THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants

Citation for published version:
Han, H, Rafiq, MK, Zhou, T, Xu, R, Mašek, O & Li, X 2019, 'A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants', *Journal of Hazardous Materials*, vol. 369, pp. 780-796. https://doi.org/10.1016/j.jhazmat.2019.02.003

Digital Object Identifier (DOI):
10.1016/j.jhazmat.2019.02.003

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Journal of Hazardous Materials

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

OPEN ACCESS

Download date: 12. Oct. 2024

Accepted Manuscript

Title: A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants

Authors: Huawen Han, Muhammad Khalid Rafiq, Tuoyu Zhou, Rong Xu, Ondřej Mašek, Xiangkai Li

PII: S0304-3894(19)30133-5
DOI: https://doi.org/10.1016/j.jhazmat.2019.02.003
Reference: HAZMAT 20272

To appear in: *Journal of Hazardous Materials*

Received date: 17 October 2018
Revised date: 23 January 2019
Accepted date: 2 February 2019

Please cite this article as: Han H, Rafiq MK, Zhou T, Xu R, Mašek O, Li X, A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants, *Journal of Hazardous Materials* (2019), https://doi.org/10.1016/j.jhazmat.2019.02.003

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants

Huawen Han[a,1], Muhammad Khalid Rafiq[b,c,1], Tuoyu Zhou[a], Rong Xu [a], Ondřej Mašek[b], Xiangkai Li[a,*]

[a] Ministry of Education Key Laboratory of Cell Activities and Stress Adaptations, School of Life Science, Lanzhou University, Tianshui South Road #222, Lanzhou, Gansu 730000, People's Republic of China

[b] UK Biochar Research Centre, School of GeoSciences, University of Edinburgh, Crew Building, King's Buildings, Edinburgh EH9 3FF, United Kingdom

[c] Rangeland Research Institute, National Agricultural Research Center, Islamabad 44000, Pakistan

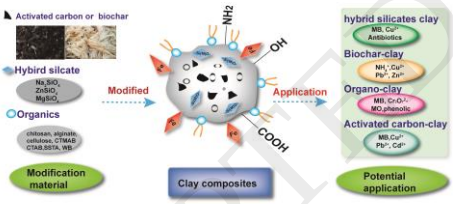
[1]These authors contributed equally to this work

* Corresponding author. E-mail address: xkli@lzu.edu.cn

Highlights

- Multi-modified clay composites show better performance than single-modified clays
- Clay composites with various modifications exhibit different absorption mechanisms
- Clay-biochar composites represent an environmentally superior alternative

Graphical abstract



Abstract: Adsorption techniques offer unique advantages owing to the use of synthetic (e.g., nanosized metal oxides and polymer-functionalized nanocomposites) and natural (e.g., clay and biochar) materials for pollutant removal. Although the most widely used adsorbent is activated carbon, extensive studies have highlighted the promising potential of modified clay minerals and biochar for removing heavy metal and organic pollutants from industrial, drinking, and eutrophic wastewater, due to their low cost and easy accessibility. However, clay modification using acids, calcination, polymers, or surfactants exhibits relatively low absorption/regeneration ability towards antibiotics, aromatics, and various dyes. The coexistence of numerous contaminants in industrial wastewater inhibited the performance of adsorbents,

ACCEPTED MANUSCRIPT

which accelerated the development of novel modified clay composites such as clay-biochar, organo-bentonite/sodium alginate beads, and enhanced biochar. This review summarizes recent studies and absorption mechanisms concerning clay composites based on various modification methods and component materials. The comparison of clay composites used for the removal of organic and inorganic contaminants provides valuable insight into real wastewater treatment. Knowledge gaps, uncertainties, and future challenges involved in the fabrication and regeneration of modified clay composites are also identified.

Key words: Biochar, clay-based composites, metal, organic pollutants, wastewater remediation

1. Introduction

As industrial and anthropogenic activities are posing an unprecedented threat to the natural environment [1], the removal and immobilization of contaminants is of crucial importance for the safety of ecosystems. Several potential technologies have been developed to remove heavy metals and organic pollutants for *in situ* remediation of industrial or domestic wastewater, including ion exchange, membrane separation, absorption, coagulation/flocculation, photocatalytic degradation, and biological treatment [2-4]. Among these approaches, adsorption offers unique advantages due to the use of synthetic and natural materials to achieve efficient pollutants removal via chemisorption and physisorption [5, 6]. The main difference between these two types of adsorption is that in the former the removal of pollutants occurs via the formation of chemical bonds through electron exchange, whereas the latter involves the adsorption of various pollutants via van der Waals forces, hydrophobicity, hydrogen bonding, polarity, as well as static and π-π interactions [3]. Current studies show that activated carbon [7], natural or modified biochar [8-10], and clay minerals [11, 12] are the main kinds of adsorbents for aqueous solutions and industrial wastewater. Clay minerals are considered superior to other commercial adsorbents such as activated carbon (AC), due to their low cost, wide availability, and excellent adsorption performance.

Generally, natural clay minerals contain montmorillonite (MMT), hectorite, sepiolite, laponite, saponite, rectorite, vermiculite (VMT), zeolite, kaolinite (KLN), and chlorite [13, 14], which mainly exist in the form of hydrous aluminum phyllosilicates along with iron, magnesium, alkali metals, and other cations [15]. Although the performance of clay minerals are mostly determined by intrinsic properties such as surface area, porosity, pH, and surface modifications, their final adsorption efficiency changed with pollutant type. Moreover, the crystal structure and negative

ACCEPTED MANUSCRIPT

charge of natural clays limit their industrial applications. Single modifications of clays through acid activation [16], calcination [17], magnetization [18], and surfactant [19] or polymer activation [20] have attracted considerable interest. These modifications can contribute to the removal of heavy metals, organic pollutants, and cytotoxins owing to their higher surface area, pore volume, and content of functional groups (e.g., $-NH_2$, -COOH, -OH) [3, 21-24]. For example, novel inorganic-organic clays (IOCs) can simultaneously eliminate both inorganic contaminants (heavy metal and oxyanions) and organic pollutants (phenolic compounds and polyaromatic hydrocarbons) [25]. Nonetheless, single-modified clays hardly meet the requirements of real wastewater treatment systems, due to the coexistence of multiple pollutants. The colloidal properties or micro-sized particles present great challenges to recover clay particles from suspensions after adsorption process, thus limiting their regeneration and reuse in fixed-bed media [26]. These limitations accelerated the emergence of granulated clay composites (e.g. activated carbon-clay composites) [27, 28] and crosslinked clay beads, such as bentonite-alginate composite and magnetic chitosan/clay beads [29, 30].

More recently, clay composites treated with a combination of modification methods have attracted widespread interest [31, 32]. For instance, acid/thermal-modified bentonite (ATA), treated with 0.1 M HCl and thermal activation (100 °C), showed larger pore size and surface area than single-modified bentonite, resulting in higher adsorption and removal of Congo red (CR) [33]. Subsequently, acid/polymer-, acid/surfactant-, anionic/cationic surfactant-, magnetic/polymer-, and surfactant/polymer-clay composites displayed a high adsorption ability for dyes, antibiotics, heavy metals, phenolic compounds, and inorganic ions (e.g., ammonia) [34-37]. In particular, clay-biochar composites incorporate the remarkable features of biochar and clay materials, and exhibit unique characteristics deriving from their high carbon content, multiple-pore structure, and compatibility [28, 38, 39], which make them also suitable for regeneration and reuse [26, 40, 41]. These combined-modification clay composites represent a promising class of adsorbent materials for the removal of pollutants from drinking water and wastewater [3, 14, 42]. However, recent developments on this class of materials have not been discussed in the literature. Hence, this review focuses on the synthesis, characteristics, toxicity, and regeneration ability of various types of modified clay minerals. Combined with a discussion of their adsorption mechanisms, we provide a critical analysis of various clay composites used in the removal of different organic and inorganic pollutants.

ACCEPTED MANUSCRIPT

Furthermore, knowledge gaps, uncertainties, and future challenges involved in the fabrication and regeneration of modified clay composites are also identified.

2. Synthesis and characteristics of clay composites with various modifications

Clay composites have received particular attention (Fig. 1) because their properties and structural performance are superior to those of their individual components [35, 36, 43]. The preparation of such composites involves the combination of two or more chemically distinct and insoluble phases [44]. According to the type of modification material, the composites can be classified into three categories: carbon material-, organo-, and hybrid silicate-clay composites. The following sections discuss the preparation procedure and characteristics of clay composites based on various combinations of modification methods and component materials. Fig. 2 and Fig. 3 show schematic diagrams of combined-modification clay composites.

2.1 Clay composites modified with carbon materials

2.1.1 Activated carbon-clay composites

Activated carbon is an adsorbent extensively used for the removal of pollutants. Due to the high cost of AC, its combination with clay minerals may allow to take advantage of their respective adsorption characteristics [45]. Activated carbon-zeolite composites synthesized from elutrilithe and pitch represent the main type of AC-clay composites. Among the raw materials employed in the synthesis, elutrilithe is a kaolinite-rich material composed of aluminosilicates and organic carbon [27], whereas pitch acts as binder and produces porous carbon. The synthesis of X-type zeolite-activated carbon composites was mainly performed via a three-step route: calcination of elutrilithe and pitch at 850 °C for 2 h, CO_2 activation of the carbonaceous material at 850 or 900 °C for 8–32 h, and hydrothermal conversion in a 3.5–5.0 mol/L NaOH solution [45]. This process resulted in the conversion of the carbon, SiO_2, and Al_2O_3 components of elutrilithe into an activated carbon-zeolite composite via an ion-exchange process in $CaCl_2$ solution (Fig. 2A). This material presented a hierarchical porosity ranging from micropores to mesopores (zeolite), a carbon content increased by 30%, and total surface area (S_{BET}) and pore volume of 615.41 m^2/g and 0.59 cm^3/g, respectively [46]. In some cases, the addition of SiO_2 facilitates the synthesis of X-type zeolite-activated carbon composites with high SiO_2/Al_2O_3 ratio ($r > 2.5$) [27]. Halim et al. developed simple methods to prepare activated carbon-zeolite composites by mixing zeolite (45.9%), limestone (15.3%), activated carbon (4.4%), rice husk carbon (4.4%), and ordinary Portland cement (OPC,

ACCEPTED MANUSCRIPT

30%) [47]. Similarly, Fig. 2B shows the preparation of calcium alginate (CA)-bentonite-activated carbon composite (ABA) beads via a simple fabrication method [28]. Despite the problems associated with AC production, such as its energy-intensive nature and high costs, the combination with clay and other materials reduces the carbon footprint and increases economic returns. These AC-clay composites have promising applications in the treatment of heavy metals, dyes, phenolic compounds, and ammonia.

2.1.2 Clay-biochar composites

Biochar is a carbon-rich solid product derived by pyrolysis of either plant or animal biomass in an oxygen-limited environment [48]. In addition to carbon sequestration and soil remediation [49], modified biochar acts as a green adsorbent for different types of pollutants, due to its porous structure, corrosion resistance, and abundant functional groups [50]. However, only few systematic studies have focused on the development of clay-biochar composites [26, 40, 41, 51]. Yao et al. first reported the preparation of six clay-biochar composites based on a simple method in 2014 [26]. Three biomass feedstocks, including bamboo (BB), bagasse [52], and hickory chips [53], were pretreated by MMT or KLN suspensions and then pyrolyzed at 600 °C in a N_2 environment (Fig. 2C). Owing to the incorporation of biochar, the pore volume and average pore width of the clay composites increased by 1.6 and 1.73 times, respectively, compared with those of pristine biochar [8]. In particular, several acidic groups (e.g., -COOH, -COO-, and -OH) of the composites crucially affected their adsorption capacity and selectivity. Subsequently, a series of studies have explored the use of clay-biochar composites for NH_4^+, PO_4^{3-}, norfloxacin (NOR), and heavy metal immobilization, such as potato stem and natural attapulgite [8], bentonite and cassava peel-based biochar [40], bamboo derived montmorillonite-biochar [51], chitosan (CTS)/clay and residual bark chips-based biochar [54], wheat straw derived montmorillonite-biochar [41], and kaolinite/jarrah-based biochar-chicken litter [55]. The adsorption ability of these composites is governed by the biomass sources and by treatment conditions such as pyrolysis temperature and activation time. Overall, non-toxic and inexpensive clay-biochar composites represent an environmentally superior alternative for wastewater treatment.

2.2 Clay composites modified with organic compounds

2.2.1 Acid /surfactant-clay composites

Acid activation (using H_2SO_4, HNO_3, or HCl) allows to partially dissolve Al_2O_3 and MgO from

ACCEPTED MANUSCRIPT

crystal lattice, resulting in an increase in internal surface area [56, 57]. However, acid-activated clays have low affinity towards organic molecules. Surfactant-modified clays can acquire hydrophobic and organophilic characteristics via the interlayer exchange between inorganic cations (e.g., Ca^{2+}, Na^{+}) and cationic surfactants such as cetyltrimethylammonium bromide (CTAB), dimethyl ammonium chloride (EA) and ethoxylated tallow amine (ETA) [6]. Thus, H_2SO_4/surfactant-activated Bent modified with a set of four alkyltrimethylammonium bromides is a typical practice of combined modification [37]. The synthesis of this material proceeded as follows: raw Bent was pretreated by a low-concentration acid (1 M H_2SO_4) at 90 °C for 4 h, and the activated solid, free of SO_4^{2-} ions, was dried at 80 °C. A 10 g amount of acid-activated Bent (AB) was dispersed into a 1 L solution of various surfactant to obtain four derivatives (Fig. 3A), labeled ABC12, ABC14, ABC16, and ABC18. The obtained samples were washed several times with distilled water to remove the residual bromide ions. Following this procedure, ABC16 was further pre-coated using sodium alginate (SA) to form activated organo-bentonite (AOBent)/SA composites [35]. After this modification, the basal spacing (d_{001}) of the clay increased from 13.84 Å (AB) to 21.50 Å (ABC18), revealing a positive correlation between d_{001} and the length of alkyl chains. Although AB generated a more developed porous structure than raw bentonite (RB), the insertion of a large molecular surfactant partially occupied the interlayer space of organo-bentonites, resulting in a decrease in porosity. The characteristics of this composite thus make it a promising candidate for the removal of dyes and aromatic compounds.

