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3 **Activated bentonite as a low-cost adsorbent for the removal of Cu(II) and**
4 **Pb(II) from aqueous solutions: Batch and column studies**
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7 Radheshyam R. Pawar¹, Lalhmunsiam², Hari C. Bajaj^{3*} and Seung-Mok Lee^{1,*}
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10 ¹Department of Energy and Environment Convergence Technology
11 Catholic Kwandong University, Gangneung–210701, South Korea.
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14 ²Department of Environmental Engineering
15 Catholic Kwandong University, Gangneung–210701, South Korea.
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18 ³Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), G.B. Marg,
19 Bhavnagar-364002, Gujarat, India.
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54 *Author for correspondence

55 Phone No.: +82-33-649-7535; Fax No: +82-33-642-7635;

56 E-Mail: leesm@cku.ac.kr, and hcbajaj@csmcri.org
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59 **Abstract**
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In this study, the effects of acid activation with high bentonite contents under mild synthetic conditions on textural and structural properties were explored. The alteration features after activation were fully characterized with the help of X-ray powder diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area, Barrett-Joyner-Halenda (BJH) pore size and volume analyses. The active sites were examined using volumetric titration and confirmed with a pyridine adsorbed FT-IR study. The activated bentonite (ABn) was further utilized for the removal of Cu(II) and Pb(II) ions from aqueous solutions. Batch reactor studies showed that the removal of these toxic metal ions was favored by increases in the pH, initial metal concentrations, contact time, and dose of the adsorbents. The equilibrium data obtained at various initial concentrations reasonably fit well with the Langmuir and Freundlich adsorption isotherms. The adsorption process was fast and the kinetic data fit better to the pseudo-second order kinetic model. The presence of other heavy metal ions, such as Cd(II), Fe(II), and Mn(II), did not significantly suppress the removal of both the Cu(II) and Pb(II); whereas the other cations, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺, caused a notable decrease in the Pb(II) removal. In addition, the breakthrough data obtained in the column studies fit well with the non-linear Thomas equation, and high loading capacities of Cu(II) and Pb(II) were obtained. Therefore, we demonstrated in this study that the low cost 'ABn' solid can be employed as a potential adsorbent for the effective treatment of aqueous waste contaminated with Cu(II) and Pb(II).

Keywords: Bentonite, Acid activation, Adsorbent, Cu(II), Pb(II), Column

Introduction

Heavy metal pollution in aquatic environments is one of the biggest concerns for environmentalists due to its high toxicity and persistency. In addition, these toxic heavy metals can accumulate in living tissues, causing various adverse effects and disorders in human beings [1][2]. Copper is a widely used metal and there are many potential sources of copper pollution. The primary sources include various industries, such as plating, mining and smelting, brass manufacturing, electroplating, petroleum refining, and the Cu-based agrichemicals industry [3]. Copper is an essential nutrient in trace amounts, but it is potentially toxic in high doses. The excess intake of copper by the human body may lead to severe mucosal irritation, renal damage, capillary damage, stomach and intestinal irritation, liver and kidney damage, and anemia [4][5]. The presence of higher concentrations (>5 mg/l) in the body has been linked to many health problems such as kidney damage, high fever, hemolysis, and vomiting. In addition, excess copper in marine systems has been found to damage marine life; primarily damaging the gills, liver, kidneys, and nervous system, as well as changing the sexual life of fishes [6].

