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Removal of pharmaceutical compounds using bentonite clay

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ABSTRACT: Wastewater contamination with pharmaceutical sources has emerged as the most significant issue concerning the environment and public health worldwide, owing to the ubiquity of pharmaceutical residues in wastewater. These pollutants originate from pharmaceutical production, human consumption and hospital waste generate a serious threat not only to aquatic systems but also to human health in the form of antibiotic resistance and endocrine disruption. The potential of bentonite clay-natural adsorbent in substitution for effective removal of pharmaceutical pollutants from water is the subject of this paper. The paper emphasizes the most relevant properties of bentonite: being absorptive, ion exchange and having a large surface area, in view of being a useful tool for the immobilization of several medicinal substance's antibiotic, analgesic and hormonals. Potential innovations such as surface modification, hybrid composites, and immobilization of bentonite with other advanced technologies like biological treatment and membrane filtration are also explored.

KEYWORDS: wastewater treatment, bentonite, adsorption, water pollution, water purification, pharmaceutical contaminants

INTRODUCTION

Water pollution is the contamination of water bodies (such as lakes, rivers, oceans, aquifers and groundwater), very often by human activities. It could be threatened by different kinds of pollutants [1], such as organic and inorganic pollutants. Many researchers have mentioned several major steps for water purification. These functions work together to dispose of pollutants and make water safe for consumption and other uses [2].

The contamination of wastewater by pharmaceutical compounds has been a rising environmental issue in recent decades. With the increase of global pharmaceutical consumption, the issue of contamination of water bodies with pharmaceutical residues has caused concerns about the impact on ecology and human health [3]. Pharmaceuticals that include both prescription drugs, over the counter-medications and personal care product are meant to be biologically active. Therefore, aquatic organisms and human health can be threatened by low concentrations of these chemicals in water [4]. The origin of pharmaceutical contamination in sewage is multifaceted, ranging from pharmaceutical production, pharmaceutical use by health facilities and households so that pharmaceutical residues are released into the sewage system. Pharmaceutical industries are one of the major causes of pharmaceutical pollutants.

Hospitals and healthcare establishments are also a major emitter of drug pollution. Pharmaceutical waste, including unused medicines, operating room waste, and excreta contaminated with medicinal products from patients, constitute a large share of total waste produced in hospitals [5]. Households are also responsible for pharmaceutical pollution, when people throw away drugs improperly. Disposal of unused or expired medication down the toilet is a common practice which bypasses acceptable disposal options.

The aquatic environment is highly susceptible to pharmaceutical pollution. Very small amounts of drugs can be highly toxic to aquatic species [6]. For instance, exposure of fish, amphibians and other aquatic organisms to hormones in wastewater results in perturbed reproductive systems and modified growth, behavior, and populations. Polymicrobial populations will tend to become resistant, however, under the selective pressures imposed by the antibiotics present in water, a major public health challenge. The emergence of resistance to antibiotics is a major problem that is spreading worldwide, and exposure to sublethal concentrations of these drugs in water can select for resistant strains and make the treatment of infections in animals and humans more difficult.

There is also the matter of potential harm for human health. Residual pharmaceuticals in the environment could plausibly enter drinking water sources and pose a health risk to humans [7]. Although traditional wastewater treatment procedures like activated sludge and filtration are meant for the upliftment of organic pollutants, still, these methods are inefficient enough to treat pharmaceutical contamination. Numerous pharmaceuticals are engineered for bioactivity and to resist biodegradation and are therefore persistent in conventional water treatment processes [8]. Therefore, traces of pharmaceuticals remain in the treated water that after consumption in a long run, is likely to cause potential health risk such as hormonal imbalance and other chronic diseases.

Considering the drawing problems of the pharmaceutical's removal, researchers are urgently in need of more convenient treatment. Some conventional sewage treatments are not very efficient at removing pharmaceutical residues, and processing treatment of pharmaceutical residues remains challenging. For this purpose, alternative water treatment techniques such as adsorption, membrane filtration, and advanced oxidation processes have been investigated. Adsorption refers to the pollutant being removed by passing air or water through a medium that attracts and binds the pollutant at its surface. This phenomenon, also known as surface phenomenon, can find application for cleansing of air and water using adsorbents such as activated carbon, bentonite, biochar or other nanomaterials. The adsorbed pollutant at the surface is called an adsorbate. Among them, the naturally available bentonite clay has gained great attention. Bentonite clay is a kind of alumina-silicate that has a high surface area and cation-exchange capacity as well as possessing sorption ability for many pollutants such as pharmaceuticals [9].