2.2.2 Anionic/cationic surfactants-clay composites

Unlike cationic surfactants, anionic surfactants are difficult to insert in the interlayer space of clay minerals in the absence of ion pairs (H_3O^{+}) or Na^{+} and Ca^{2+} as counterions. Co-modification with anionic and cationic surfactants can effectively overcome this issue [58], resulting in a higher organic carbon content compared to that of single-modified clays. In the typical experimental procedure, a given amount of cationic surfactant was added into clay suspensions with mechanical stirring for 1 h (Fig. 3B). After adding the anionic surfactant, the obtained mixture was continuously stirred for 4 h at 70 °C and the final clay composites was separated via centrifugation and ethanol washing at 60 °C [59]. This process resulted in clay particles with a 3.44 times higher basal spacing compared with that of raw clay (1.54 nm), excellent heat resistance, as well as lower hydrophilicity and surface energy. In addition, mixed micelles present in this type of composites exhibited

ACCEPTED MANUSCRIPT

synergistic effects for the removal of organic compounds [60]. Although possible risks caused by the potential release of the surfactants into the environment should be evaluated, anionic/cationic surfactant-modified clays may offer significant advantages in the adsorption of cationic dyes (e.g., methyl orange, MO) and *p*-nitrophenol (PNP) [34, 61].

2.2.3 Acid/polymer-clay composites

The intrinsic colloidal properties of clay minerals severely affect their regeneration and recovery from aqueous solutions. The embedding of pristine clay into natural polymeric materials, including chitosan [20], alginate [62], peanut hull [63], and cellulose [36], are considered as an effective strategy to address this challenge. Such crosslinked clay beads have been widely used in many fields [64, 65]. Acid/polymer-clay composites have recently attracted interest because of their biocompatibility and low cost. The corresponding modification method is suitable for almost all types of clays, including poly(acrylic acid) [66]/chitosan-vermiculite [67], HCl/SA-bentonite [30], wheat bran (WB)/*g*-PAA-palygorskite (PAL) [68], and H_2SO_4/$Al(OH)_3$/SA-Malaysia clay [69]. Taking H_2SO_4/chitosan-natural clay as an example, 1 g chitosan and 1 g H_2SO_4-activated clay were dispersed into acetic acid (1 mol/L) and then dried for 3 h to remove air bubbles [70]. The resulting solution was syringed dropwise into a neutral solution (15% NaOH and 95% ethanol) for 24 h to form composite beads (Fig. 3C). The beads facilitated separation and regeneration in wastewater treatment. More importantly, this modification integrated additional functional groups (-NH_2 and -OH) into the raw clay: the FTIR spectrum provided evidence of -OH stretching, COO^- stretching, CH_2 bending, and R-O-R stretching vibrations. While the acid-activated clay was smooth and rigid, the surface morphology of the composites showed some porosity. Therefore, we believe that acid/polymer-modified clay composites are widely applicable to various substrates.

2.2.4 Surfactant/polymer-clay composites

Surfactant-modified clays have been previously shown to possess a much higher affinity for humic acid than raw clays. Few studies attempted to utilize a surfactant and a polymer for the co-modification of clays [36, 71]. Previous studies investigated the use of cetylpyridinium bromide (CPB)/chitosan-based clay composites for humic acid remediation [72]. These composites were prepared by a two-step procedure involving chitosan-modified zeolite (CSZ) and surfactant-modified CSZ (SCMZ). Namely, a chitosan solution was dispersed in a zeolite suspension with stirring for 1.5 h, and a 2 mol/L NaOH solution was used to adjust the pH of the reaction system.

ACCEPTED MANUSCRIPT

The resulting CSZ was mixed with a CPB solution (25 mmol/L) in a shaker at 40 °C for 48 h. The supernatant mixture was then removed by centrifugation and the final SCMZ was washed with distilled water until no Br^- residue was detected by $AgNO_3$ solution (Fig. 3D). This composite exhibited two pronounced adsorption bands, corresponding to the asymmetric and symmetric $-CH_2$ stretching vibrations. SCMZ showed a lower surface area and pore volume than CSZ; the possible reason for this difference is that the surfactant molecules partially blocked the main pore channels of CSZ. It is worth noting that all clay minerals treated by surfactants require an additional $AgNO_3$ test for the real-time monitoring of the surfactant residue before their use. In addition, this surfactant/polymer-clay composite was used for the remediation of heavy metals and phenolic compounds [20].

2.2.5 Magnetic/polymer-clay composites

The separation of adsorbents from the aqueous solution is the main challenge that limits their broader industrial application. Aside from flotation as for fine particle separation technique [73, 74], magnetic treatment is also alternative solution to this issue. Magnetic composites have been widely synthesized by pretreating a clay using iron or chemical co-precipitation of iron oxides (Fe_3O_4 or γ-Fe_2O_3) [18]. In this section, we focus on the encapsulation of γ-Fe_2O_3-modified MMT in cross-linked chitosan beads [29]. Briefly, a certain amount of ferrofluid was mixed under stirring with an acetic acid solution containing chitosan, and the resulting mixture was dropped into an alkaline epichlorohydrin solution to form beads. The beads were then washed with ethanol to remove residual chloride ions (Fig. 3E). Through these procedures, magnetic adsorbents can provide active sites with good affinity for organic and/or inorganic compounds [75]. Considering the different charges of their components, including chitosan (bearing a positive charge in acid medium), clay (bearing a permanent negative charge), and magnetic nanoparticles (with a pH-dependent charge), the present composites maintained a high removal efficiency in a broad pH range (3–12). Once the pollutants were adsorbed on the surface of the magnetic clay materials, a magnetic field could easily separate the composite without affecting the turbidity of water. Owing to its high stability and reusability, the magnetic clay composites can be employed as multifunctional adsorbents for the removal of both cationic and anionic pollutants, either separately or together.

2.3 Clay composites modified with hybrid silicates

The preparation of inorganic-inorganic hybrids, especially hybrid silicate-clay composites [39],

ACCEPTED MANUSCRIPT

is considered a promising strategy to create new materials, owing to their excellent stability, non-toxicity, and compatibility. These composites were synthesized by a one-step hydrothermal route (Fig. 2D). Briefly, a homogeneous suspension containing Na_2SiO_3 and PAL was mixed with $MgSO_4$ or $ZnSO_4$ solution to form white solid and then reacted in Teflon Tank at 180 °C for 8 or 24 h [76, 77]. Furthermore, the presence of monochloroacetic acid [78] in hybrid silicate-clay composites contributed to the growth of PAL nanorods and formed -Si(M)O^- groups [76]. This process resulted in the appearance of some amorphous or plate-shaped particles due to the transformation from Si-O-Si bonds to -Si-O groups, which contributed to reduce the surface potential of PAL. Upon increasing the Si/Mg ratio, the total pore volume reached the maximum value at Si/Mg ration of 1:2. Furthermore, the presence of wide hysteresis loops revealed that multilayer adsorption occurred in the mesopores and macropores of the adsorbents. These non-toxic hybrid adsorbents composites, resulting from natural clay minerals and environment-compatible elements (e.g., Si, Mg, Na), could be considered perfect candidates for the removal of dyes and heavy metal ions.

3. Application of modified clay composites in aquatic environments

Water pollution is one of the most critical environmental issues causing serious problems to living organisms [79, 80]: approximately 2.3 billion people in the world suffer from diseases related to water pollution, over 95% lives in developing countries (e.g. India, Pakistan). In China, 70% of the population feels threatened by water pollution and over 60,000 people die from a range of other diseases and injuries associated with water pollution each year [81]. The ubiquity of various contaminants has accelerated the development of microorganism resistance, with increasing risks for the human health associated with opportunistic pathogens [78, 82]. Raw or modified clay materials have a promising potential for the removal or immobilization of inorganic (heavy metals, ammonia, phosphate) and organic (dyes, antibiotics, aromatic compounds) pollutants, as well as cytotoxins. However, the integration of an adsorbent with other materials via impregnation, chelation, and crosslinking leads to better adsorption properties compared with the individual components [10]. Thus, in the following we critically analyze the performance and adsorption mechanism of combined-modification clay composites, single-modified clays, and raw clays.

3.1 Removal of dyes from wastewater

Dye effluents are among of the most important water pollution sources associated with textile, paper, food processing, and dye manufacturing industries [83]. According to incomplete statistics,

ACCEPTED MANUSCRIPT

over 35,000 metric tons of dyes are released into the hydrosphere worldwide, with a total annual production of 10,000 different dyes [84]. Typical cationic and anionic dyes such as methylene blue (MB) and methylene orange (MO) are considered common pollutants due to their carcinogenic, mutagenic, and high coloring effects on the entire ecosystem [85]. Although commercial activated carbon (CAC) shows the highest MB removal of 980.3 mg/g [86], the price of available clays (e.g., vermiculite, with 0.04–0.12 USD/kg) is about 20-fold lower than that of activated carbon. Rafatullah et al. presented a detailed analysis of the MB adsorption capacities of different AC and raw clay minerals [87]; coal-derived AC (400–588 mg/g) showed a much higher MB adsorption capacity compared to raw clays (6.3–289.2 mg/g) [88, 89]. This large difference is related to the layered structure of the pristine clays, which results in different adsorption mechanisms. In fact, adsorption is a complicated process that depends on particle size and electrostatic or hydrophobic interactions [90].

Various studies have attempted to improve the MB removal capabilities of single-modified clays via acid [57], thermal [91], surfactant, and polymer activation [92]. For instance, low acid concentrations (≤ 1 M) caused an increase in the surface area and pore volume of attapulgite owing to decarbonation processes, while the crystal structure was preserved [56]. Natural Moroccan clay modified by thermal (300 °C for 2 h) and acid activation (0.5 mol/dm^3 HNO_3) showed adsorption capacities up to 500 mg/g [17], 1.43 times higher than that of the pristine clay. Dodecyl sulfobetaine-modified MMT (SB12-modified MMT) exhibited a clearly enhanced MB removal capacity (254.0 mg/g) [93]. The role of low-cost adsorbents in the removal of MB from a solution has been discussed in a recent review [87], which provided a comparative analysis of the costs and adsorption ability of AC and clays.

Recently, there has been increasing interest in the use of combined-modification clay composites for the simultaneous uptake of different dyes [70]. For example, the introduction of H_2SO_4/CTAB-activated bentonite (AOBent) [37] into SA had no impact on the basal spacing of clays [35], indicating that SA is only adsorbed on the positively charged side surfaces of bentonite. With increasing pH, the -OH and -COOH groups of the beads are gradually deprotonated, enhancing the electrostatic interaction between MB and AOBent/SA. The q_e of this novel AOBent/SA adsorbent for MB reached 769 mg/g within 200 min, which is four times higher than the corresponding value of AOBent. Conversely, the encapsulation of AOBent strongly inhibited the MO removal because

ACCEPTED MANUSCRIPT

of weak hydrophobic interactions. To improve the MO removal efficiency, anion-cationic composites by integrating the cationic surfactants cetyltrimethylammonium bromide (CTMAB) and anionic surfactants sodium stearate (SSTA) into MMT [34], which has a higher organic carbon content and is a highly effective partition medium. Intriguingly, the MO adsorption capacity of CTMAB/SSTA-MMT (CTMAB/SSTA ratio =1:10) was 149.25 mg/g after 40 min, and increased by 16.4% for CTMAB-MMT and 249% for SSTA-MMT. This stronger adsorption is closely related to the cation exchange capacity [94], and the d_{001} of this composites decreases with an increase in CEC [95]. Compared with acid/surfactant-clay composites such as AOBent/SA [35], anionic/cationic-clay composites exhibit improved MO adsorption.

Moreover, novel ABA beads showed the highest MB adsorption capacity, reaching 994.06 mg/g at 50 °C. These composites presented a higher number of bulges on their surface compared with bentonite/alginate (BA) and activated carbon/alginate (AA) beads [28]. Furthermore, this composite showed 75% MB removal efficiency after six regeneration cycles. In another study of acid/polymer composites (CTS-*g*-PAA/VMT), the introduction of 10 wt.% VMT into the chitosan-*g*-poly (acrylic acid) polymeric network resulted in the highest uptake ability (1,685.56 mg/g) for MB after 60 min (Table 1, Fig. 4A) [67]. Although high pH, contact times, and initial dye concentrations facilitated the MB adsorption, increasing ionic strength and sodium dodecyl sulfate (SDS) concentration reduced its performance. The adsorption equilibrium of MB onto these composites follows the Langmuir isotherm model; the electrostatic attraction between -COOH groups and MB represents the main adsorption process in these systems. However, clay-biochar composites showed exceptional performance for the adsorption of MB (Fig. 4A) [26]. For example, a bagasse derived clay-biochar composite (BG-MMT) did show a five-fold enhancement in MB adsorption compared to three pristine biochars (i.e., bamboo, bagasse, and hickory chips), but it could only remove approximately 11.94 mg/g MB. Similarly, γ-Fe_2O_3-modified MMT/chitosan beads exhibited favorable MB removal performance in the 3–12 pH range, with a maximum adsorption activity of 82 mg/g at R = 1.3 (where R is the clay/chitosan weight ratio) [29], as well as 90% MB removal after 1.7 h. The dye removal performances of clay composites are shown in Table 1.

The marked differences in the adsorption properties of clay composites can be attributed to the types of clay (Fig. 5A) and to the biochar/clay ratio [96]. The most critical aspect is that clay

ACCEPTED MANUSCRIPT

composites subjected to different modification processes exhibit different adsorption mechanisms (Fig. 6). Benhouria et al. showed that multiple adsorption mechanisms (electrostatic interactions, organic partitioning, and hydrogen bonding) controlled the ABA adsorption process, while film diffusion controlled the adsorption rate under the tested conditions [28]. Apparently, the presence of biochar in clay-biochar composites provides a porous texture and results in a high surface area. In fact, no direct correlation was found between adsorption ability and surface area. The clay modification with biochar can't alter its native ion-exchange ability, resulting in a relatively low MB adsorption capacity. Regardless of the q_e parameter, the regeneration of clay-biochar composites is similar to that observed in ABA; the composites still delivered 70% MB removal after six regeneration cycles (Fig. 5B), which denotes a higher removal rate compared with activated carbon (40%–60% after three cycles) [97]. The regeneration of the adsorbent is a crucial economic factor for industrial applications; clay-biochar composites have advantages such as simple manufacturing processes, low hydrolysis temperature, and reduced cost, along with the use of various recycled waste materials (Table 1, Fig. 2C). Following encapsulation of clay minerals by sodium or calcium alginate, the SA content in the composites makes a greater contribution to their performance [35] (Fig. 5C). This process can explain the high adsorption ability of ABA, which in turn illustrates how the coating process using SA may effectively improve the performance of clay-biochar composites. Clearly, other biochar modification methods can also be employed for the fabrication of clay-biochar composites [98, 99]. Although adsorbents such as CTS-*g*-PAA/VMT exhibit the highest MB adsorption ability, the carcinogenicity of PAA severely hinders their application.