Lead is another toxic heavy metal which is widely employed in process industries, such as battery manufacturing, metal plating, industries engaged in lead–acid batteries, as well as paint, oil, metal, phosphate fertilizer, electronic, and wood production [7]. Lead is highly toxic to organisms, including humans, even at extremely low concentrations [8]. The Pb^{2+} ion has a high affinity for the enzymes containing thio (-SH) and phosphate ions (PO_4^{3-}), ligands and biomolecules, which inhibit the biosynthesis of haeme units and thus, affect the membrane permeability of the kidney, liver, and brain cells. In addition, Pb forms complexes with the oxo-groups in enzymes, which affects virtually all of the steps in the process of hemoglobin synthesis and porphyrin metabolism. Lead poisoning in humans causes severe damage to the kidneys, nervous system, reproductive system, liver, and brain. Severe

1 exposure to lead has been associated with mental retardation, sterility, abortion, stillbirth, and
2 neonatal deaths [9][10]. Therefore, when considering the toxicity and the environmental
3 risks, Cu(II) and Pb(II) are the heavy metals that are of the most interest for removal or
4 recovery.
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9 To date, many techniques have been reported for the effective elimination of
10 hazardous heavy metals from aqueous solutions such as adsorption, flocculation, coagulation,
11 membrane filtration, electrochemical operations, solvent extraction, bio sorption, as well as
12 various other processes [11][12][13]. Some of these methods are costly and inefficient for
13 controlling heavy metal ion levels in wastewater, and all of these methods have advantages
14 and disadvantages in terms of their effectiveness, cost, and environmental impact. Among the
15 methods noted above, adsorption is preferred as a well-organized technique for the removal
16 of heavy metals from aqueous wastes. This adsorption technique has advantages over other
17 methods due to its unique properties, such as simple design, the use of non-toxic and low cost
18 materials, and the high efficiency in removing pollutants at low level concentrations [6][14].
19 The primary disadvantage of the adsorption process is the high cost of the adsorbent material,
20 which may further increase the price of the wastewater treatment. However, the use of
21 naturally abundant materials offers cost effective and environmentally friendly treatment
22 technologies.
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43 Clays are abundantly available as a natural resource and they are non-toxic to the
44 ecosystem. The cost of clay is relatively low in comparison to other alternative adsorbents,
45 including activated charcoal, natural and synthetic zeolites, and ion exchange resins., Clay
46 minerals have great potential as inexpensive and efficient adsorbents due to their large
47 quantities, chemical and mechanical stability, and structural properties [15]. Clay minerals,
48 such as montmorillonite, bentonite, attapulgite, vermiculite, illite, sericite, and kaolinite, are
49 among the natural materials that have been investigated as potential adsorbents for metals.
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Bentonite has several advantages over other clay minerals due to its intrinsic properties, such as a high cation exchange capacity, high specific surface area, excellent physical and chemical stability, and surface properties [16][17][18]. Bentonite is primarily composed of montmorillonite, which is a 2:1-type aluminosilicate [19]. The inner layer is composed of an octahedral sheet situated between two SiO_4 tetrahedral sheets. Substitutions within the lattice structure of the trivalent aluminum for quadrivalent silicon in the tetrahedral sheet, as well as substitutions of the ions of the lower valence for the trivalent aluminum in the octahedral sheet, result in a net negative charge on the clay surfaces. The charge imbalance is offset by exchangeable cations, such as H^+ , Na^+ , or Ca^{2+} , on the layer surfaces. In aqueous solutions, water molecules are intercalated into the interlamellar space of bentonite, leading to an expansion of the minerals. The chemical nature and pore structure of bentonite generally determine their adsorption ability [20][21].

During recent years, the modification of clay to increase its adsorption capacity for the removal of contaminants from aqueous media has been studied [22]. Several research groups have focused on the improvement of the structural and textural properties of smectite clays and their applications in waste water treatments [22][16]. One of the common methods for the modification of smectite clay is through acid activation, in which clays are treated with a mineral acid solution, usually HCl or H_2SO_4 , at a suitable temperature [23]. It has been reported that the activation of clay by acidification can significantly enhance the adsorption capacity of raw clay [24][25]. The general protocol for the acid activation of bentonite clay minerals involves the treatment of clay with sulphuric or hydrochloric acid at moderately high to high temperatures, followed by washing, drying, and extruding into the desired shape and size [26]. The acid treatments result in a number of metal ions in the octahedral layer and impurities, such as calcite, and are removed by leaching with an inorganic acid at elevated temperatures [27]. In addition, the edges of the platelets are opened and consequently, the

pore diameters and surface area are increased [28][29].