In the following sections, we present and analyze the sources and the ecological effects of pharmaceutical contamination in the same medium, alert on the drawbacks of using conventional methods of these contaminants elimination and discuss the potential of the bentonite clay as an efficient solution of pharmaceutical pollution. In compiling an inventory of existing studies and recent developments, we performed an extensive literature review across several major databases such as Scopus, Google Scholar, PubMed, Web of Science, IEEE Xplore, and DOAJ, from 2013 to 2025. The search approach integrated terms and keywords associated with bentonite clay, adsorption kinetic data, adsorption equilibrium, the Freundlich isotherm, the Langmuir model, wastewater treatment, water purification, removal efficiency, and pharmaceutical compounds. Through this review, we hope to stimulate new developments in a more efficient, cheaper and more environmentally sound treatments of pharmaceuticals in wastewater.

PHARMACEUTICAL CONTAMINANTS

In the last few years, pharmaceutical contaminants in water have become an important environmental and public health problem. The worldwide application of pharmaceuticals is increasing and so is the concentration of pharmaceutical residue in wastewater, which poses a threat to the aquatic ecosystem and the life of human beings as well as indicating a challenge to existing wastewater treatment processes [10].

Antibiotics are the most detected pharmaceutical contaminants in wastewater. Antibiotics are commonly used in humans and animals to cure bacterial infections. These include amoxicillin, tetracycline, ciprofloxacin and sulfamethoxazole [11]. Antibiotics are environmentally poisonous, being chemically stable, they tend to remain in the wastewater system and water body and contribute to the increasingly discovered global problem of antibiotic resistance. In terms of analgesics and anti-inflammatory drugs, this group encompasses pain relievers and anti-inflammatory medications such as acetaminophen, ibuprofen, aspirin and others. These drugs are commonly taken by people for self-medication and residue from their use may be present in wastewater [12]. While these drugs are not as hazardous as some other pharmaceuticals to aquatic life, their general distribution remains of concern about the potential for long-term impacts upon aquatic organisms.

Hormones, like estrogen and testosterone and steroids as well as synthetic hormones, found from contraceptives were the most widespread compounds found in wastewater. These substances can disrupt aquatic organisms' endocrine system, resulting in reproductive dysfunction, changed development patterns and decreasing number in population. Estrogens are also problematic, as they can lead to feminization in male fish, a disruption of the normal reproductive process [13]. Antidepressants and psychotropic medications like selective serotonin reuptake inhibitors and benzodiazepines are widely used for mental health, depression and anxiety. These substances have been detected in wastewater and may modify behavior of aquatic animals including feeding activity and agonistic interactions [14]. The possibility that psychotropic drugs could impact human beings when released into the environment through contamination of drinking water is also problematic.

Anticancer drugs, such as cyclophosphamide, methotrexate and doxorubicin are some of these highly active drugs that consistently emerged in wastewater, which potentially toxic to aquatic organisms and human [15]. This can be problematic as many of these compounds are present in trace amounts in effluent from hospitals, and difficult to remove due to their chemical structures. Hospitals and health care units are also important sources of pharmaceuticals as developing pollutants in wastewater [16]. In such environments, vast amounts of drugs are consumed, and the wasted and/or active drug residues are frequently thrown or washed into wastewater channels [17]. Proponents for chemotherapy and oncology departments, and intensive care units contribute large volumes of pharmaceuticals to effluent discharges are proliferation of chemotherapy units where strong cytotoxic are used.

Pharmaceutical contaminants are difficult to remove from water through traditional wastewater treatment routes [18]. The conventional methods, including activated sludge, filtration and biological treatment, have mainly been applied to eliminate organic matters, nutrients, and suspended solids in wastewater, and no apparent performance is observed for removal of pharmaceuticals that are chemically recalcitrant and biologically persistent [19].