3.2 Removal of aromatic compounds from wastewater

Aromatic pollutants contain one or more fused benzene rings of natural or anthropogenic origin [100]. Phenolic compounds, such as phenol, *p*-nitrophenol, and polychlorinated biphenyls (PCBs), are among the most prevalent aromatic pollutants, due to their low solubility and degradation resistance [101]. Alginate/MMT beads can remove 95% of tri-, tetra-, penta-, and hexachlorobiphenyls [43]**.** In a flow-through reactor system, the single modification of palygorskite with dioctadecyl dimethylammonium bromide (DODMA) produced a positive surface charge and enabled the modified composite to adsorb 42 mg/g of the anionic *p*-nitrophenol (PNP) contaminant via electrostatic attraction [102]. However, alginate-MMT beads exhibited a lower PNP adsorption

ACCEPTED MANUSCRIPT

ability than raw MMT [103], which is consistent with the results obtained by the Ely group [65]. The only difference is that the later study provided further insights into the Cu^{2+}/ PNP competition isotherms. The addition of PNP in solution had no influence on the Cu^{2+} removal ability of ZS26 Mauritanian clay/alginate and activated carbon/alginate beads. On the other hand, the removal of PNP from all types of clay beads was greatly affected by the presence of Cu^{2+}, presumably because Cu^{2+} alters the steric interactions of the clay or increases the phenol acidity to inhibit adsorption of PNP [65].

The PNP removal properties of anion-cation organo-bentonite were first reported by the Zhu group in 2000 [58]. In a series of anion-cation modified palygorskites [61], the hexadecyltrimethylammonium bromide (HDTMAB)/SDS-PAL (in 1:4 or 3:10 mass ratio) composite achieved the best PNP removal performance (137.74 mg/g) at 313 K within 60 min (Table 2), which is superior to that of DODMA-modified PAL [102]. This spontaneous adsorption of HDTMAB/SDS-PAL followed a pseudo second-order kinetic model with a rate constant of 0.0045 mg/min. Recent research focused on understanding how the anionic and cationic surfactants intercalate into the interlayer space of MMT [59], revealed that the sequential addition of cetyltrimethylammonium chloride (CTAC) and SDS influences the d_{001}-value and thermal stability of CTAC/SDS-MMT. By taking advantage of combined H_2SO_4/surfactant treatments, organo-bentonite treated with octadecyl trimethylammonium bromide (ABC18) adsorbed 200.6 mg/g of 2,4,5-trichlorophenol (TCP) after 10 min via the Langmuir model [37]; this adsorption capacity is almost an order of magnitude higher than that of poly-4-vinylpyridine-co-styrene (PVPcoS)-modified MMT [104]. This can be explained by the fact that the adsorption mechanism of ABC18 is dominated by surface adsorption and intra-particle diffusion, whereas electrostatic attraction controls the adsorption on PVPcoS-modified MMT. In addition, acid-activated bentonites (AB) with higher porosity still show an inferior TCP adsorption performance in comparison to ABC18.

There are no available studies on the application of clay-biochar composites in the removal of phenol compounds. However, zeolite X/activated carbon (X/AC) composites effectively removed 40.31 mg/g of phenol [105]; this capacity is orders of magnitude higher than that of HDTMA/SA-modified MMT composites (Table 2, Fig. 4B) [71]. The Redlich-Peterson and Freundlich equations provided the best fitting to the phenol removal process of the X/AC composite, indicating the presence of various functional groups on its surface. On the other hand, electron donor-acceptor

ACCEPTED MANUSCRIPT

complexes, π- π dispersion interactions, and solvent effects dominate the process of phenol adsorption on activated carbon (Fig. 6). Overall, acid/surfactant- and anionic/cationic surfactant-clay composites exhibit better properties for the removal of aromatic pollutants [37]. On the other hand, many surfactants used in clay composites, such as dodecyl-, tetradecyl-, hexadecyl-, and octadecyl- trimethyl ammonium bromides (DTAB, TTAB, HTAB, OTAB), pose possible risks to human health; therefore, an additional $AgNO_3$ test to detect the residual surfactants is required before using these composites.

3.3 Removal of antibiotics from wastewater

The overuse of antibiotics in stockbreeding and aquaculture is a cause of public concern because these synthetic chemicals (e.g., fluoroquinolone antibiotics) are not easily biodegradable. Their ubiquity in aquatic environments leads to toxic effects on biota and changes in the antibiotic-resistant microorganism populations [106]. Biomass-based activated carbon is the preferred adsorbent for the removal of norfloxacin [107, 108]. In order to reduce the cost of activated carbon or biochar, Li et al. evaluated the possible use of a clay-biochar composite (APB) derived from the pyrolysis of potato stem and natural attapulgite, which greatly improved the NOR removal from aqueous solutions [8]. The q_e values for NOR adsorption of APB composites and pristine biochar [109] are 5.24 and 3.12 mg/g, respectively. APB composites may be more effective than PB for NOR removal from three different types of water (distilled, tap, and river water). The functional groups and SiO_2 particles of this composite control its NOR adsorption process, which further explains the enhanced NOR adsorption ability of biochar. However, a wheat straw-derived MMT-biochar composite (MT-BC) presented a higher q_e value (25.53 mg/g) than APB, because of its higher surface area (112.6 m^2/g) and total pore volume (0.604 cm^3/g) [41]. Upon addition of Cu^{2+} and dissolved humic acid (DHA), the NOR adsorption capacity of the MT-BC composite was significantly reduced due to the competitive adsorption processes. Intriguingly, Cu^{2+} led to a smaller decrease in NOR adsorption compared with DHA; it has been speculated that NOR-Cu^{2+} complexes slightly offset this inhibitory action. Overall, these two types of clay-biochar composites maintained 85% of the NOR removal efficiency after five regeneration cycles. The main interactions involved in the NOR adsorption mechanisms of biochar-clay composites are electrostatic attraction, hydrogen bonding, pore-filling, π-π electron donor-acceptor (EDA), hydrophobic interactions, and others (Fig. 6).

ACCEPTED MANUSCRIPT

Antibiotics such as chlortetracycline (CTC), oxytetracycline (OTC), aureomycin (AMC), and tetracycline (TC) are commonly used for human therapy and farming [110, 111]. $NaSiO_3/ZnSO_4$ hybrid palygorskite exhibited increased average pore volumes (10.62–11.50 nm) and a negative surface charge (-42.54 mV) due to the formation of -Si(M)O^- groups [77]. This simple hydrothermal-activated silicate (Si/Zn ratio = 3:1) removed 384 mg/g AMC and 337 mg/g TC after 6 h (Table 2), which far exceeded the performance of raw KAL and PAL [112]. The introduction of MCA resulted in the dispersion of large amounts of -COOH groups in hybrid silicate clay adsorbents [76]. Thus, relatively high removal efficiencies of CTC (329.84 mg/g) and OTC (207.47 mg/g) were obtained for Si/Zn/MCA hybrid PAL. The adsorption kinetics was fitted well by a pseudo second-order model, revealing that electrostatic, hydrogen bonding, and pore adsorption are the main driving forces for the adsorption process [76]. Although the evaluation of the clay performance cannot exclude the influence of the composite type or adsorbates, hybrid silicate clays could represent the best adsorbents to remove antibiotics (Fig. 4B), due to their high adsorption ability and non-toxicity [77]. In addition, the colloidal properties of hybrid silicate-clay need to be improved via natural polymer (e.g. chitosan and SA) modification in order to further facilitate their regeneration and reuse.

3.4 Removal of heavy metals from wastewater

Non-biodegradable and soluble heavy metals or metalloid ions have attracted considerable interest due to the associated risks to ecosystems and human health [113], which create a high demand for effective removal treatments of heavy metals. Batch adsorption experiments provided some insight into the removal of Pb^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+} species by Na-MMT and Ca-MMT via ion exchange [114]. Addy et al. showed that a single-modified clay, obtained by treatment with SiO_2 or Fe_2O_3 and grafting with a chelating ligand (*N*-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid, TMS-EDTA), exhibited excellent performance in model wastewater containing either individual or mixed heavy metal ions [115]. Activated carbon-clay composites such as AC/zeolite have been used for Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and $Cr_2O_7^{2-}$ removal since 2006 [116]. Nevertheless, a novel chitosan/clay/biochar (MTCB) nanobiocomposite showed similar performances in the simultaneous immobilization of Cu, Pb, and Zn metal ions [54]. Among these ions, MTCB has highest affinity towards Pb^{2+} (336 mg/g). The adsorption isotherm of Pb^{2+} fitted Temkin model, while the isotherms of Cu^{2+} and Zn^{2+} were best represented by a Freundlich model. Although certain

ACCEPTED MANUSCRIPT

functional group (e.g., $-NH_2$) in this composite are mainly involved in the immobilization of metals, its performance dramatically exceeded that of epichlorohydrin/chitosan-modified Bent [117]. Si/Mg-modified PAL is another low-cost and efficient adsorbent, with a Cu^{2+} adsorption capacity of 210.64 mg/g [39]. A Si/Mg dosage ratio of 2:1 and alkaline conditions contribute to the whole adsorption process. These silicate materials exhibit an ideal surface charge distribution and higher BET surface areas (407.3 m^2/g), which enable them to separate various heavy metals or dyes from contaminated water [118]. As a result, these hybrid silicate-clay composites exhibited a better capacity in the adsorption of Cu^{2+} than biochar-clay [54] and organo-clay [119] composites (Table 2, Fig. 4A). The possible reason is that the -Si(M)O- groups of hybrid silicate-clay composites play a key role in pollutant adsorption via electrostatic attraction, ion exchange, and chemical adsorption.

Hexavalent chromium (CrO_4^{2-}, $Cr_2O_7^{2-}$) is considered as one of the most harmful metallic species because of its carcinogenicity. The hydroxyl groups of the cellulose macromolecule play a vital role in the adsorption of metal ions, thus enabling the use of cellulose/CTAB-activated MMT composites as adsorbents of $Cr_2O_7^{2-}$ ions [36]. This material presented a maximum adsorption capacity of 22.2 mg/g and a 99% recovery within 10 cycles. Another quaternary ammonium-activated MMT/chitosan composite (CNC) exhibited a $Cr_2O_7^{2-}$ uptake of 128.43 mg/g over 50 min, which is six times higher than that of chitosan [20]. This material also retained about 70% of its removal efficiency after five regeneration cycles. As a whole, the performance of CNC is superior to that of single-modified bentonite with alkyl ammonium surfactants (8.51–14.64 mg/g) [120] and of zeolite X/activated carbon composites [121], indicating that CNC provides a larger number of cationic adsorption sites for chromate via ion-exchange forces, electrostatic attraction, and chelation. The organo-clays discussed in this section may also be used for the removal of other contaminants such as arsenate, selenate, antimonate, molybdate, nitrate, phosphate, and anionic dyes.

The removal of radioactive elements such as Cs^+ and Sr^{2+} has caused great attention since a total of approximately 3.3×10^{16} Bq Cs was released into environment after Fukushima Daiichi Nuclear Power Plant Disaster [122, 123]. Various efforts have been made to desorb Cs from contaminated clays via polymeric cation-exchange agent [124] or flotation [125]. In aqueous condition, novel organo-MMT composites containing potassium copper hexacyanoferrate (KCuHCF) showed a superior Cs^+ adsorption capacity (206 mg/g), twice that of the pristine clay. Such enhanced performance led to two orders of magnitude greater Cs^+ selectivity than the pristine

ACCEPTED MANUSCRIPT

MMT. More importantly, recovery efficiencies of the Cs-loaded composite particles of up to 90% via flotation [74]. Poly (acrylamide-acrylic acid)/kaolin composite (P(AM-AA)/K) showed high adsorption capacity for Co^{2+} and Cs^{+} [126]. A simple synthesis of montmorillonite-prussian blue (MMT-PB) hybrid adsorbents showed the maximum adsorption capacity of 57.47 mg/g [127], and it still sustained high selectivity toward Cs^{+} adsorption in the presence of competing cations such as Na^{+}, K^{+}, Mg^{2+}.

3.5 Removal of other pollutants from wastewater

Humic acid (HA) dissolved in drinking water can cause color, taste, and odor problems. As early as 2004, H_2SO_4-activated natural clay/chitosan composites were found to exhibit maximum adsorption capacities of HA (232 mg/g) and tannic acid (1,395 mg/g), respectively [70]; these values are much higher than those obtained for the raw clay (138 and 26.4 mg/g, respectively). It was initially reported that the adsorption capacities of clay composites for TA, HA, and the RR222 dye are comparable to those of chitosan beads. A surfactant/chitosan-modified zeolite (SMCSZ) showed a maximum monolayer HA adsorption of 164 mg/g [72], but its performance was poorer than that of acid/polymer-clay composites and single-modified clays (CSZ). Three coupling mechanisms (electrostatic interaction, organic partitioning, and hydrogen bonding) control the HA adsorption process of SMCSZ, while only electrostatic and hydrophobic interactions are involved in the adsorption of CSZ on HA. The different adsorption mechanisms further illustrate the advantages of these surfactant/polymer-clay composites.

While current studies focus on the benefits associated with available chitosan/alginate-clay composites for pollutant removal [62, 128], there is increasing interest in the use of natural agricultural byproducts (e.g., WB) to prepare eco-friendly WB-*g*-PAA/clay superabsorbent composites [68]. Among these materials, WB-*g*-PAA/laterite exhibited the maximum urea loading capacity (694 g/g), which fitted Schott's second-order kinetic model. After six cycles, all clay composites only retained about 50% of their initial water absorbency. This study thus suggests a new strategy for utilizing WB and laterite, especially in agricultural and horticultural applications.

Additionally, AC/zeolite composites have been used for the adsorption of ammonia [47], COD, and *N*-nitrosamines [129]. Ammonia was preferentially adsorbed on AC/zeolite composites rather than on zeolite and activated carbon [47], which is consistent with the results obtained for cassava peel derived bentonite-hydrochar composites [40]. The ammonia adsorption capacity measured in

ACCEPTED MANUSCRIPT

the latter study decreased in the order bentonite-hydrochar (23.67 mg/g) > bentonite (12.37 mg/g) > biochar (9.49 mg/g) [40]. Despites the small increase observed in AC-clay composites, all composites showed a synergistic enhancement of the ammonium removal capacity, whereas antagonistic effects of AC/zeolite composites hindered COD removal [130]. A possible explanation for this finding is that the high proportion of activated carbon and biochar in the composites contributes to COD removal [38, 129]. Chen et al. investigated the resultant NH_4^+- and PO_4^{3-}-laden MBC (bamboo-derived MMT-biochar) samples can be used as an effective slow-release fertilizer of nitrogen and phosphorus[51]. According to the Langmuir model, the q_e of MBC samples for NH_4^+ and PO_4^{3-} were 12.52 and 105.28 mg/g, respectively. While electrostatic attraction or ionic bonding controlled the adsorption of PO_4^{3-} onto the MBC sample, the adsorption capacity of NH_4^+ was determined by surface adsorption.