The effects of the acid concentration, time, and temperature during the acid treatment on the physicochemical properties and the adsorptive properties of the activated clays **that are obtained** have been well reported in the literature [29]. However, there is little information **in the literature regarding systematic** efforts to develop an optimized acid activation protocol under mild synthetic conditions with **a** high clay content, which is important for the production of high **yields** of the adsorbent. It is also important to take into account the mineral composition of **the** starting materials from various deposits. Therefore, the objective of this study **was** to investigate the structural and textural changes in bentonite with a high clay content by acid treatment and the application of **an** activated sample for **the** efficient removal of Cu(II) and Pb(II) from aqueous solutions under various physico-chemical parameters.

Materials and Methods

Materials and chemicals

The raw bentonite lumps were collected from the Kutch region, which is located in Western India. Approximately 500 g of a raw bentonite lump was dried in a hot air oven, milled in a mixer, and then the fine powder was collected by passing **it** through a 100-mesh **British standard sieve (BSS)**. The obtained sample was designated as BnR (bentonite raw). The BnR was utilized for certain important properties and physiochemical characterization. The important properties of natural bentonite are **presented** in **Table 1**.

The chemicals *viz.*, nitric acid, sodium hydroxide, iron sulphate, and copper(II) sulphate were obtained from Duksan Pure Chemicals Co. Ltd., Korea, and the manganese nitrate, cadmium(II) sulphate, and lead(II) nitrate were obtained from the Junsei Chemical Co. Ltd., Japan. The concentrated H₂SO₄ (98%) was procured from Qualigens Fine Chemicals, India. The stock solutions (1,000 mg/L) of the Cu(II) and Pb(II) were prepared by

dissolving the exact quantity of the respective salts in double distilled water. The stock solutions were diluted further to reach the required experimental concentrations. The other chemicals used for the experiments were of analytical reagent (A.R.) grade and were obtained from Merck, SD Fine, and Spectrochem. All of the chemicals were used without further purification.

Acid activation

An acid activation experiment was performed with a clay concentration of 6% (w/v), which was optimized by varying the clay concentration. In addition, a clay concentration greater than 6% (w/v) resulted in the unsuitable mixing of the acid and clay, due to swelling and the high viscous nature of the clay slurry. Therefore, a clay concentration of 6% (w/v) was selectively used to achieve a homogenous mixture for the experiments. In the detailed experiments, precisely 60 g of natural bentonite lumps were soaked overnight in the calculated amount of de-ionized water, and they were treated with a calculated amount of 6 N sulphuric acid at 65 °C for 10 h. After the completion of the reaction, the solid product was separated by centrifugation (Kubota 6,500 centrifuge) and washed with deionized water. The washing cycle was repeated until the solid product was free from sulphate ions and the sample was subsequently dried at 110 °C overnight. The activated solid product was milled and passed through a 100 mesh BSS sieve. The obtained product was designated as ABn (acid activated bentonite). The results of the alteration of the textural properties along with the acid activation conditions are summarized in **Table 2**.

Characterization

The powder X-ray diffraction analysis was carried out using the Philips X pert MPD system in a 2θ range of 2–70° using Cu K α ($\lambda = 1.54178\text{\AA}$) radiation. The nitrogen adsorption/desorption measurements for the evaluation of the textural properties (surface area, total pore volume, and pore size distribution) were performed at 77 K using ASAP 2010

(Micrometrics USA). Prior to the measurements, the samples were degassed at 423 K for 4 h to remove any residual moisture. The BET specific surface areas were calculated from the adsorption data in the relative pressure (P/P_0). The pore size and pore volume were calculated using the BJH method applied to the desorption leg of the isotherms. The FT-IR spectroscopic measurements were carried out using a Perkin Elmer GX spectrophotometer. The chemical analysis for the elemental compositions in the samples was carried out by XRF analysis, using an S4 pioneer Bruker AXS XRF analyzer. In order to determine the morphologies of the samples, SEM micrographs were obtained from a Leo series 1430 VP. The loss of ignition was determined separately at 1,000 °C (2 h).