Several medications such as antibiotics, hormones, and other biologically active compounds are chemically stable, and they show poor degradation in standard treatment processes [20]. Pharmaceutical pollutants are typically found at very low concentrations from ng/l to µg/l, making it difficult to detect and to eliminate them via conventional wastewater treatment techniques. Because wastewater is in fact a combination of several pharmaceutical compounds and as they are only a category, or a broad classification, then a single treatment may not work for all kinds of pharmaceutical pollutants complicating the cost and scalability of the process. To solve these problems, it is necessary to use some advanced treatments such as advanced oxidation treatment, photolysis, Ozonation, and reverse osmosis for waste treatment, which not only give more accurate results in low concentrations but also are cheap, chemically stable, not only at the pharmaceutical level but also at the toxic metals level as well [21].

BENTONITE AS ADSORBENTS

Bentonite as a naturally occurring material has attracted considerable attention for its wide range of applications, especially in environment and industry. It is a good, fine-grained silty clay soil spread and deposited primarily by minerals from the smectite group, among which montmorillonite is the most common and distinctive mineral [22]. The extraordinary properties of bentonite are a result of its mineralogical composition, and as such this clay is an extremely valuable material for use in various industries such as agriculture, water treatment, and pharmaceuticals.

The adsorption capacity of bentonite is primarily based on surface area, typically being high from 50 to 800 m^2/g that is adequate to absorb drugs. Because of its high surface, more adsorbed material can be accommodated, leading to greater effectiveness in the removal of contaminants from water or other media. It is also more efficiently applicable than other conventional time-consuming, expensive and even sometimes toxic methods for the elimination of pharmaceuticals by virtue of its great ion exchange process [23].

COMPARISON OF BENTONITE WITH OTHER ADSORBENT MATERIALS

As compared to other materials, nanomaterials are known for their small size and high aspect ratio, strong adsorption capacity, rich reactivity [24]. Different types of nanomaterials can eliminate metal particles, bacteria, organic and inorganic fluid impurities. Selecting the right adsorbent [25] involves properly aligning its properties with the specific material to be removed, operational parameters and economic and safety factors.

Activated carbon, a porous material, along with other carbon can absorb a wide variety of substances from liquids, gases and even inside solid materials [26]. To produce activated carbon, heating carbonizes the carbon from the pyrolysis process in an inert atmosphere [27]. Then, in a second step, activate the char by heating it to high temperatures with an oxidizing agent such as steam or carbon dioxide or by impregnating it with chemicals and then heating it so that pores develop in the structure having a large surface area [28].

Bentonite clay is generally the more economical option compared to activated carbon. It is readily available, comes without many manufacturing processes and is therefore cheaper. Because bentonite is found naturally in minerals and the extraction process is relatively easy [29], it is lower than activated carbon in price as well. While this varies depending on where consumers buy and how much consumers purchase, one source indicates that bentonite clay might be at least 20 times less expensive than activated carbon.

Bentonite clay can swell and bind impurities, it comes in handy for detoxification. Zeolite also has a remarkable ability to adsorb toxins, heavy metals at the molecular level [30]. Bentonite change of volcanic ash resulting from the transformation, weathering by water/precipitation becomes hardening into loose pumice ash. Such deposits typically form within areas of previous volcanic activity and subsequent contact with fresh water. In contrast, zeolites naturally form when volcanic ash reacts with alkaline water or in some cases with hydrothermal ground water [31] where it forms crystalline aluminosilicate edifice.

Bentonite is a type of clay with remarkable absorbent and binding properties, while fly ash is byproduct from the combustion of coal that happens to have pozzolanic properties [32]. Bentonite is a naturally occurring clay mineral that is noted for its swelling and absorbent properties, whereas fly ash is used as a cementitious material in construction and elsewhere. Fly ash was made up of silica, alumina, iron and calcium oxides [33]. Fly ash, as a substance, had the appearance of fine powder with pozzolanic properties. Fly ash is often cheaper than bentonite clay. It is typically easier to come by due to the widespread use of coal for power generation. It is priced in tons or quantities such as bulk and is generally regarded as a low-cost material.