3.6 Comparative analysis of activated carbon, raw clays, and clay composites

In addition to natural biomass, coal is the most commonly used precursor for CAC production. This carbonaceous material has high porosity, physicochemical stability, adsorption capacity, and mechanical strength, as well as a huge surface area (124.3–1390 m^2/g) [131]. The surface of activated carbon exposes protonated (C-OH^{2+}), neutral (COH), and ionized (CO^-) groups, resulting in high affinity for organic pollutants. For example, the MB removal capacity of coal-derived AC ranges from 230 to 588 mg/g, depending on the precursor types and the activation treatment [87]. Similarly, PNP is preferentially adsorbed onto activated carbon; the adsorption capacity decreases in the order AC > AC/SA > Na-MMT > Na-MMT/SA. By contrast, clays are hydrous aluminosilicates and their surface contain many exchangeable ions suitable for pollutant removal, such as Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-, and others [87]. Among all raw clays, the MB adsorption capacity on kaolin, palygorskite, and pyrophyllite is less than 70 mg/g; this low adsorption efficiency accelerates the development of modified clays. When heavy metals such as Cu^{2+} were employed as model pollutants, the Cu^{2+} adsorption efficiency varied in the following order: SA > composite microbeads > clays and activated carbon [103]. The different adsorption efficiency of AC and clays can be attributed to their different adsorption mechanisms. Surface complexation, hydrophobic, and π-electron donor-acceptor interactions participate in the adsorption on AC, whereas the adsorption mechanism of the clay involves ion exchange, hydrogen bonding, partition adsorption, and electrostatic attraction.

ACCEPTED MANUSCRIPT

In addition, many factors control the cost of the different adsorbents, such as availability, source, synthesis method, recycle, and stability. Generally, the price of biochar (0.35–1.2 USD/kg) is lower than activated carbon (PAC, 1.8–2.1 USD/kg) [132]. However, natural clays (montmorillonite, bentonite, etc.) have a low average price of 0.04 USD/kg, which represents an obvious advantage compared to AC. Other adsorbents (e.g., chitin and chitosan) are approximately 12 times more expensive than natural adsorbents such as clay, ash, and peat [131, 133]. Therefore, clay composites modified using biochar or natural polymers can be considered low-cost adsorbents. Regeneration is another crucial parameter to enable the rapid recycling or recovery of adsorbents using inexpensive methods. Momina et al. described a series of regeneration methods, including thermal, steam, pressure, vacuum, and chemical regeneration [133], which depend on the nature and type of adsorbates/adsorbents. The most common method used for clay composites is chemical regeneration using methanol, H_2O, H_2SO_4, or NaOH solutions, which maintains a 23%–85% removal rate after five cycles (Tables 1–3). On the other hand, the performance of AC obtained by thermal or electrochemical regeneration depends on the temperature and current, respectively, with 80%–90% regeneration rates [134-136]. In most cases, combined regeneration methods may also represent an effective alternative for the recovery of tested adsorbents.

4. Future directions in the development of multi-modified clay composites

There has been a huge increase in the demand of modified clay composites for the removal of various organic or inorganic pollutants [68, 85]. We provide a comprehensive understanding of organo-clay composites, clay-biochar composites, activated carbon-clay composites and silicate modified clay (Fig. 7). Inexpensive and eco-friendly clay composites modified using biochar or silicate can't alter the colloidal nature of raw clay, thus using flotation or encapsulation of these composites in micro-gels facilitates the regeneration and reuse. Among organo-clay composites, polymer-modified clay composites are more eco-friendly and less expensive for the removal of various pollutants, due to the use of natural polymers such as alginate, cellulose, and chitosan. In contrast, surfactant-modified clay composites should further evaluate potential toxicity of surfactant to environment, resulting in more comprehensive fabrication and detection procedures. Magnetic clay composites and crosslinked polymer-clay beads facilitate their separation from the medium with 42%–99% regeneration ability. Unlike the excellent adsorption ability of organo-clay

ACCEPTED MANUSCRIPT

composites and hybrid silicate-clay composites, the only drawback of clay-biochar composites is their poor adsorption ability. Therefore, clay-biochar composites derived from hybrid silicate clays and biomass-based biochar may be promising candidates to enable the application of these materials. The study of an enhanced biochar, composed by 30% kaolinite, 30% Jarrah-based biochar, and 30% chicken litter, supplemented with rock phosphate, basalt dust, calcium carbonate, and ilmenite, has highlighted the promising potential of clay composites based on multiple materials [55]. Furthermore, the unique structural properties of composites combining two clay minerals, such as bentonite/zeolite and struvite/attapulgite (MAP/APT), may also open up new interesting possibilities [31, 32].

The MB removal ability of combined-modification clay composites varies in a wide range (Table 1 and Table 2), partial composites show lower adsorption capacities than raw clays or single-modified clay composites [36, 37, 68], which indicates that the source and type of raw clays play a crucial role in the composite performance. Hence, standardized manufacturing processes are a prerequisite for industrial development. Many parameters (e.g., pH, temperature, contact time, initial concentration of contaminants, adsorbent dose) and inorganic salts (e.g., sodium salts) influence the adsorption behavior of clay composites [137]. In particular, the presence of one type of pollutant suppresses the adsorption of another pollutant. For example, the maximum adsorption abilities of SB12-modified MMT in pure Cu^{2+} or MB solutions were 10.2 and 254.2 mg/g, respectively [93]; in binary systems, a high concentration (>150 mg/L) of MB dramatically inhibited the Cu^{2+} removal (Fig. 8A-8B). However, MB adsorption slightly decreased (by 20%) with increasing Cu^{2+} concentration. This indicates that SB12-modified MMT provides similar active sites for Cu^{2+} and MB adsorption, but with a higher affinity for MB. A similar competitive adsorption [41] was observed for the removal of NOR in the presence of DHA and Cu^{2+} (Fig. 8C–8D). Thus, further research is needed on competitive adsorption effects in combined-modification clay composites used in real wastewater systems [93, 138], as well as on improving the selectivity of clay composites in the adsorption of targeted pollutants. Moreover, the fabrication of a novel poly(methyl methacrylate) plastic-based fluidized bed reactor (FBR) system facilitated the removal of nitrate (10–15%), COD (20–40%) and phosphate (100%) from municipal primary effluent samples [139]. Another future research direction may involve the exploration of new approaches for the synthesis of the composites. For example, rapid microwave heating has been used fabricating

ACCEPTED MANUSCRIPT

an HCl-activated bentonite-alginate composite [30]. This irradiation method contributed to the formation of adsorbent pores, thus favoring the permeation of the dye solution.

Besides various types of industrial wastewater, eutrophic lakes or rivers severely disrupt the microbial community structure of aquatic ecosystems and the potential water use because of the release of toxic metabolites (cytotoxins) from cyanobacteria [140]. Several studies found that chitosan-modified local soil and octadecyltrimethyl ammonium (ODTMA)-bentonite complex can simultaneously eliminated cyanobacteria and cyanotoxins from an aquatic environment [24, 141]. However, it is crucial to obtain dynamic information on the release of ODTMA from the granulated micelle-clay complex owing to the biocidal effect of ODTMA on cyanobacteria and on other bacteria [142], thus it is essential to examine the impact of clay composites on the indigenous microbial community structure. On the other hand, more researches focus on the removal of Cs^{+} and Sr^{2+} via raw clay or single-modified clay composites such as (P(AM-AA)/K and MMT-PB [126, 127, 143], multi-modified clay composites may have promising application in the remediation of radionuclide contaminated soils.

5. Conclusions

Vast amounts of industrial, agricultural, and domestic wastewater need to be treated before being discharged into the hydrosphere. Combined-modification clay composites exhibited significant advantages over single-modified clays, due to their high adsorption ability and low cost. Among organo-clay composites, anionic-cationic modified clay composites are more suitable for removing anionic dyes and phenolic compounds, whereas polymer-modified clay composites remain the adsorbents of choice for heavy metal and cationic dye removal. Furthermore, non-toxic and environmentally compatible hybrid silicate-clay and clay-biochar composites represent a superior alternative for Cu^{2+} and antibiotics remediation. The specificity and selectivity of clay composites for tested pollutants mainly depends on the corresponding adsorption mechanism, which in turn is determined by the modification method employed. Ion exchange, electrostatic attraction, hydrogen bonding, and pore-filling are the predominant mechanisms controlling the adsorption of targeted pollutants. Overall, combined-modification clay composites represent promising candidates for the removal of heavy metals, antibiotics, phenolic compounds, and dyes from various types of industrial wastewater.

Conflict of Interest

ACCEPTED MANUSCRIPT

The authors declare no conflict of interest.

Acknowledgements

The work was supported by National Natural Science Foundation grant (31470224); Gansu province major science and technology projects (No: 17ZD2WA017); Central Universities grant [grant number lzujbky-2018-103].

References

[1] X. Mao, R. Jiang, W. Xiao, J. Yu, Use of surfactants for the remediation of contaminated soils: a review, Journal of hazardous materials, 285 (2015) 419-435.

[2] Y. Zhu, H. Zhang, W. Wang, X. Ye, Z. Wu, A. Wang, Fabrication of a magnetic porous hydrogel sphere for efficient enrichment of Rb + and Cs + from aqueous solution, Chemical Engineering Research and Design, 125 (2017) 214-225.

[3] T. Ngulube, J.R. Gumbo, V. Masindi, A. Maity, An update on synthetic dyes adsorption onto clay based minerals: A state-of-art review, Journal of environmental management, 191 (2017) 35-57.

[4] B. Van Aken, Transgenic plants for phytoremediation: helping nature to clean up environmental pollution, Trends in biotechnology, 26 (2008) 225-227.

[5] K.S. Abou-El-Sherbini, M.M. Hassanien, Study of organically-modified montmorillonite clay for the removal of copper(II), Journal of hazardous materials, 184 (2010) 654-661.

[6] S. Jia, Z. Yang, K. Ren, Z. Tian, C. Dong, R. Ma, G. Yu, W. Yang, Removal of antibiotics from water in the coexistence of suspended particles and natural organic matters using amino-acid-modified-chitosan flocculants: A combined experimental and theoretical study, Journal of hazardous materials, 317 (2016) 593-601.

[7] R.B. Akshay Jain, M.P. Srinivasan, Hydrothermal Conversion of Biomass Waste to Activated Carbon with High Porosity: A Review, Chemical Engineering Journal, 283 (2016) 789–805.

[8] Y. Li, Z. Wang, X. Xie, J. Zhu, R. Li, T. Qin, Removal of Norfloxacin from aqueous solution by clay-biochar composite prepared from potato stem and natural attapulgite, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 514 (2017) 126-136.

[9] M. Auta, B.H. Hameed, Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue, Chemical Engineering Journal, 198-199 (2012) 219-227.

[10] B. Li, L. Yang, C.Q. Wang, Q.P. Zhang, Q.C. Liu, Y.D. Li, R. Xiao, Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes, Chemosphere, 175 (2017) 332-340.

[11] E.I. Unuabonah, B.I. Olu-Owolabi, E.I. Fasuyi, K.O. Adebowale, Modeling of fixed-bed column studies for the adsorption of cadmium onto novel polymer-clay composite adsorbent, Journal of hazardous materials, 179 (2010) 415-423.

[12] M. Overesch, J. Rinklebe, G. Broll, H.U. Neue, Metals and arsenic in soils and corresponding vegetation at Central Elbe river floodplains (Germany), Environmental pollution, 145 (2007) 800-812.

[13] Y. Zhang, W. Wang, J. Zhang, P. Liu, A. Wang, A comparative study about adsorption of natural palygorskite for methylene blue, Chemical Engineering Journal, 262 (2015) 390-398.

[14] M.K. Uddin, A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, Chemical Engineering Journal, 308 (2017) 438-462.

[15] M. Kotal, A.K. Bhowmick, Polymer nanocomposites from modified clays: Recent advances and

ACCEPTED MANUSCRIPT

challenges, Progress in Polymer Science, 51 (2015) 127-187.
[16] M. Pentrák, A. Czímerová, J. Madejová, P. Komadel, Changes in layer charge of clay minerals upon acid treatment as obtained from their interactions with methylene blue, Applied Clay Science, 55 (2012) 100-107.
[17] Y. El Mouzdahir, A. Elmchaouri, R. Mahboub, A. Gil, S.A. Korili, Equilibrium modeling for the adsorption of methylene blue from aqueous solutions on activated clay minerals, Desalination, 250 (2010) 335-338.
[18] L. Cottet, C.A.P. Almeida, N. Naidek, M.F. Viante, M.C. Lopes, N.A. Debacher, Adsorption characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media, Applied Clay Science, 95 (2014) 25-31.
[19] J.L. Alves, P.d.T.V.e. Rosa, A.R. Morales, Evaluation of organic modification of montmorillonite with ionic and nonionic surfactants, Applied Clay Science, 150 (2017) 23-33.
[20] H.T. Kahraman, Development of an adsorbent via chitosan nano-organoclay assembly to remove hexavalent chromium from wastewater, International journal of biological macromolecules, 94 (2017) 202-209.
[21] N.T. Stephen Baker, François-Xavier Weill, Kathryn E. Holt, Genomic insights into the emergence and spread of antimicrobial-resistant bacterial pathogens, Science, 360 (2017) 733–738
[22] I.S.-A. Siavash Atashgahi, Hermann J. Heipieper, Jan R. van der Meer, Alfons J. M. Stams, Hauke Smidt, Prospects for harnessing biocide resistance for bioremediation and detoxification, Science, 360 (2018) 743–746
[23] N.J.H. Matthew C. Fisher, Dominique Sanglard, Sarah J. Gurr, Worldwide emergence of resistance to antifungal drugs challenges human health and food security, Science, 360 (2018) 739–742
[24] A. Sukenik, Y. Viner-Mozzini, M. Tavassi, S. Nir, Removal of cyanobacteria and cyanotoxins from lake water by composites of bentonite with micelles of the cation octadecyltrimethyl ammonium (ODTMA), Water research, 120 (2017) 165-173.
[25] S.I. Rathnayake, W.N. Martens, Y. Xi, R.L. Frost, G.A. Ayoko, Remediation of Cr (VI) by inorganic-organic clay, Journal of colloid and interface science, 490 (2017) 163-173.
[26] Y. Yao, B. Gao, J. Fang, M. Zhang, H. Chen, Y. Zhou, A.E. Creamer, Y. Sun, L. Yang, Characterization and environmental applications of clay–biochar composites, Chemical Engineering Journal, 242 (2014) 136-143.
[27] Z. Li, X. Cui, J. Ma, W. Chen, W. Gao, R. Li, Preparation of granular X-type zeolite/activated carbon composite from elutrilithe by adding pitch and solid SiO2, Materials Chemistry and Physics, 147 (2014) 1003-1008.
[28] A. Benhouria, M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala, B.H. Hameed, Calcium alginate–bentonite–activated carbon composite beads as highly effective adsorbent for methylene blue, Chemical Engineering Journal, 270 (2015) 621-630.
[29] A. Bée, L. Obeid, R. Mbolantenaina, M. Welschbillig, D. Talbot, Magnetic chitosan/clay beads: A magsorbent for the removal of cationic dye from water, Journal of Magnetism and Magnetic Materials, 421 (2017) 59-64.
[30] R. Fabryanty, C. Valencia, F.E. Soetaredjo, J.N. Putro, S.P. Santoso, A. Kurniawan, Y.-H. Ju, S. Ismadji, Removal of crystal violet dye by adsorption using bentonite – alginate composite, Journal of Environmental Chemical Engineering, 5 (2017) 5677-5687.
[31] H. Wang, X. Wang, J. Ma, P. Xia, J. Zhao, Removal of cadmium (II) from aqueous solution: A comparative study of raw attapulgite clay and a reusable waste-struvite/attapulgite obtained from