Titrateable acidity and pyridine adsorption FT-IR study

In general, activated clay has many attractive features regarding its structure, including active sites such as hydroxyl groups, surface acidity (i.e., an acidity resulting from adsorbed sulphuric acid and aluminum sulphate), and Lewis and Brønsted acidity. The acidity of the acid-activated clay was measured using the so-called “boil-out” volumetric titration method, and was expressed in milligrams of KOH per gram of the sample. More specifically, 1 g of the sample (previously dried at 110 °C for 6 h) was boiled and stirred for 15 min with 20 ml of distilled water. Then, the clay water suspension was titrated with a 0.01 N potassium hydroxide (KOH) solution using phenolphthalein as an indicator. The acidity was then determined in mg of KOH used per gram of clay using Equation (1), as follows:

$$\text{Acidity} = [(V \times N \times 56.10) / \text{Wt.}] \times 100, (1),$$

where V is the volume of KOH used in the titration (ml), N is the normality of the potassium hydroxide solution, and Wt. is the weight of clay (g) [30][31].

The nature of the Brønsted and Lewis acid sites of ABn was determined using pyridine adsorption with spectroscopic measurements. For the FT-IR analysis of the adsorbed pyridine, the samples were oven dried at 373 K for 3 h. The oven-dried samples (0.2 g) were

placed in a sample cup and exposed to pyridine vapors in vacuum desiccators with 25 ml of dry pyridine. The sample cup was then kept in a vacuum for 4 h. Subsequently, the samples were evacuated for 30 min at room temperature to desorb the physisorbed pyridine, and the FT-IR spectrum was recorded in the spectral range of 1,200–1,900 cm^{-1} using a KBr disc [30][32].

pH pzc measurement

The pH point of zero charge (pzc) of ABn was obtained by following a previously reported method [23][33]. In details 500 mL of double distilled water was boiled in an Erlenmeyer flask for 20 min to remove all of the dissolved CO_2 . The flask was immediately capped to prevent the re-absorption of atmospheric CO_2 . 50 mL of 0.01 mol/L NaCl solution was prepared using this water, and the pH of the solution in each flask was adjusted to the pH levels of 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 by adding 0.1 mol/L HNO_3 or 0.1 mol/L NaOH solutions. Then, 0.15 g of the ABn was added to each flask and the flasks were agitated at 25 ± 1 °C for 24 h. the final pH of the solution was measured again using the pre-calibrated pH meter. The pH pzc was determined to be the point at which the pH_{final} was equal to the $\text{pH}_{\text{initial}}$.

Batch reactor studies

Batch experiments were carried out to study the effects the of sorptive pH, initial metal concentration, contact time, dose of the adsorbents, and presence of other cations on the removal of Cu(II) and Pb(II) using ABn. The adsorption of Cu(II) and Pb(II) was investigated by taking 0.1 g of ABn in 50 ml of Cu(II)/Pb(II) solution, i.e., 2.0 g/L. The effects of the initial metal concentrations and the contact time were studied under two different ABn doses, 2 g/L and 4 g/L. The solution mixture was equilibrated using an automatic shaker at 25 ± 1 °C for 12 h in order to complete all of the sorption processes, except for the effects of the contact time studies. The equilibrated solutions were filtered using a cellulose mixed ester syringe filter (0.45 μ) and the final pH was measured. The bulk sorptive concentration of the filtered

solutions were determined using an atomic absorption spectrometer (AAS) (Fast Sequential AAS: Model AA240FS, Varian). The solution pH was adjusted by adding drops of 0.1 M HNO₃ and 0.1 M NaOH for the entire experiment.