Both bentonite and layered double hydroxides (LDHs) are sorbent materials with different characteristics and applications. However, bentonite clay is cheaper than LDH material. LDHs possess a large surface area [34] and significant anion exchange properties and are, therefore, excellent candidates for the removal of anionic pollutants from water. Composite materials with better properties have also been produced by combining bentonite with LDH to satisfy special requirements, for example with better adsorption of anionic pollutants [35].

EFFICIENT REMOVAL OF OTHER POLLUTANTS WITH BENTONITE

At a radioactive waste treatment station, cesium-137 (Cs-137) laden fluid contaminates the environment [36]. Various treatment methods such as adsorption, ion-exchange, evaporation, chemical precipitation, filtration, reverse osmosis and solvent extraction can be used to treat severely radioactive and radio nuclides of long half-life waters. Heavy-metal contamination is common in many industrial effluents like metal plating plants, mining, battery manufacturing process, production of paints and pigments, and glass manufacturing industry. Lead may be absorbed into the body through inhalation, skin absorption, or ingestion, and may have an impact on nearly every system in the body. Low levels of Pb(II) ions have been associated with anemia and high levels of kidney damage. Accordingly, the concentration of the heavy metals in sewage, potable water, and water for agriculture should be decreased to the maximum allowed limit level.

Dyestuffs of various kinds are employed in many industries, and they are present in wastewater [37]. Dye compounds represent a fascinating category of organic chemicals, specifically designed to add vibrant hues to various substrates. Unlike pigments, which remain insoluble and create color through the scattering of light, dyes have a distinct mechanism of action. They operate by dissolving in a liquid medium, allowing them to bind effectively to the materials they are intended to color.

EFFICIENT REMOVAL OF PHARMACEUTICAL COMPOUNDS WITH BENTONITE

The hybrid of ZnO and bentonite generally shows a synergistic relationship; this composite material maintains better performances than those of the single counterpart upon some processes such as photocatalytic degradation. In this regard, the bentonite plays a supporting role that can alleviate agglomeration of ZnO nanoparticles and enlarge surface area of the catalysts for better stability in addition to adsorption of target molecules prior to photocatalysis. In scanning electron microscopy image (Fig. 1), the growth of spherical nanoparticles with average size of 40 nm to 50 nm could be observed. The best performance came from ZnO/Bentonite, which, at room temperature, under solar light irradiation, and at near-neutral pH (pH=6.5), took out 95% of ciprofloxacin 5 mg/l

Table 1 Several types of contaminants that could be removed using bentonite.

Contaminant	**Highlighted results**
Cesium	The highest removal efficiency was 98% and supported by pseudo second order [36].
Lead ion	The highest adsorption capacity [38] in manganese oxide coated (58.8%) if compared to raw bentonite (16.7%) and acid activated (8.9%).
Lead ion	The highest adsorption capacity was 26.3 mg/g [39].
Lead ion	Higher adsorption capacity [40] in modified with hexadecyl trimethyl ammonium bromide (18.75 mg/g) if compared to unmodified bentonite (14.71 mg/g).
Copper and lead ions	Adsorption capacities were 0.6 mg/g and 0.22 mg/g for lead and copper removal [41].
Lead ion	Maximum adsorption capacity was 54.6 mg/g [42].
Lead ion	The highest adsorption capacity [43] was 0.59 mmol/g.
Cadmium, lead ions	Maximum adsorption capacity [44] was recorded for lead (31.04 mg/g) and cadmium (25.03 mg/g) ions in aliquot bentonite. Maximum adsorption capacity was recorded for lead (29.35 mg/g) and cadmium (17.6 mg/g) ions in purified bentonite.
Methylene blue, Crystal violet, Rhodamine B	The highest removal efficacy [45] was 99.99% (methylene blue), 95% (crystal violet) and 83% (Rhodamine B) when the pH was 9.
Malachite green	Adsorption efficiency [46] increases (95.2% to 99.4%) when dye concentration increases (25 to 500 mg/l).
Crystal violet	The highest adsorption capacity [47] was observed (601.9 mg/g) at 70 °C when using bentonite alginate composites.
Reactive Red 120	Adsorption capacity was found to be 1, 2.1, 0.6, and 0.45 mg/g for Tabarka, KGa-2, Fouchana, and Palygorskite, respectively [48].
Disperse blue 56, pigment blue 60	The percentage of removal achieved 85% (disperse blue) and 78% (pigment blue) when using organo-bentonite [49]. The percentage of removal reached 52% (disperse blue) and 45% (pigment blue) when using ordinary bentonite.