ACCEPTED MANUSCRIPT

nutrient-rich wastewater, Journal of hazardous materials, 329 (2017) 66-76.
[32] M. Shaban, M.R. Abukhadra, M.G. Shahien, S.S. Ibrahim, Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes, Environmental Chemistry Letters, 16 (2017) 275-280.
[33] M. Toor, B. Jin, Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye, Chemical Engineering Journal, 187 (2012) 79-88.
[34] D. Chen, J. Chen, X. Luan, H. Ji, Z. Xia, Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange, Chemical Engineering Journal, 171 (2011) 1150-1158.
[35] N. Belhouchat, H. Zaghouane-Boudiaf, C. Viseras, Removal of anionic and cationic dyes from aqueous solution with activated organo-bentonite/sodium alginate encapsulated beads, Applied Clay Science, 135 (2017) 9-15.
[36] A.S.K. Kumar, S. Kalidhasan, V. Rajesh, N. Rajesh, Application of Cellulose-Clay Composite Biosorbent toward the Effective Adsorption and Removal of Chromium from Industrial Wastewater, Industrial & Engineering Chemistry Research, 51 (2011) 58-69.
[37] H. Zaghouane-Boudiaf, M. Boutahala, S. Sahnoun, C. Tiar, F. Gomri, Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing the 2,4,5-trichlorophenol, Applied Clay Science, 90 (2014) 81-87.
[38] Z.L. Liao, H. Chen, B.R. Zhu, H.Z. Li, Combination of powdered activated carbon and powdered zeolite for enhancing ammonium removal in micro-polluted raw water, Chemosphere, 134 (2015) 127-132.
[39] W. Wang, G. Tian, Z. Zhang, A. Wang, A simple hydrothermal approach to modify palygorskite for high-efficient adsorption of Methylene blue and Cu(II) ions, Chemical Engineering Journal, 265 (2015) 228-238.
[40] S. Ismadji, D.S. Tong, F.E. Soetaredjo, A. Ayucitra, W.H. Yu, C.H. Zhou, Bentonite hydrochar composite for removal of ammonium from Koi fish tank, Applied Clay Science, 119 (2016) 146-154.
[41] J. Zhang, M. Lu, J. Wan, Y. Sun, H. Lan, X. Deng, Effects of pH, dissolved humic acid and Cu^{2+} on the adsorption of norfloxacin on montmorillonite-biochar composite derived from wheat straw, Biochemical Engineering Journal, 130 (2018) 104-112.
[42] E.I. Unuabonah, A. Taubert, Clay–polymer nanocomposites (CPNs): Adsorbents of the future for water treatment, Applied Clay Science, 99 (2014) 83-92.
[43] S. Barreca, S. Orecchio, A. Pace, The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies, Applied Clay Science, 99 (2014) 220-228.
[44] Y.L.a.A.C. Balazs, Modeling the Phase Behavior of Polymer-Clay Composites, Macromolecules, 31 (1998) 6676-6680.
[45] J. Ma, J. Tan, X. Du, R. Li, Effects of preparation parameters on the textural features of a granular zeolite/activated carbon composite material synthesized from elutrilithe and pitch, Microporous and Mesoporous Materials, 132 (2010) 458-463.
[46] W.A. Khanday, F. Marrakchi, M. Asif, B.H. Hameed, Mesoporous zeolite–activated carbon composite from oil palm ash as an effective adsorbent for methylene blue, Journal of the Taiwan Institute of Chemical Engineers, 70 (2017) 32-41.
[47] A.A. Halim, H.A. Aziz, M.A.M. Johari, K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination, 262

ACCEPTED MANUSCRIPT

(2010) 31-35.
[48] X.F. Tan, Y.G. Liu, Y.L. Gu, Y. Xu, G.M. Zeng, X.J. Hu, S.B. Liu, X. Wang, S.M. Liu, J. Li, Biochar-based nano-composites for the decontamination of wastewater: A review, Bioresource technology, 212 (2016) 318-333.
[49] R. Chintala, T.E. Schumacher, L.M. McDonald, D.E. Clay, D.D. Malo, S.K. Papiernik, S.A. Clay, J.L. Julson, Phosphorus Sorption and Availability from Biochars and Soil/Biochar Mixtures, CLEAN - Soil, Air, Water, 42 (2014) 626-634.
[50] M.T. Moreira, I. Noya, G. Feijoo, The prospective use of biochar as adsorption matrix - A review from a lifecycle perspective, Bioresource technology, 246 (2017) 135-141.
[51] L. Chen, X.L. Chen, C.H. Zhou, H.M. Yang, S.F. Ji, D.S. Tong, Z.K. Zhong, W.H. Yu, M.Q. Chu, Environmental-friendly montmorillonite-biochar composites: Facile production and tunable adsorption-release of ammonium and phosphate, Journal of Cleaner Production, 156 (2017) 648-659.
[52] G. Pillot, E. Frouin, E. Pasero, A. Godfroy, Y. Combet-Blanc, S. Davidson, P.P. Liebgott, Specific enrichment of hyperthermophilic electroactive *Archaea* from deep-sea hydrothermal vent on electrically conductive support, Bioresour Technol, 259 (2018) 304-311.
[53] R. Karimi Aghcheh, Z. Németh, L. Atanasova, E. Fekete, M. Paholcsek, E. Sándor, B. Aquino, I.S. Druzhinina, L. Karaffa, C.P. Kubicek, The VELVET A orthologue VEL1 of *Trichoderma reese*i regulates fungal development and is essential for cellulase gene expression, PloS one, 9 (2014) e112799.
[54] H. Arabyarmohammadi, A.K. Darban, M. Abdollahy, R. Yong, B. Ayati, A. Zirakjou, S.E.A.T.M. van der Zee, Utilization of a Novel Chitosan/Clay/Biochar Nanobiocomposite for Immobilization of Heavy Metals in Acid Soil Environment, Journal of Polymers and the Environment, 26 (2017) 2107-2119.
[55] Y. Lin, P. Munroe, S. Joseph, A. Ziolkowski, L. van Zwieten, S. Kimber, J. Rust, Chemical and structural analysis of enhanced biochars: thermally treated mixtures of biochar, chicken litter, clay and minerals, Chemosphere, 91 (2013) 35-40.
[56] L. Boudriche, R. Calvet, B. Hamdi, H. Balard, Effect of acid treatment on surface properties evolution of attapulgite clay: An application of inverse gas chromatography, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 392 (2011) 45-54.
[57] G.K. Sarma, S. Sen Gupta, K.G. Bhattacharyya, Adsorption of Crystal violet on raw and acid-treated montmorillonite, K10, in aqueous suspension, Journal of environmental management, 171 (2016) 1-10.
[58] C.B. Zhu LZ, Sorption Behavior of p-Nitrophenol on the Interface between Anion-Cation Organobentonite and Water, Environ. Sci. Technol., 34 (2000) 2997-3002.
[59] M. Fu, Z. Zhang, L. Wu, G. Zhuang, S. Zhang, J. Yuan, L. Liao, Investigation on the co-modification process of montmorillonite by anionic and cationic surfactants, Applied Clay Science, 132-133 (2016) 694-701.
[60] Z. Zhang, J. Zhang, L. Liao, Z. Xia, Synergistic effect of cationic and anionic surfactants for the modification of Ca-montmorillonite, Materials Research Bulletin, 48 (2013) 1811-1816.
[61] Y. Chang, X. Lv, F. Zha, Y. Wang, Z. Lei, Sorption of p-nitrophenol by anion–cation modified palygorskite, Journal of hazardous materials, 168 (2009) 826-831.
[62] A.A. Edathil, P. Pal, F. Banat, Alginate clay hybrid composite adsorbents for the reclamation of industrial lean methyldiethanolamine solutions, Applied Clay Science, 156 (2018) 213-223.
[63] Q.L. Mengmeng Diao, Haiyan Xiao, Ningjing Duan, Junjun Xu, Synthesis and adsorption properties of superabsorbent hydrogel and peanut hull composite, Journal of Environmental Chemical Engineering 2(2014) 1558–1567.
[64] A.A. El-Zahhar, N.S. Awwad, E.E. El-Katori, Removal of bromophenol blue dye from industrial waste

ACCEPTED MANUSCRIPT

water by synthesizing polymer-clay composite, Journal of Molecular Liquids, 199 (2014) 454-461.

[65] A. Ely, M. Baudu, M.O.S.A.O. Kankou, J.-P. Basly, Copper and nitrophenol removal by low cost alginate/Mauritanian clay composite beads, Chemical Engineering Journal, 178 (2011) 168-174.

[66] H. Li, A. Kankaanpaa, H. Xiong, M. Hummel, H. Sixta, H. Ojamo, O. Turunen, Thermostabilization of extremophilic *Dictyoglomus thermophilum* GH11 xylanase by an N-terminal disulfide bridge and the effect of ionic liquid [emim]OAc on the enzymatic performance, Enzyme Microb Technol, 53 (2013) 414-419.

[67] Y. Liu, Y. Zheng, A. Wang, Enhanced adsorption of Methylene Blue from aqueous solution by chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites, Journal of Environmental Sciences, 22 (2010) 486-493.

[68] J. Gao, Q. Yang, F. Ran, G. Ma, Z. Lei, Preparation and properties of novel eco-friendly superabsorbent composites based on raw wheat bran and clays, Applied Clay Science, 132-133 (2016) 739-747.

[69] M. Auta, B.H. Hameed, Acid modified local clay beads as effective low-cost adsorbent for dynamic adsorption of methylene blue, Journal of Industrial and Engineering Chemistry, 19 (2013) 1153-1161.

[70] M.Y. Chang, R.S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, Journal of colloid and interface science, 278 (2004) 18-25.

[71] K.A. Hernández-Hernández, J. Illescas, M.d.C. Díaz-Nava, S. Martínez-Gallegos, C. Muro-Urista, R.E. Ortega-Aguilar, E. Rodríguez-Alba, E. Rivera, Preparation of nanocomposites for the removal of phenolic compounds from aqueous solutions, Applied Clay Science, 157 (2018) 212-217.

[72] J. Lin, Y. Zhan, Adsorption of humic acid from aqueous solution onto unmodified and surfactant-modified chitosan/zeolite composites, Chemical Engineering Journal, 200-202 (2012) 202-213.

[73] Y. Gao, Gao, Z., Sun, W., Yin, Z., Wang, J., & Hu, Y. , Adsorption of a novel reagent scheme on scheelite and calcite causing an effective flotation separation, Journal of colloid and interface science, 512 (2018) 39-46.

[74] H. Zhang, Kim, Y. K., Hunter, T. N., Brown, A. P., Lee, J. W., & Harbottle, D., Organically modified clay with potassium copper hexacyanoferrate for enhanced Cs+ adsorption capacity and selective recovery by flotation, Journal of Materials Chemistry A, 5 (2017) 15130-15143.

[75] J. Chang, J. Ma, Q. Ma, D. Zhang, N. Qiao, M. Hu, H. Ma, Adsorption of methylene blue onto Fe3O4/activated montmorillonite nanocomposite, Applied Clay Science, 119 (2016) 132-140.

[76] G. Tian, W. Wang, L. Zong, Y. Kang, A. Wang, A functionalized hybrid silicate adsorbent derived from naturally abundant low-grade palygorskite clay for highly efficient removal of hazardous antibiotics, Chemical Engineering Journal, 293 (2016) 376-385.

[77] W. Wang, G. Tian, L. Zong, Q. Wang, Y. Zhou, A. Wang, Mesoporous hybrid Zn-silicate derived from red palygorskite clay as a high-efficient adsorbent for antibiotics, Microporous and Mesoporous Materials, 234 (2016) 317-325.

[78] C. Baker-Austin, M.S. Wright, R. Stepanauskas, J.V. McArthur, Co-selection of antibiotic and metal resistance, Trends in microbiology, 14 (2006) 176-182.

[79] Y. Lu, S. Song, R. Wang, Z. Liu, J. Meng, A.J. Sweetman, A. Jenkins, R.C. Ferrier, H. Li, W. Luo, T. Wang, Impacts of soil and water pollution on food safety and health risks in China, Environment international, 77 (2015) 5-15.

[80] N. Saha, M.S. Rahman, M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, Industrial metal pollution in water and probabilistic assessment of human health risk, Journal of environmental management, 185 (2017) 70-78.