Fixed-bed column reactor studies

The column experiments were performed using a glass column that had a 1 cm inner diameter, packed with 1.0 g of ABn in the middle of the column, and the rest of the column was filled with glass beads. The solution concentration of Cu(II) and Pb(II) was approximately 25 mg/L and the pH was maintained at 5.0. The sorptive solution was pumped upward from the bottom of the column using an Acu-flow Series II High-Pressure liquid chromatograph at a constant flow rate of 1.00 mL/min. The effluent samples were then collected using a Spectra/Chrom CF-2 fraction collector and the total bulk sorptive concentration was measured using AAS.

Results and Discussion

Characterization of the sample

X-ray diffraction studies

Powder X-ray diffraction (XRD) is one of the primary techniques used for tracking changes in the layer spacing of clay minerals [34]. The structural changes that occurred in the clay material due to the acid treatment were studied using the X-ray diffraction technique. **Fig. 1** depicts the XRD profiles of the natural and acid activated bentonite samples. A typical characteristic peak of the '001' plane of bentonite was at a 2 θ value of 6.80° (d spacing of 12.98 Å). The presence of montmorillonite (M), kaolinite (K), and quartz (Q) in the XRD profile of the BnR sample confirmed the presence of the smectite phase [35]. The presence of the smectite phase was also confirmed with the ethylene glycol experiments that resulted in the expansion of the basal d spacing of 17Å, which is characteristic of smectite. In general, the '001' reflection appeared broad and weak after acid activation due to the partial

destruction of the layered structure of the smectite [36]. The reduction in the intensity and the increase in the width of the '001' peak indicated that the crystallinity of the BnR was considerably affected by the acid activation. The activated clay sample (ABn) obtained under optimized conditions (6 N H₂SO₄ 6% w/v clay concentration) showed a 2 θ reflection at 6.80°, which was shifted towards the lower angle with a decrease in the peak intensity (2 θ value of 5.85° and spacing of 19.77 Å). If the activation was conducted under harsh acidic conditions, then the '001' reflection would completely disappear, favoring the production of the amorphous phase by the decomposition of the clay structure [27][37]. The acid treatment conditions that were applied for the activation of the BnR did not damage the inherent layered structure of the bentonite. This result implied that the pristine clay structure was partially destroyed. The balance between the acid attack and the structural preservation hold the key for the establishment of optimal adsorbent parameters. However, the '020' and '060' peaks of the BnR remained unchanged after the 6 N H₂SO₄ acid treatments.

Infra-red spectroscopic studies

The spectra of the original bentonite and the ABn are shown in **Fig. 2**. The spectrum of the original clay exhibited absorption bands at 3,417 and 1,640 cm⁻¹ assigned to the stretching and bending vibrations of the -OH groups, respectively, for the water molecules adsorbed onto the clay surface. Further, a band at 3,638 cm⁻¹ representing the stretching vibration of the -OH groups coordinated with the octahedral Al³⁺ cations. The Si-O bands were strongly evident in the silicate structure of the original clay and could easily be recognized in the infrared spectrum as very strong absorption bands in the 1,100–1,000 cm⁻¹ region. The most intensive band at 1,031 cm⁻¹ was attributed to the Si-O in the plane stretching, and the band at 1,125 cm⁻¹ was due to the Si-O outside of the plane stretching vibration. The bands at 530 and 464 cm⁻¹ corresponded to the Si-O-Al (octahedral) and Si-O-Si bending vibrations,

respectively. The treatment of bentonite with 6 N H₂SO₄ acid resulted in the formation of slender amorphous silica, which complemented the data obtained from the XRD. These results suggested the partial depletion of Al, Mg, and Fe from the clay structure, in accordance with the changes in the chemical composition. The intensity of the bands at 3,417 and 1,640 cm⁻¹ for water used in the hydration, as well as the hydroxyl stretching band at 3,617 cm⁻¹, also showed a significant change after acid activation. However, the persistence of a weak band at 1,039 cm⁻¹ indicated that the layered structure of the original clay was not fully destroyed, which was in agreement with the XRD results. The progressive widening of the 1,041 cm⁻¹ band, together with the increase in intensity of the 793 cm⁻¹ band (tridymite), indicated the formation of amorphous silica. In conclusion, the IR spectrum of the activated clays indicated that acid leaching affects both the octahedral and the tetrahedral sheets [27][38].