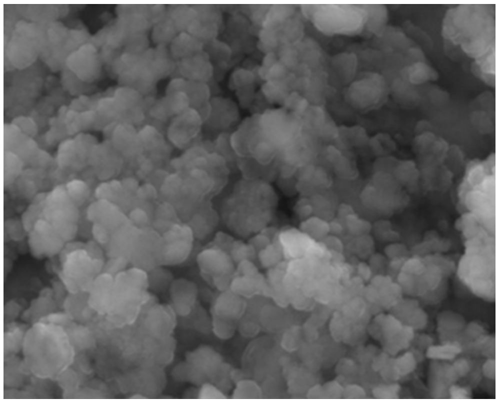

Fig. 1 SEM image for zinc oxide/bentonite [50], reprinted with permission from "Molecules" under the Creative Commons Attribution License CC BY.

in 30 min with 0.5 g/l ZnO/bentonite dosage. The composite also showed efficient simultaneous removal of ciprofloxacin (98%, 5 mg/l) and sulfamethoxazole (97%) within 30 min with only a small 5% decrease in the carbamic acid compound titrated separately from these two pharmaceutical substances at all stages of their development [50]. Further investigation also showed that H^+ (67%), OH (18%) and O_2^- (10%) contribute to the degradation of ciprofloxacin by photocatalytic means and that with holes (H^+) as the dominant oxidizer found in such systems, this type of behavior can be expected for other covalent compounds containing electron affinity.

Montmorillonite is a widely used clay mineral [51], one of the principal components of bentonite. It was used to combine with other polymer-based methods of drug administration. This way, montmorillonite could be used to develop various types of drug delivery systems to control and/or to modify pharmaceuticals, in which aspects such as solubility, release rate and uptake would all be improved. Researchers have prepared bentonite/magnetite composite via coprecipitation of shortened forms for coprecipitate magnetite/bentonite and will then separate back using magnetic field. Particle size was found to be 3.2 µm and showed ferromagnetic properties [52]. Adsorption of nitrofurazone obeyed pseudo second order model and adsorption capacity was 3.2×10^{-2} mmol/g. Nitrofurazone is an antimicrobial organic compound belonging to the nitrofuran class [53].

Morphology of municipal solid waste (MSW) biochar-clay was studied and showed disorder structure [54]. However, the bentonite clay could be identified by intermediate layers or platelike shapes. The nonuniform, flakey structures and many pores were observed. The Hill model supposes that the adsorption of one species on the homogenous substrate, and adsorption capacity was 286.6 mg/g. It was noted that the presence of clay significantly improves the removal. With regards to SEM [54], there are distinguishing features which can be noted between raw bentonite (RBN) and treated bentonite (RBN-1). The raw bentonite consisted of large pseudospherical aggregates of smectite in the range of 5–100 µm with most particles not connected to others. The raw bentonite displayed compact, smooth morphology, resulting in a decrease of the surface porosity. The surface morphology has been transformed after being washed with NaCl. However, the surfaces of RBN-1 sample (677.7 m^2/g) were more porous than those of RBN sample (474.6 m^2/g), as could be seen from the measurement of BET surface area. An exchange capacity between 61.76 and 88.20 meq/100 g was obtained for RBN-1. This can be attributed to the mineralogical transformation of clay minerals.

