^{2+} ions	[34]
Polypyrole/ Montmorillonite (PPy-OMMTNC)	Preparation of exfoliated polypyrrole- modified organically montmorillonite with adsorption capacity of 209.6 mgg^{-1} at 318K	Cr (VI)	[35]
Montmorillonite (Mt) / Biochar	Herein, (Mt) acted as a solid as a catalyst. The maximum adsorption capacity of NH_4^+ and PO_4^{3-} was reported as 12.52 $mg \cdot g^{-1}$ and 105.28 $mg \cdot g^{-1}$.	NH_4^+ and PO_4^{3-}	[36]
Carboxymethyl chitosan (CMC)/montmorillonite	Montmorillonite act as nanofiller. The adsorption capacity was found to be 92 mg $Pb.g^{-1}$ resin at pH 6.	Pb (II)	[37]
L-methionine/ montmorillonite (MMT)	L-methionine MMT encapsulated guar gum-g-polyacrylonitrile (GPCM) hybrid nanocomposite was synthesized by free radical graft copolymerisation. Maximum adsorption capacity of 125.00 mg g^{-1} for Pb (II) and 90.91 mg g^{-1} for Cu (II).	Pb (II) and Cu(II)	[38]
CTAB-Montmorillonite (CTAB-MMT)	Synthesized dextrin oxalic acid/(CTAB-MMT).Maximum adsorption capacity was found to be 4.731 mg g^{-1} at pH- 5.1 .	Pb (II)	[39]
Magnetite-ethylamine-Montmorillonite	Synthesized hybrid nanocomposite with sodium rich Montmorillonite (MMT) with magnetite nanoparticles (40nm, Fe_3O_4 NPs) coated with Polyethylenimine polymer having maximum amount of adsorption capacity of 8.8 $mg.g^{-1}$.	Cr(VI)	[40]

Table 1: Highlighted the few montmorillonite nanocomposites for heavy metal removal.

Towards Colorant Adsorption

Chang, et al. [41] prepared Fe_3O_4 /activated montmorillonite nanocomposite of good stability and reusability for the removal of methylene blue. It was noticed that within the time span of 25 min (0.5g) of nanocomposite removed 99.47%of MB from 120mgL^{-1} solution at pH 7.37. The reusability was assured to be 83.73% after 5 cycles of MB. In an another study, surfactant modified montmorillonite was assessed as adsorbent for the removal of methylene blue and Cu(II) in singles and binary systems [42]. The dodecyl sulfobetaine surfactant-modified montmorillonite was found to be more beneficial in adsorbing methylene blue is 9.5mg.g-1 and Cu (II) is 15.02 $mg.g^{-1}$ of adsorption capacities. Olad, et al. [43] synthesized effective starch -montmorillonite /polyaniline (St-MMT-/PANI) nanocomposites to get rid of reactive dyes .The adsorption capacity of reactive dye onto the nanocomposite were 91.74mgg^{-1}. Another study reveals the Cr (III) intercalated montmorillonite as an potential adsorbent for the removal of a synthetic dye supranol Yellow 4GL. XRD data of montmorillonite revealed that after modification the interlayer spacing (d001) of was increased from 12.35 to 23.06 Å. The separator factor RL revealed the favourable nature of this adsorption process [44]. Mahdavinia, et al. [45] reported crystal violet removal from water by solution polymerization of sodium acrylate in presence sodium montmorillonite and carrageenan biopolymer. APS was employed as initiator and MBA as crosslinker produced a 3D network.

Nanocomposite	AIM	Colorant/Dye	References
Graphene oxide/ Montmorillonite	Prepared via facile chemical route with adsorption capacity of 746.27mgg^{-1}	Crystal violet	[46]
Montmorillonite clay/starch/$CoFe_2O_4$	Montmorillonite was magnetically modified by starch and cobalt-ferrite with sorption efficienc 98.67% (MB) and 99.45% (MV)	Methylene blue (MB) and Methyl Violet (MV)	[47]
Montmorillonite/ hydrogel	synthesized via a simple solution copolymerization of acrylic acid and 2-acrylamido-2-methylpropanesulfonic acid monomers in the presence of MMT by using ammonium persulfate as an initiator	Methylene Blue(MB)	[48]

Table 2: Highlighted the few Montmorillonites nanocomposite for colorant removal.

Conclusion

This mini review encompassed various montmorillonite nanocomposites which have been efficient in removal of both dyes and heavy metals from the aqueous media. The paper compiled and categorized various montmorillonite adsorbents refashioned for the sequestration toxic heavy metals and dyes efficiently, cost-effectively, and environmentally friendly from water. The paper provided literature information about the synthesis of various nanocomposite-based adsorbents by employing adsorption technique.

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