Textural properties

The N₂ adsorption–desorption isotherms of the raw, purified, and acid activated bentonite samples are presented in **Fig. 3 (A)**. The isotherms of these samples were of type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification. In addition, all of the samples contained a pronounced type of H₃ hysteresis loops. Such hysteresis is usually found on solids consisting of aggregates or agglomerates of particles forming slit-shaped pores, with non-uniform size or shape, which confirmed the isotherm for layered clay material that can be attributed to the multilayer formation and capillary condensation in mesopores [39][40]. The most important textural changes caused by acid-activation were an increase in the specific surface area (SA) and the pore volume (PV) of the clay due to the splitting of particles within the dissolved octahedral sheets [41]. The extent of these changes depended on the activation conditions, i.e., the acid strength, temperature, and time of the treatment [29]. The textural properties of the samples before and after the acid treatments are

shown along with the raw bentonite in **Table 2**. An approximately 3.3 times increase in SA and an approximately 2.75 times increase in the PV were observed after treatment with the 6 N H₂SO₄ acid. The pore size distribution curves of the raw bentonite (BnR) and the acid treated bentonite (ABn) samples are given in **Fig. 3 (B)**. It was observed that the dominant pore fell in the diameter range from 3 to 6 nm. The acid treatment caused the formation of smaller pores in the solid particles, resulting in a higher surface area. The acid activation caused variation in the morphology of the solid particles, which were responsible for the enhancement of the adsorption properties of the activated samples due to an increase in the porosity of the original material [42][43].

XRF analysis for chemical composition

The XRF analysis was carried out to determine the chemical compositions of the clay before and after the acid treatment. **Table 3** shows the results of the chemical analysis of the pristine and acid activated bentonite samples. Pristine clay contains SiO₂, Al₂O₃, and Fe₂O₃ in large quantities, whereas the other oxides, such as MgO, CaO, Na₂O, K₂O, and TiO₂, are present in trace amounts. It was observed that the chemical composition of the parent clay was considerably changed during the acid treatment. The acid treatment resulted in a gradual increase in the amount of SiO₂ in the ABn samples at the expense of the octahedral cations and tetrahedral Al from the smectite structure. The majority of the exchangeable cations and most of the Fe, Mg, and Al atoms in the octahedral sheet of the ABn sample were removed and, therefore, the relative quantity of the Fe₂O₃, Al₂O₃, MgO, CaO, K₂O, and Na₂O contents in the acid treated material decreased [37].

Scanning electron microscope (SEM) study

The SEM was used to probe the changes in the morphological features of the natural bentonite and the activated samples. **Figures 5 (A)** and **5(B)** show the SEM micrographs of the BnR and ABn samples. The surface morphology of the natural clay was different from

that of the acid treated samples. The ABn (**Figure. 5B**) had larger pores between the particles than the BnR (**Figure. 5A**). In addition, the BnR appeared to be highly compact, so the inter-particle pores were smaller in the BnR sample than those in the ABn sample. The micro-graphs of the acid treated bentonite indicated the disaggregation and decrease in the size of the clay structure by the acid treatment [44].