The highest removal efficiency for sulphamethoxazole (27.85%), metronidazole (37.3%) and trimethoprim (52.4%) were reported. This work presented that the Kenyan pharmaceutical industries established drug preparation, mixing, and the formulation, which generate weak wastewater [55]. Treatment processes varied between factories, but all plants applied coagulation/flocculation (aluminum or iron salts). Among the other treatment processes used in this industry sector were carbon treatment and ozonation. The conventional treatment facilities had to be upgraded because of high doses of chemicals used with low quality of floc formation. Bentonite pre-treatment was efficient since the quality of effluent was better in terms of pharmaceutically active compounds removal, than the one generated using the optimum coagulation with no bentonite, with a lower usage of coagulants. Mesoporous structure in bentonite showed specific surface area (91.6 m^2/g) and average pore width (20 and 80 Å). Adsorption capacity of amoxicillin [56] could be observed greatly affected by pH values such as pH 2.31 (53.9 mg/g), 3.85 (49.99 mg/g) and 7.01 (47.37 mg/g).

The bentonite was organically modified with specific surfactant namely hexadecyl trimethyl ammonium bromide to produce hydrophobic bentonite from the hydrophilic bentonite. The maximum removal of amoxicillin (93%) was obtained [57] at the following optimized conditions such as pH=10, contact time=4 h, agitation speed=200 rpm, adsorbent dosage=3 g and initial concentration=30 ppm. The isotherm models were also studied, and the Freundlich isotherm model fitted better with the experimental results ($R^2 = 94.77\%$), indicating that amoxicillin was heterogeneously adsorbed onto modified bentonite. The adsorption dynamics was investigated. Experimental data fitted well to the pseudo-first-order kinetic model ($R^2 = 95.1$). Thermodynamic analysis revealed that the adsorption process was endothermic physisorption.

Hexadecyl trimethyl ammonium modified

organobentonite is the product obtained after native cation adsorption at planar sites then exchanged with hexadecyl trimethyl ammonium (HDTMA) which is a cationic surfactant. So, the bentonite surface negative charge is converted to a positive surface charge, thus facilitating its removal from wastewater of organic compound like dyes, phenols and drugs. The long hydrophobic tails of the HDTMA molecules intercalated in the bentonite layers leading to an increase on basal spacing, and created a new surface with affinity for organic molecules. Amoxicillin adsorption onto the modified bentonite best fits a pseudo second-order kinetic model and rates were calculated as 0.0187 g/mg min at 20 °C in batch system. The maximum adsorption capacity (26.18 mg/g at 20 °C) was determined by the Langmuir isotherm. The enthalpy values (2.28 kJ/mol) implied that the adsorption of amoxicillin onto hexadecyl trimethyl ammonium modified organobentonite was endothermic and physical in nature, the higher temperature is more favorable for adsorption. Meanwhile, the entropy values (−1.868 J/kmol) indicated that during adsorb amoxicillin, randomness at the solid/solution interface decreased. In general, the magnitudes of the changes in the free energy of physisorption are smaller than those associated with chemisorption. The calculated values of the Gibbs free enthalpy (ΔG°) were 2.83, 2.85 and 2.86 kJ/mol for 20 °C, 30 °C and 40 °C, respectively. The ΔG° values were positive and increased with temperature, indicating that adsorption was spontaneous at higher temperatures. Finally, this modified bentonite was employed for the removal of amoxicillin from wastewaters and effectiveness was reached to 81.9% and 87.5% at 19.0 mg/l and 2.0 mg/l of amoxicillin, respectively [58].

In general, 17α-ethinylestradiol is a laboratory synthesized estrogen which is an active ingredient in birth control pill and has also been detected in surface waters at ng/l levels. It has a toxicity 50 times greater than estrone and 17β-estradiol. The maximum adsorption of 17α-ethinylestradiol with the initial concentration 10 mg/l was 4.2 mg/g and the equilibrium adsorption was attained at 2 h. Correlation coefficient (R^2) values greater than 0.98 show the best fit results for the Langmuir model and Dual-mode model [59]. On the other hand, the obtained results reveal that the pseudo-second order model is proper to express the adsorption kinetic process. The rate controlling step of the latter process was chemisorption in adsorbent-adsorbate interaction using model assumptions of pseudo-second order kinetic.