ACCEPTED MANUSCRIPT

[81] Q. Wang, Z. Yang, Industrial water pollution, water environment treatment, and health risks in China, Environmental pollution, 218 (2016) 358-365.
[82] K. Poole, At the Nexus of Antibiotics and Metals: The Impact of Cu and Zn on Antibiotic Activity and Resistance, Trends in microbiology, 25 (2017) 820-832.
[83] B. Mu, A. Wang, Adsorption of dyes onto palygorskite and its composites: A review, Journal of Environmental Chemical Engineering, 4 (2016) 1274-1294.
[84] M.T. Yagub, T.K. Sen, H.M. Ang, Equilibrium, Kinetics, and Thermodynamics of Methylene Blue Adsorption by Pine Tree Leaves, Water, Air, & Soil Pollution, 223 (2012) 5267-5282.
[85] R. Elmoubarki, F.Z. Mahjoubi, H. Tounsadi, J. Moustadraf, M. Abdennouri, A. Zouhri, A. El Albani, N. Barka, Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics, Water Resources and Industry, 9 (2015) 16-29.
[86] M.M.S. Nagarethinam Kannan, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, Dyes and Pigments, 51 (2001) 25-40.
[87] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, Journal of hazardous materials, 177 (2010) 70-80.
[88] C.A. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, Journal of colloid and interface science, 332 (2009) 46-53.
[89] A. Gürses, S. Karaca, Ç. Doğar, R. Bayrak, M. Açıkyıldız, M. Yalçın, Determination of adsorptive properties of clay/water system: methylene blue sorption, Journal of colloid and interface science, 269 (2004) 310-314.
[90] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresource technology, 97 (2006) 1061-1085.
[91] H. Chen, J. Zhao, A. Zhong, Y. Jin, Removal capacity and adsorption mechanism of heat-treated palygorskite clay for methylene blue, Chemical Engineering Journal, 174 (2011) 143-150.
[92] I.A. Shabtai, Y.G. Mishael, Catalytic polymer-clay composite for enhanced removal and degradation of diazinon, Journal of hazardous materials, 335 (2017) 135-142.
[93] H. Fan, L. Zhou, X. Jiang, Q. Huang, W. Lang, Adsorption of Cu2+ and methylene blue on dodecyl sulfobetaine surfactant-modified montmorillonite, Applied Clay Science, 95 (2014) 150-158.
[94] H. Baaziz, C. Gambari, A. Boyeldieu, A. Ali Chaouche, R. Alatou, V. Méjean, C. Jourlin-Castelli, M. Fons, ChrASO, the chromate efflux pump of Shewanella oneidensis, improves chromate survival and reduction, PloS one, 12 (2017) e0188516.
[95] W. Sanqin, Z. Zepeng, W. Yunhua, L. Libing, Z. Jiansheng, Influence of montmorillonites exchange capacity on the basal spacing of cation–anion organo-montmorillonites, Materials Research Bulletin, 59 (2014) 59-64.
[96] S. Chen, M. Zhou, H.-F. Wang, T. Wang, X.-S. Wang, H.-B. Hou, B.-Y. Song, Adsorption of Reactive Brilliant Red X-3B in Aqueous Solutions on Clay–Biochar Composites from Bagasse and Natural Attapulgite, Water, 10 (2018) 703.
[97] P.-J. Lu, H.-C. Lin, W.-T. Yu, J.-M. Chern, Chemical regeneration of activated carbon used for dye adsorption, Journal of the Taiwan Institute of Chemical Engineers, 42 (2011) 305-311.
[98] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, M. Chen, Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater, Bioresource technology, 214 (2016) 836-851.
[99] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok,

ACCEPTED MANUSCRIPT

Biochar as a sorbent for contaminant management in soil and water: a review, Chemosphere, 99 (2014) 19-33.
[100] A.K. Haritash, C.P. Kaushik, Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review, Journal of hazardous materials, 169 (2009) 1-15.
[101] Z. Chen, Y. Niu, S. Zhao, A. Khan, Z. Ling, Y. Chen, P. Liu, X. Li, A novel biosensor for p-nitrophenol based on an aerobic anode microbial fuel cell, Biosensors & bioelectronics, 85 (2016) 860-868.
[102] B. Sarkar, M. Megharaj, Y. Xi, R. Naidu, Surface charge characteristics of organo-palygorskites and adsorption of p-nitrophenol in flow-through reactor system, Chemical Engineering Journal, 185-186 (2012) 35-43.
[103] A. Ely, M. Baudu, J.P. Basly, M.O. Kankou, Copper and nitrophenol pollutants removal by Na-montmorillonite/alginate microcapsules, Journal of hazardous materials, 171 (2009) 405-409.
[104] R. Ganigar, G. Rytwo, Y. Gonen, A. Radian, Y.G. Mishael, Polymer–clay nanocomposites for the removal of trichlorophenol and trinitrophenol from water, Applied Clay Science, 49 (2010) 311-316.
[105] W.P. Cheng, W. Gao, X. Cui, J.H. Ma, R.F. Li, Phenol adsorption equilibrium and kinetics on zeolite X/activated carbon composite, Journal of the Taiwan Institute of Chemical Engineers, 62 (2016) 192-198.
[106] I. Máthé, T. Benedek, A. Táncsics, M. Palatinszky, S. Lányi, K. Márialigeti, Diversity, activity, antibiotic and heavy metal resistance of bacteria from petroleum hydrocarbon contaminated soils located in Harghita County (Romania), International Biodeterioration & Biodegradation, 73 (2012) 41-49.
[107] W. Liu, J. Zhang, C. Zhang, L. Ren, Sorption of norfloxacin by lotus stalk-based activated carbon and iron-doped activated alumina: Mechanisms, isotherms and kinetics, Chemical Engineering Journal, 171 (2011) 431-438.
[108] H. Liu, W. Ning, P. Cheng, J. Zhang, Y. Wang, C. Zhang, Evaluation of animal hairs-based activated carbon for sorption of norfloxacin and acetaminophen by comparing with cattail fiber-based activated carbon, Journal of Analytical and Applied Pyrolysis, 101 (2013) 156-165.
[109] E.C. Campbell, G.J. Correy, P.D. Mabbitt, A.M. Buckle, N. Tokuriki, C.J. Jackson, Laboratory evolution of protein conformational dynamics, Current opinion in structural biology, 50 (2018) 49-57.
[110] M.E. Parolo, M.J. Avena, G.R. Pettinari, M.T. Baschini, Influence of Ca2+ on tetracycline adsorption on montmorillonite, Journal of colloid and interface science, 368 (2012) 420-426.
[111] A.L. Filgueiras, D. Paschoal, H.F. Dos Santos, A.C. Sant'Ana, Adsorption study of antibiotics on silver nanoparticle surfaces by surface-enhanced Raman scattering spectroscopy, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy, 136 Pt B (2015) 979-985.
[112] P.H. Chang, Z. Li, T.L. Yu, S. Munkhbayer, T.H. Kuo, Y.C. Hung, J.S. Jean, K.H. Lin, Sorptive removal of tetracycline from water by palygorskite, Journal of hazardous materials, 165 (2009) 148-155.
[113] G. Lofrano, M. Carotenuto, G. Libralato, R.F. Domingos, A. Markus, L. Dini, R.K. Gautam, D. Baldantoni, M. Rossi, S.K. Sharma, M.C. Chattopadhyaya, M. Giugni, S. Meric, Polymer functionalized nanocomposites for metals removal from water and wastewater: An overview, Water research, 92 (2016) 22-37.
[114] C. Chen, H. Liu, T. Chen, D. Chen, R.L. Frost, An insight into the removal of Pb(II), Cu(II), Co(II), Cd(II), Zn(II), Ag(I), Hg(I), Cr(VI) by Na(I)-montmorillonite and Ca(II)-montmorillonite, Applied Clay Science, 118 (2015) 239-247.
[115] M. Addy, B. Losey, R. Mohseni, E. Zlotnikov, A. Vasiliev, Adsorption of heavy metal ions on mesoporous silica-modified montmorillonite containing a grafted chelate ligand, Applied Clay Science,

ACCEPTED MANUSCRIPT

59-60 (2012) 115-120.
[116] K.Y. Foo, B.H. Hameed, The environmental applications of activated carbon/zeolite composite materials, Advances in colloid and interface science, 162 (2011) 22-28.
[117] V.N. Tirtom, A. Dinçer, S. Becerik, T. Aydemir, A. Çelik, Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan–clay composite beads in aqueous solution, Chemical Engineering Journal, 197 (2012) 379-386.
[118] T. Xiong, X. Yuan, X. Chen, Z. Wu, H. Wang, L. Leng, H. Wang, L. Jiang, G. Zeng, Insight into highly efficient removal of cadmium and methylene blue by eco-friendly magnesium silicate-hydrothermal carbon composite, Applied Surface Science, 427 (2018) 1107-1117.
[119] V.K. Jha, M. Matsuda, M. Miyake, Sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}, Journal of hazardous materials, 160 (2008) 148-153.
[120] B. Sarkar, Y. Xi, M. Megharaj, G.S. Krishnamurti, D. Rajarathnam, R. Naidu, Remediation of hexavalent chromium through adsorption by bentonite based Arquad(R) 2HT-75 organoclays, Journal of hazardous materials, 183 (2010) 87-97.
[121] R.A. Shawabkeh, Adsorption of chromium ions from aqueous solution by using activated carbo-aluminosilicate material from oil shale, Journal of colloid and interface science, 299 (2006) 530-536.
[122] K. Sasaki, K. Takeno, H. Shinkawa, K. Sasaki, N. Das, Removal of Radioactivity and Recovery of Radioactive Cs from Sediment Mud and Soil in Fukushima, Japan Using Immobilized Photosynthetic Bacteria, Advanced Materials Research, 1091 (2015) 125-130.
[123] X. Liu, G.R. Chen, D.J. Lee, T. Kawamoto, H. Tanaka, M.L. Chen, Y.K. Luo, Adsorption removal of cesium from drinking waters: a mini review on use of biosorbents and other adsorbents, Bioresource technology, 160 (2014) 142-149.
[124] C.W. Park, B.H. Kim, H.M. Yang, B.K. Seo, K.W. Lee, Enhanced desorption of Cs from clays by a polymeric cation-exchange agent, Journal of hazardous materials, 327 (2017) 127-134.
[125] H. Zhang, S. Tangparitkul, B. Hendry, J. Harper, Y.K. Kim, T.N. Hunter, J.W. Lee, D. Harbottle, Selective separation of cesium contaminated clays from pristine clays by flotation, Chemical Engineering Journal, 355 (2019) 797-804.
[126] M.I. El-Dessouky, H.H. Ibrahiem, E.H. El-Masry, G.E. Sharaf El-deen, N.M. Sami, M.E. Moustafa, E.M. Mabrouk, Removal of Cs^{+} and Co^{2+} ions from aqueous solutions using poly (acrylamide-acrylic acid)/kaolin composite prepared by gamma radiation, Applied Clay Science, 151 (2018) 73-80.
[127] H.A. Alamudy, K. Cho, Selective adsorption of cesium from an aqueous solution by a montmorillonite-prussian blue hybrid, Chemical Engineering Journal, 349 (2018) 595-602.
[128] U. Soni, J. Bajpai, S.K. Singh, A.K. Bajpai, Evaluation of chitosan-carbon based biocomposite for efficient removal of phenols from aqueous solutions, Journal of Water Process Engineering, 16 (2017) 56-63.
[129] R. Xue, A. Donovan, H. Zhang, Y. Ma, C. Adams, J. Yang, B. Hua, E. Inniss, T. Eichholz, H. Shi, Simultaneous removal of ammonia and N-nitrosamine precursors from high ammonia water by zeolite and powdered activated carbon, Journal of environmental sciences, 64 (2018) 82-91.
[130] A.A. Halim, H.A. Aziz, M.A. Johari, K.S. Ariffin, M.N. Adlan, Ammoniacal nitrogen and COD removal from semi-aerobic landfill leachate using a composite adsorbent: fixed bed column adsorption performance, Journal of hazardous materials, 175 (2010) 960-964.
[131] S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review, Sustainable Materials and Technologies, 9 (2016) 10-

ACCEPTED MANUSCRIPT

40.
[132] K.A. Thompson, K.K. Shimabuku, J.P. Kearns, D.R. Knappe, R.S. Summers, S.M. Cook, Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment, Environmental science & technology, (2016).
[133] M. Momina, M. Shahadat, S. Isamil, Regeneration performance of clay-based adsorbents for the removal of industrial dyes: a review, RSC Advances, 8 (2018) 24571-24587.
[134] M.J. Lashaki, M. Fayaz, H.H. Wang, Z. Hashisho, J.H. Philips, J.E. Anderson, M. Nichols, Effect of adsorption and regeneration temperature on irreversible adsorption of organic vapors on beaded activated carbon, Environmental science & technology, 46 (2012) 4083-4090.
[135] R.M. Narbaitz, A. Karimi-Jashni, Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter, Environmental technology, 30 (2009) 27-36.
[136] B. Ledesma, S. Román, A. Álvarez-Murillo, E. Sabio, J.F. González, Cyclic adsorption/thermal regeneration of activated carbons, Journal of Analytical and Applied Pyrolysis, 106 (2014) 112-117.
[137] S. Lu, J. Hu, C. Chen, X. Chen, Y. Gong, Y. Sun, X. Tan, Spectroscopic and modeling investigation of efficient removal of U(VI) on a novel magnesium silicate/diatomite, Separation and Purification Technology, 174 (2017) 425-431.
[138] E.I. Unuabonah, M.I. El-Khaiary, B.I. Olu-Owolabi, K.O. Adebowale, Predicting the dynamics and performance of a polymer–clay based composite in a fixed bed system for the removal of lead (II) ion, Chemical Engineering Research and Design, 90 (2012) 1105-1115.
[139] V. Vimonses, B. Jin, C.W.K. Chow, C. Saint, Development of a pilot fluidised bed reactor system with a formulated clay–lime mixture for continuous removal of chemical pollutants from wastewater, Chemical Engineering Journal, 158 (2010) 535-541.
[140] T.J. Alexander, P. Vonlanthen, O. Seehausen, Does eutrophication-driven evolution change aquatic ecosystems?, Philosophical transactions of the Royal Society of London. Series B, Biological sciences, 372 (2017).
[141] N.T. Joutey, H. Sayel, W. Bahafid, N. El Ghachtouli, Mechanisms of Hexavalent Chromium Resistance and Removal by Microorganisms, in: D.M. Whitacre (Ed.) Reviews of Environmental Contamination and Toxicology Volume 233, Springer International Publishing, Cham, 2015, pp. 45-69.
[142] A. Shtarker-Sasi, S. Castro-Sowinski, O. Matan, T. Kagan, S. Nir, Y. Okon, A.M. Nasser, Removal of bacteria and Cryptosporidium from water by micelle–montmorillonite complexes, Desalination and Water Treatment, 51 (2013) 7672-7680.
[143] C.B. Durrant, J.D. Begg, A.B. Kersting, M. Zavarin, Cesium sorption reversibility and kinetics on illite, montmorillonite, and kaolinite, The Science of the total environment, 610-611 (2018) 511-520.
[144] M. Auta, B.H. Hameed, Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue, Chemical Engineering Journal, 237 (2014) 352-361.
[145] L. Ai, Y. Zhou, J. Jiang, Removal of methylene blue from aqueous solution by montmorillonite/CoFe2O4 composite with magnetic separation performance, Desalination, 266 (2011) 72-77.
[146] L. Mouni, L. Belkhiri, J.-C. Bollinger, A. Bouzaza, A. Assadi, A. Tirri, F. Dahmoune, K. Madani, H. Remini, Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies, Applied Clay Science, 153 (2018) 38-45.