Titrateable acidity and pyridine adsorption FT-IR study

The total acidity of the activated clays was higher than that of the pristine bentonite sample, because of the replacement of exchangeable cations with protons and due to the fact that the aluminum and iron exsolved from the octahedral sites were relocated in the interlamellar space and acted as acid centers. The titrateable acidity for ABn was found to be 29-30 mg KOH/g clay. The alkali titration results of the ABn evidenced the presence of surface acidity (Table 2). Pyridine as an adsorbed molecule is an important tool for the confirmation of surface acidity because, it interacts differently with solid surface acid sites depending on the nature of the acid sites, i.e., the Brønsted or Lewis sites. Fig. 5 shows the spectra, recorded after the pyridine adsorption on the acid activated clay sample ABn. The FT-IR spectra of the adsorbed pyridine showed the bands described in literature at 1,600, 1,545, 1,492, and 1,446 cm^{-1} . The bands at 1,545-48 cm^{-1} were assigned to the Brønsted pyridine sites and those at 1,445-47 and 1,600 cm^{-1} were assigned to the hydrogen bonding between the pyridine atom and the -OH groups of the clay mineral. A strong band at 1,492 cm^{-1} indicated the combined presence of all of the acid sites, i.e., Lewis py+Bronsted py+Hydrogen. However, according to previous reports the unmodified bentonite after pyridine adsorption shows weak acid sites and broad band due to -OH at 1,638 cm^{-1} , which was attributable to the presence of interlayer water [30][45].

Batch Reactor Operations

Effects of the pH

The pH of a solution is the most influential parameter in metal removal because it greatly affects the surface charge of the adsorbent as well as the speciation of the metals in the solution [46]. Therefore, the effects of the pH were studied between the initial pH values of 2.0 and 9.0, and the pH of the solutions of Cu(II) and Pb(II) were determined to be 8.20 and 9.79 mg/L, respectively. It was observed that the pH of the metal solutions significantly affected the removal of these two metal ions and the results obtained were plotted as the percent removal of the metals as a function of the initial pH of the solution. These results are shown in **Fig. 6**. In the highly acidic solution, the percentage removal of these two ions was extremely low due to the competition that occurred between the excess of hydrogen ions and the positively charged metal ions towards the same active sites of the solid surface, which consequently suppressed the metal ion adsorption from the solution [47]. The increase in the solution pH gradually reduced the H^+ ion concentrations, which resulted in greater electrostatic attraction of the metal cations towards the negatively charged surface of the ABn. Therefore, with an increase in the initial pH from 2.0 to 4.0, there was a drastic increase in the removal of both the Cu(II) and Pb(II). However, there was a slight increase in the percent removal between the pH values of 4.0 to 7.0, and the percentage removal remained almost constant beyond a pH value of 7.0. In addition, the pH_{PZC} of ABn was found to be 4.32. This result suggested that the activated material carried the surface net positive charge below this pH value and it possessed a net negative charge beyond this pH value. Therefore, the uptake of Cu(II) and Pb(II) at low pH values was not favored due to the strong repulsive forces operating between the positively charged surface and the divalent cations of these two metal. The percentage removals of Cu(II) and Pb(II) were also extremely low. On the other hand, the electrostatic attraction between the solid surface and the metal ions significantly increased the removal of Cu(II) and Pb(II) within the pH range of 4 to 10. Similar effects of the pH were previously reported for the removal of Cu(II) and Pb(II) using AC and iron impregnated

AC [48].