Removal of ivermectin from aqueous media using bentonite-based organophilic clay. Elovich kinetic model is the best fitted model for the adsorption data, showing that chemisorption is the rate limiting step in the removal of the given drug [60]. The Langmuir and Sips isotherms seem to be suitable for the experimental equilibrium data. The process was found to be spontaneous ($\Delta G^\circ_{\text{ads}} < 0$), endothermic ($\Delta H^\circ_{\text{ads}} > 0$), increase in disorderliness at the solid-liquid interface ($\Delta S^\circ_{\text{ads}} > 0$) and consistent with a physical-chemical adsorption ($E_a = 11.065$ kJ/mol) process under the experimental conditions. Adsorption was favorable at the natural pH of the solution and the organoclays could be successfully regenerated with water and reused in consecutive adsorption cycles. Quantity of ivermectin adsorbed on the organophilic clay varied between 1.78 and 3.88 mg/g.

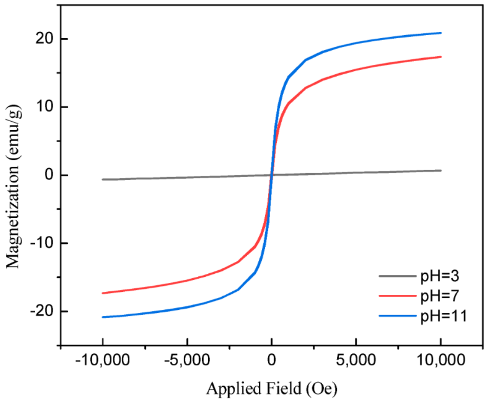

Fig. 2 Magnetization versus applied magnetic field for magnetized bentonite [61], reprinted with permission from "Molecules" under the Creative Commons Attribution License CC BY.

Erythromycin is an efficient antibiotic in the treatment of a variety of bacterial infections. A new adsorbent was prepared by using Fe_3O_4 nanoparticles to modify calcined natural bentonite through magnetization and it showed the superior performance for adsorption of antibiotics. Natural bentonite was calcined to eliminate the hydroxyl groups of natural bentonites, while magnetization changes the crystalline by causing formation of a new composites composite between Fe_3O_4 and infiltration with it. The magnetic characteristics after magnetization of magnetic calcined bentonite at pH values of 3, 7 and 11 are shown in Fig. 2. The results of the data clearly indicate that magnetic behavior is strongest in alkaline environment at pH 11, followed by pH 7 and pH 3, respectively. Surface area was enhanced [61] by the change, and the maximum adsorption was found at pH 11. Optimum conditions interpreted by the quadratic model of 41.9 mg adsorbent, 29.1 °C and 9.6 h for maximum efficiency of the antibiotic removal with 96.2%. The SEM images show that the natural bentonite and bentonite calcined at 500 °C (CB) have an amorphous and dispersed feature. In the XRD pattern of magnetized bentonite (MCB), the characteristic diffraction peaks of Fe_3O_4 can be observed, especially the characteristic peak at $2\theta \approx 35.38^\circ$, which indicates that the Fe_3O_4

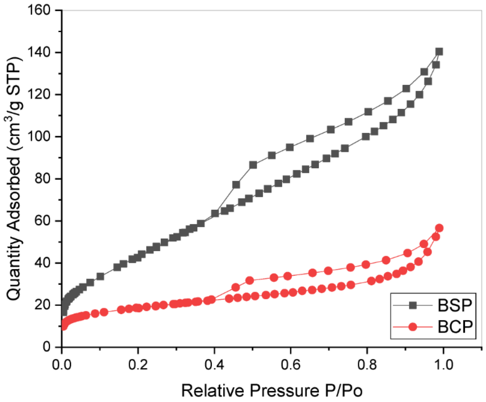

Fig. 3 Nitrogen Adsorptiondesorption isotherms of BSP (pillared sodium bentonite) and (BCP) pillared calcium bentonite [62], reprinted with permission from "Water" under the Creative Commons Attribution License CC BY.

particles were successfully inserted into the bentonite matrix. In contrast to CB, the XRD peaks of MCB display more broadening and weaker intensity, suggesting that the crystallinity has decreased with the introduction of Fe_3O_4 nanoparticles. Surface area of the CB is 41.4 m^2/g, while that of the magnetization one is 61.6 m^2/g. This slight increment implies that the Fe_3O_4 coating is beneficial in enhancing the structural dispersion as well as inhibiting the particle aggregation, leading to an increase in the accessible surface area. The average pore size is reduced from 11.9 nm to 7.6 nm, due to partial blockage of the pore or the structural reorganization by the magnetic modification.