ACCEPTED MANUSCRIPT

Figure legend

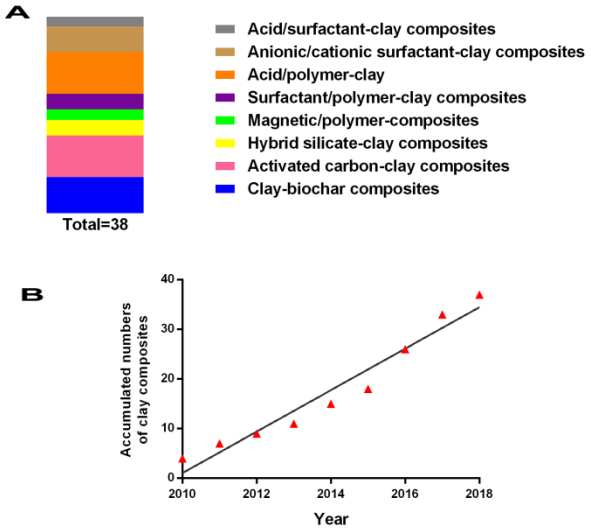


Fig.1 Core areas of published research on multi-modified clay composites treated by carbon materials, organics and hybrid silicates published between 2010 and 2018. B, Cumulative number of published papers on clay composites between 2010 and 2018.

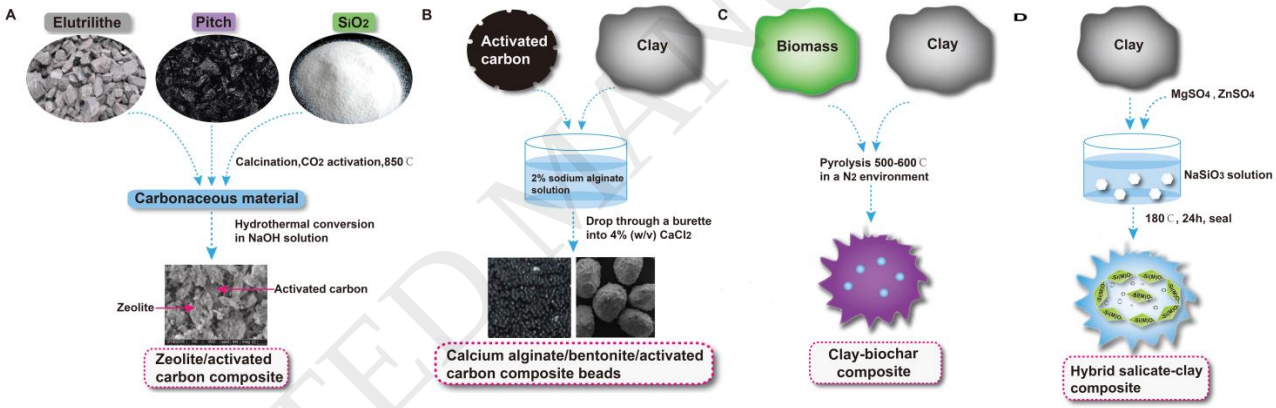


Fig.2 Schematic diagrams of synthesizing activated carbon/clay composites (A,B), clay-biochar composites(C) and hybrid silicate-clay composites (D)

ACCEPTED MANUSCRIPT

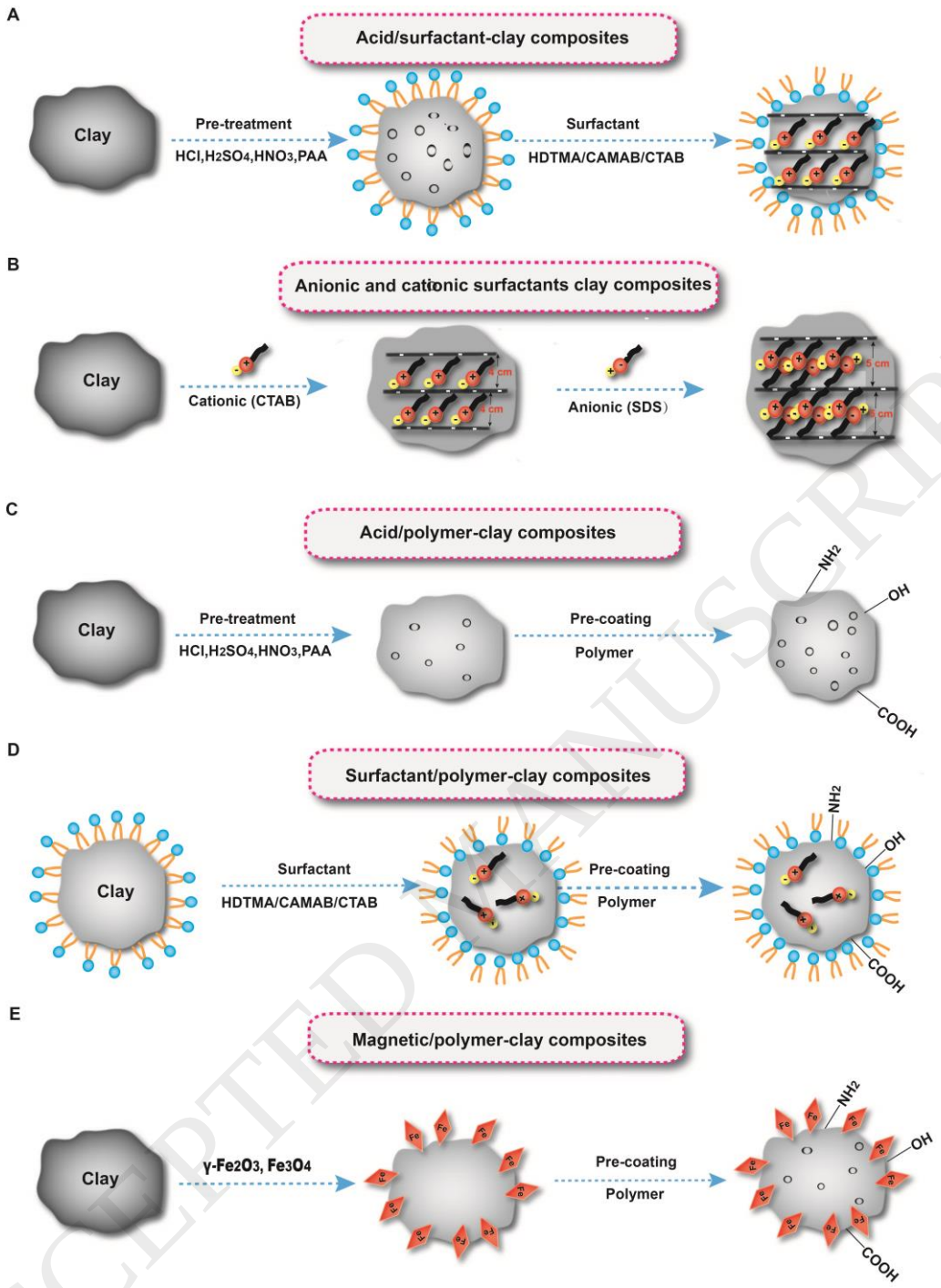


Fig.3 Schematic diagrams of synthesizing various organo-clay composites based on combined modification.

ACCEPTED MANUSCRIPT

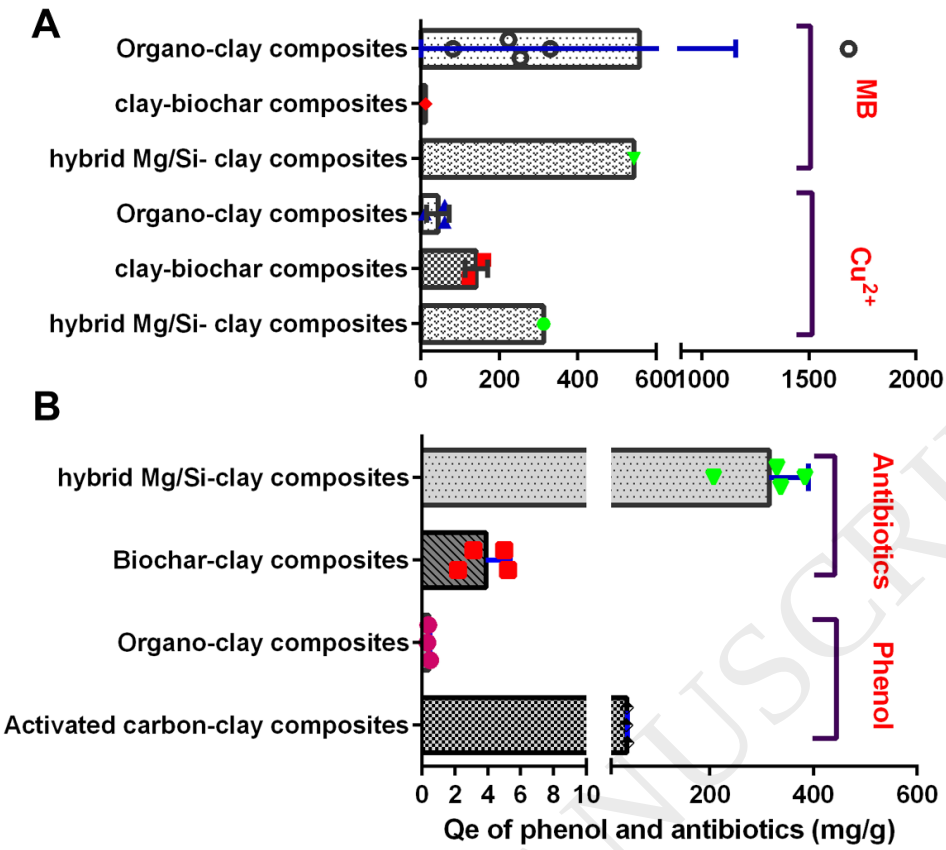


Fig. 4 A, Comparative analysis of various clay composites for the removal of MB [26, 29, 35, 39, 67, 69, 70, 93] and Cu^{2+} [39, 54, 93, 119]; B. The adsorption ability of various clay composites on phenol [71, 105] and antibiotics [8, 41, 76, 77].

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

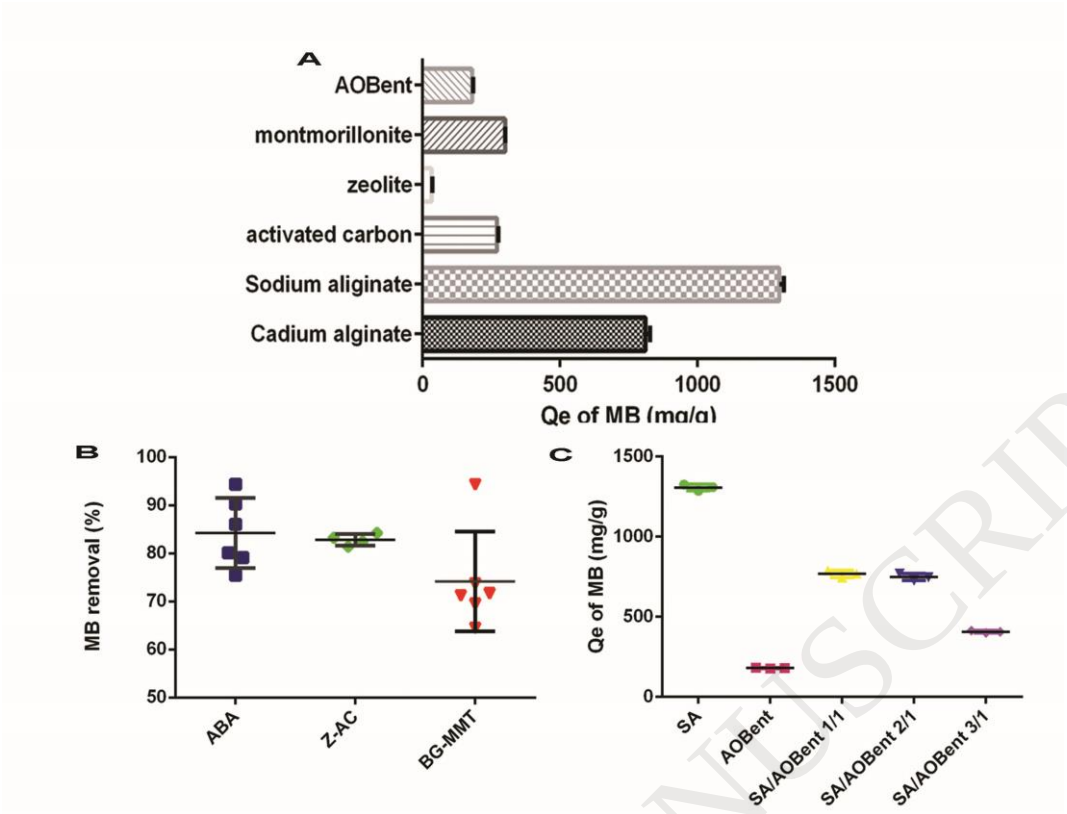


Fig.5 A, Maximum MB adsorption capacity from various types of raw materials[28, 87]; B. MB removal efficiency of regenerated activated carbon-clay composites (ABA and Z-AC) and biochar-clay composites (BG-MMT) [26, 28, 46]; C, The proportion of clay and SA in organo-clay composites changes their performance [35].

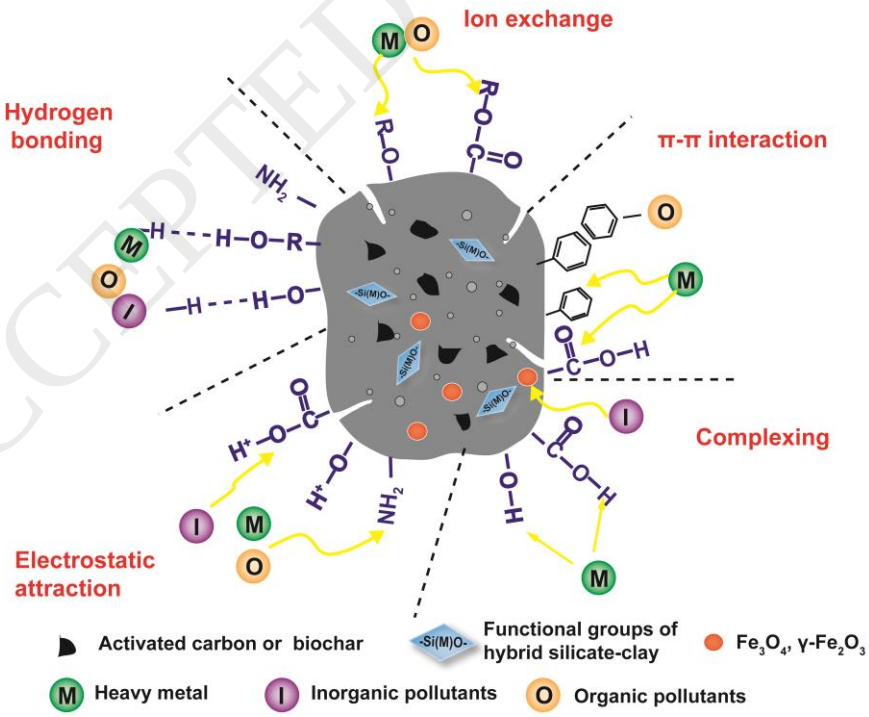


Fig.6 Adsorption mechanisms of combined modification clay composites for various pollutants

ACCEPTED MANUSCRIPT

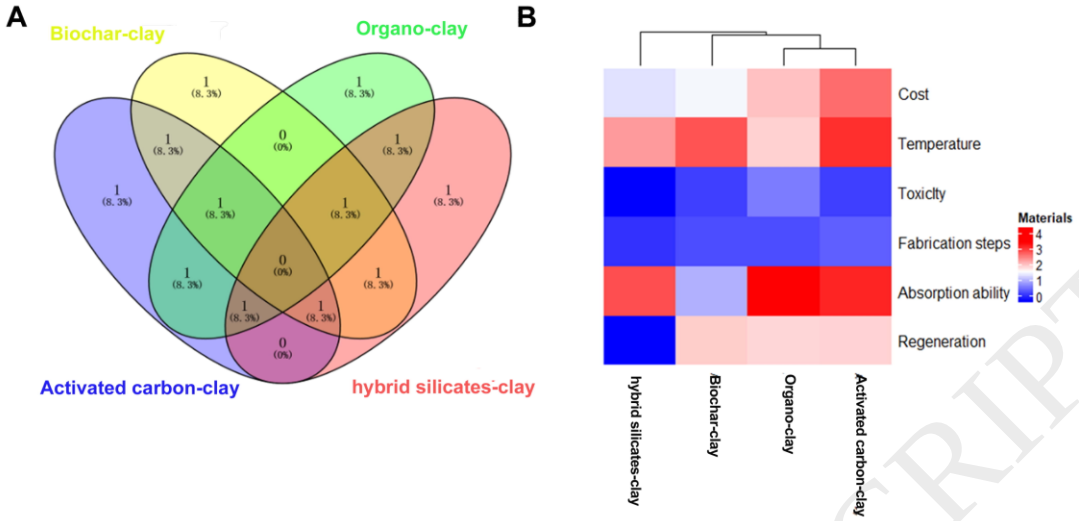


Fig. 7 Venn diagram (A) and heat map (B) of biochar modified clay (BC-clay), activated carbon modified clay (AC-clay), organic modified clay (Organo clay) and silicate modified clay from the prospective of adsorption ability, regeneration, toxicity, cost and preparation condition.