Two kinds of pillared bentonites, namely BSP (pillared sodium bentonite) and BCP (pillared calcium bentonite). They were calcined for 3 h at 500 °C. In the nitrogen (N_2) adsorption isotherm measurements, type IV or type I-type II mixed adsorption isotherms are observed (Fig. 3), indicating that multilayer adsorptions could be accomplished on micro-mesoporous materials having orderly chemical structures. The hysteresis of both samples is of $H4$ type characteristic to mesoporous materials. More quantity of N_2 adsorbed in BSP shows that the structure of BSP has a bigger pore size. The textural characterization of the pillared bentonites indicates an increase in their surface areas compared with the natural bentonites. Surface area of natural calcium bentonite increased from 42 to 63 m^2/g, in case of sodium bentonite from 28 to 162 m^2/g. The increase in the surface area could be ascribed to the increment of pores, where the larger specific surface area was exhibited in columnar clays for it performed better adsorption and increase of the surface area resulted in an enhancement on micropore volume. This could be attributed to the physicochemical changes when intercalation and calcination processes occur while preparing BCP and BSP. BSP has a greater surface area when compared to BCP. The adsorption kinetics of ciprofloxacin on pillared bentonite fit the mixed second-order kinetic model. The BSP isotherm is well described by the Freundlich model. This suggests multi-layer adsorption. Dubinin-Radushkevich model showed that, for the two adsorbents, mostly physical adsorption occurs on ciprofloxacin. The pH-effect test of ciprofloxacin adsorption showed that at a pH range of 6 to 8, it is best absorbed by the two adsorbents, thus suitable to be used in wastewater treatment in this pH range. It is known that the higher specific surface area of BSP followed the order of ciprofloxacin (CIP) adsorption capacity BSP > BCP. For two reasons this can be explained [62]. A sparingly soluble solid, CIP adsorbs better on hydrophobic adsorbates. The most adsorption capacity, in accordance with the Langmuir model, was 106.4 mg/g and 196.1 mg/g for BCP and BSP, respectively. The XRD pattern of BCP and BSP showed that the crystalline degree significantly decreased after the pillar formation, especially in BSP with the introduction of amorphous TiO2 into the structure. In the BCP spectrum, the presence of clear diffraction peaks at 2θ equal to 20°, 23°, 27°, and 50° shows a crystalline structure than BSP. BCP has a higher amount of SiO_2 as quartz and elite or precious inclusions than BSP.

CONCLUSION AND OUTLOOK

Pharmaceutical pollution in water has recently been identified as an environmental and public health concern. This problem stems from the frequent presence of pharmaceutical residues in wastewater. Toxins from pharmaceutical manufacturing, human use, and hospital waste pose significant risks to aquatic ecosystems and human health. This paper looks at how bentonite, a natural adsorbent, can serve as an alternative method for removing pharmaceutical pollutants from water. Bentonite clay is an ultra-fine, natural clay made mainly from montmorillonite and formed from volcanic ash. It is known for its ability to absorb and swell when it encounters water. The results show that key features of bentonite, such as its adsorbing ability, ion exchange capacity, and large surface area, are effectively demonstrated through the prepared nanocomposite, making it a strong material for trapping medications. This works demonstrated how the bentonite-based composites can be used as sustainable materials for the adsorption of hazardous pollutants. However, the following issues hindered the use of bentonite-based composites: (i) The poor regeneration and low adsorption capacity of bentonite-loaded composites. As of right now, bentonite-containing composites have the potential to pollute the environment, come with high treatment costs, and have a limited capacity for adsorption; (ii) their environmental adaptability and biocompatibility are still in their infancy. Consequently, the following are the prospects of bentonite-based composites: First, the development of efficient and recyclable bentonite-bearing composites through large-scale green synthesis technology; second, the investigation of the molecular mechanism of pollutants' reactions with bentonite-bearing composites.

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