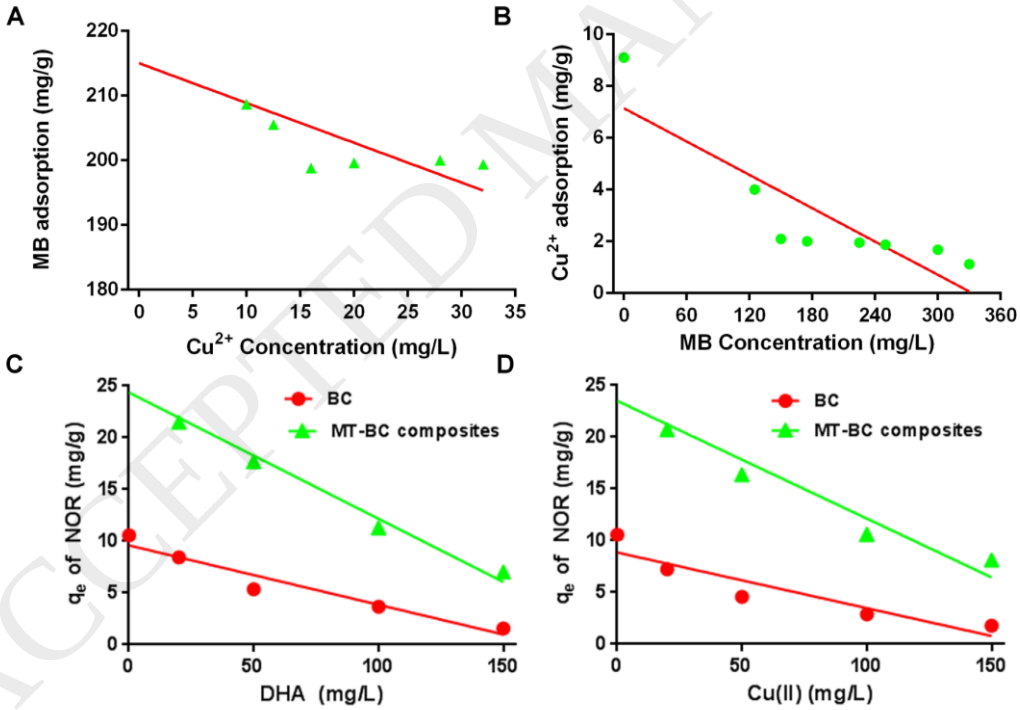


Fig.8 Competitive adsorption in pure solution and binary system. A, B The MB (A) or Cu^{2+} (B) adsorption capacity of MMT-SB12 in the presence of $Cu^{2+}$and MB, respectively [93]. C, D, Effects of DHA and Cu(II) on the adsorption of NOR on BC (A) and MTP-BC composite (B) [41].

ACCEPTED MANUSCRIPT

Table1 Removal of Dye from various clay composites

Raw clay	Modification	Basal space (nm)	Surface area (m^2/g)	Pore size (nm)	Adsorbents dose	Initial pollutants concentration	Contact time	pH	Temperature (℃)	Regeneration Solution and recovery	Targeted pollutants	q_e (mg/g)	References
Bentonite,	Calcium alginate, hydrodarco C	-	185.3	5.97	1 g/L	25-500 mg/L	30 h	3-11	30-50	Methanol, 75% recovery after 6 cycles	MB	756.97-994.06	[28]
Kaolinite	oil palm ash, aluminum oxide	-	615 .4	3.05	1 g/L	25-400 mg/L	29 h	3-13	30-50	acidic ethanol, 80% recovery after 4 cycles	MB	143.47-285.71	[46]
MMT Kaolinite	Bamboo, bagasse, hickory chips	-	224-408	-	2 g/L	20 mg/L	48 h	5.7	22	ddH_2O/KCl, 70% recovery after 4 cycles	MB	11.94	[26]
Attapulgite	Bagasse	-	63.9-178	3-4	1 g/L	40-200 mg/L	24 h	6-7	25	Methanol, 85% recovery after 5 cycles	Brilliant red X-3B.	65.1-72.2	[96]
Bentonites	H_2SO_4/HTAB/SA	1.84	-	-	0.4 g/L	50-2000 mg/L 50-800 mg/L	12-15h-	2-11	23	-	MB MO	414-769 28.7-116.3	[35]
Bentonites	H_2SO_4/HTAB	1.84	-	-	0.4 g/L	50-2000 mg/L 50-800 mg/L	12-15h-	2-11	23	-	MB MO	183 141	[35]
MMT	CTMAB /SSTA CTMAB SSTA	4.76-4.8 2.01 4.80	-	-	2 g/L	120 mg/L	2 h	3-10	30-60	-	MO	149.25 128.21 42.73	[34]

ACCEPTED MANUSCRIPT

	-	1.29										24	
Natural clay	H_2SO_4 /chitosan	-	-	-	1 g/L	600 mg/L 900 mg/L	10 h	7.14 6.47	30	-	MB RR222	330 1912	[70]
Ball clay	H_2SO_4 /chitosan H_2SO_4	-	-	-	1 g/L	30-300 mg/L	100 min	4-12	30	ddH_2O, 50% recovery after 5 cycles	MB	142 140	[144]
Malaysia clay	H_2SO_4/ $Al(OH)_3$/SA		19.32	2.2	2 g/L	30-300 mg/L	12 h	3-12	30	ddH_2O, 33% recovery after 3 cycles	MB	223.19	[69]
Vermiculite	PAA/chitosan	-	-	-	0.5 g/L	700-1200 mg/L	10 h	2-9	30-50	-	MB	1685.56	[67]
activated MMT	Fe_3O_4	1.54	147.9	47.4	2.5 g/L	100-250 mg/L	-	3-11	30	Magnetics, 84% recovery after 5 cycles	MB	106.38	[75]
	-	1.23	187.3	46.4	2.5 g/L	100-250 mg/L	-	3-11			MB	64.43	[75]
MMT	γ-Fe_2O_3/chitosan	-	-	-	5 g/L	100 mg/L	1.7	3.7- 9.4	20	-	MB	52-82	[29]
Palygorskite	$MgSO_4$, $NaSiO_3$ -	- -	- -	3.4- 3.7	1 g/L	100-1500 mg/L	2 h	7	30	-	MB	11.94 212.77	[39]
Bentonite	- Thermal HCl HCl/ Thermal Thermal HNO_3	-	25.7 34.6 75.5 84.6	5.02 5.16 5.38 5.61	1 g/L	100-1000 mg/L	24 h	7.0	25	-	Congo red	- 54.64 69.44 74.5	[33]
Moroccan clay		-	-	-	2 g/L	100-1200 mg/L	2 h	5.6	30	-	MB	500 500	[17]

ACCEPTED MANUSCRIPT

	-											350	
	-	1.55				120mg/L						150.2	
MMT	dodecyl		-	-	1 g/L		2 h	5.0	18-35	-	MB		[93]
	sulfobetaine	1.73				120mg/L						254	
MMT	$CoFe_2O_4$	-	-	-	2 g/L	40-200 mg/L	40 min	3-9	25-45	-	MB	97.5	[145]
MMT clay	-	-	62	9.16	2 g/L	200-1500 mg/L	4 h	5.5-7.5	45-60	-	MB	289-300	[88]
Kaolin	-	-	21.3	15	0.5 g/L	80-250 mg/L	3 h	2-10	25	dH_2O, 23% recovery after 5 cycles	MB	52.76	[146]

q_e (mg/g) is the amount of targted pollutants adsorbed at Langmuir equilibrium

ACCEPTED MANUSCRIPT

Table2 Removal of organic pollutants from various clay composites

Raw clay	Modification	Basal space (nm)	Surface area (m^2/g)	Pore size (nm)	Adsorbents dose	Initial pollutants concentration	Contact time	pH	Temperature (℃)	Regeneration Solution and recovery	Targeted pollutants	q_e (mg/g)	References
Elutrilithe	Activated carbon	-	872	0.59	6 g/L	103-552 mg/L	20 h	6.5	25-55	-	Phenol	37.9-40.3	[105]
Bentonites	H_2SO_4/(DTAB,TTAB,HTAB, OTAB)	1.42-2.15	1.1-161	4.6-7.4	0.4 g/L	10-250 mg/L	2 h	4	24	-	trichloropheno l	85-201	[37]
Bentonites	H_2SO_4	1.38	282	4.6								0	[37]
Bentonites	-	1.33	45	6.2								-	[37]
Palygorskite	HTAB/SDS, HDTMAB/SDS, DDMAB/SDS	-	-	-	1 g/L	200 mg/L	1 h	5.7-13.6	20-40	-	p-nitrophenol	137.74	[61]
MMT	HDTMA/SA	-	-	-	10 g/L	10 mg/L	24 h	-	25	-	Phenol 4-chlorophenol	0.334 0.118	[71]
Attapulgite,	potato stem -	- -	90.40 99.43	5.42 3.12	4 g/L	10 mg/L	0.2-36 h	2-11	15-35	Methanol, 82% recovery after 5 cycles	Norfloxacin	4.99-5.24 2.18-3.12	[8]
MMT	wheat straw-biochar	-	112.6	21.7	2.5 g/L	0.4-15 mg/L	48 h	3-11	25	Methanol, 82% recovery after 5 cycles	Norfloxacin	25.53	[41]
Red Palygorskite	$ZnSO_4$, $NaSiO_3$ -		157 43	11.5 8.95	0.5 g/L	200 mg/L	4 h	3.5	30	-	Aureomycin tetracycline	384 337	[77]
Palygorskite,	$MgSO_4$, $NaSiO_3$, monochloroacetic	-	410.61	15-30	1 g/L	50-800 mg/L	25 h	2-10	25	-	chlortetracycline	329.8 207.5	[76]

ACCEPTED MANUSCRIPT

	acid										oxytetracycline		
Zeolite	CPB/chiotosan Chiotosan	- -	5.56 9.82	- -	0.4-2 g/L	80 mg/L 50 mg/L	24 h	4-12	18-30	NaOH, 66% recovery After desorption	Humic acid	164	[72]
Natural clay	H_2SO_4 /chitosan	-	-	-	1 g/L	500 g/L 100 g/L	6 h 6 h	4.62 7.86	30	-	tannic acid humic acid	1395 232	[70]

ACCEPTED MANUSCRIPT

Table3 Removal of heavy metal from various clay composites

Raw clay	Modification	Surface area (m^2/g)	Pore size (nm)	Adsorbents doseq	Initial pollutants concentration	Contact time	pH	Temperature (℃)	Regeneration Solution and recovery	Targeted pollutants	q_e (mg/g)	References
Kaolinite	HNO_3/polyvinyl	-	-	20 g	300 mg/L	20 h	5.5	25	HCl	Cd^{2+}	21.11	[11]
MMT	CTAB/cellulose	87.09	1.8	20 g/L	20 mg/L	50 min	3.8-5.5	25	-	$Cr_2O_7^{2-}$	22.2	[36]
MMT	Quaternary ammonium /chitosan	-	-	0.2-3 g/L	0.2-6 mM/L	135 min	1-7	30	H_2SO_4, 66% recovery after 5 cycles	$Cr_2O_7^{2-}$	128.43	[20]
Clay	bark chips/ chitosan	272.49	1.98	1 g/L	0.5-51 mM/L	24 h	5.0	25-60	-	Cu^{2+} Pb^{2+} Zn^{2+}	121.5 336 134.6	[54]
Activated carbon-zeolite composite	coal fly ash	-	-	2 g/L	500 ppm 500 ppm 500 ppm 1000 ppm	24 h	7.0	25	-	Ni^{2+} Cu^{2+} Cd^{2+} Pb^{2+}	70.43 161.87 109.30 549.08	[119]
Palygorskite	$MgSO_4$, $NaSiO_3$	39.8	3.47	1 g/L	50-200 mg/L		5.0	30	-	Cu^{2+}	313.38	[39]

ACCEPTED MANUSCRIPT

Table4 Removal of ammonia and phosphate from various clay composites

Raw clay	Modification	Surface area (m^2/g)	Pore volume (cm^3/g)	Adsorbents dose	Initial pollutants concentration	Contact time	pH	Temperature (℃)	Targeted pollutants	q_e (mg/g)	References
Zeolite	Coconut shell activated carbon, limestone, rice husk carbon	60.94	-	1-5 g/L	1010-2740 mg/L 1478-3540 mg/L	105 min	8.1-8.7	25	Ammonia COD	24.39 22.99	[47]
Bentonite,	cassava peel	152.3	0.23	1-10 g/L	200 mg/L	6 h	6.0	30	ammonia	23.67	[40]
Montmorillonite	bamboo powder	-	-	20 g/L	200 mg/L	40 h	7.0	30	ammonium phosphate	12.52 105.28	[51]