Effects of the initial metal concentration

In the batch reactor experiment, the initial concentration of metal ions in the solution played an important role as a driving force to overcome the mass transfer resistance between the aqueous and solid phases. The effects of the initial metal concentration study were carried out by changing the initial concentration between 1.0 mg/L and 20.0 mg/L for both the Cu(II) and Pb(II) at a pH value of 5.0 using two different solid doses, i.e., 2 g/L and 4 g/L. The results obtained were plotted as the percentage removal against the initial metal concentration (mg/L) as shown in **Fig. 7**. It was observed that a high percentage removal at a low metal concentration gradually decreased with an increase in the initial sorptive concentration. This result was due to the fact that a relatively larger number of active sites were available on the solid surface for a smaller number of sorbing ions at a low concentration of metal ions. However, an increase in the sorptive concentration for the same dose of solids with a relatively smaller number of active sites resulted in a lower percentage removal of the metal ions [49]. However, a high percentage uptake of Pb(II) was obtained even at higher concentrations using a 4 g/L solid dose. The amount of Pb(II) removal was increased from 0.536 to 5.955 mg/g and 0.501 to 5.21 mg/g using 2 g/L and 4 g/L, respectively, while increasing the initial Pb(II) concentration from 1.0 to 20 mg/L. Similarly, the amount of Cu(II) adsorbed was found to increase from 0.548 to 3.410 mg/g and 0.499 to 2.76 mg/g using 2 g/L and 4 g/L, respectively, while increasing the initial Cu(II) concentration from 1.0 to 20 mg/L.

The concentration dependence data obtained were analyzed using Langmuir adsorption isotherm [50] and the Langmuir adsorption equation was taken in its linear form (Eq.2).

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o}, (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g) at equilibrium; C_e is the equilibrium bulk concentration (mg/L); q_o is the Langmuir monolayer adsorption capacity, i.e., the amount of solute required to occupy all of the available sites in the unit mass of the solid sample (mg/g); and K_L is the Langmuir constant (L/g). The graphs were plotted between the C_e/q_e versus C_e values and a fairly straight line was obtained. The regression coefficient, i.e., R^2 values, indicated a good fit to the Langmuir adsorption model for both the Cu(II) and Pb(II). The values of the Langmuir monolayer adsorption capacity (q_o), Langmuir constant (K_L), and the R^2 values were obtained, and are shown in **Table 4**. The Langmuir monolayer adsorption capacity obtained for Pb(II) was higher than that obtained for Cu(II) and the adsorption capacity obtained for Cu(II) and Pb(II) decreased with an increase in the dose of the adsorbents from 2 g/L to 4 g/L. A similar decrease in the adsorption capacity with an increase in the adsorbent dose was previously reported for the removal of malachite green using zinc nanoparticles loaded onto activated carbon [51]. The higher values of the Langmuir constant may be further reflected in the strength and affinity of the ABn towards these two metal ions [52].

Similarly, the equilibrium sorption data obtained from the concentration dependence study were further evaluated using the Freundlich adsorption isotherm model [53]. The Freundlich adsorption equation was taken in its linear form (Eq. 3) as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (3),$$

where q_e and C_e are the amount adsorbed (mg/g) and bulk sorptive concentration (mg/L) at equilibrium, respectively, and K_f and $1/n$ are the Freundlich constants referring to the adsorption capacity and the adsorption intensity, respectively. The graph was plotted as $\log q_e$ versus $\log C_e$ and it was observed that the fitting of the concentration dependence data to the Freundlich equation was relatively low in comparison to the Langmuir adsorption isotherm.

The calculated constants value along with the R^2 values are shown in **Table 4**. The fractional values of $1/n$ ($0 < 1/n < 1$) obtained for these systems indicates a heterogeneous surface structure of the material employed with an exponential distribution of the active sites. Further, a strong affinity of ABn towards these two metal ions was inferred by the relatively higher values of the Freundlich sorption capacity that were obtained [52]. The **Langmuir monolayer adsorption capacities of the various adsorbents along with the ABn are presented in Table 5.** The difference in the adsorption capacity of the various adsorbents was due to the difference in the various physical-chemical properties of the adsorbents as well as the experimental factors including the concentration range of the metal ions, pH, temperature, estimation method, and ionic strength, etc. [23].

Effects of the contact time

The time dependence study provided information about the rate at which the pollutant was removed from the solutions and the time required to achieve adsorption equilibrium. These parameters are important for designing an adsorption process. The effects of the contact time in the removal of Cu(II) and Pb(II) using ABn were studied at various initial concentrations with two different adsorbent doses. The solution was maintained at a pH of 5.0. In this study, a 2 g/L solid dose was used to treat the Cu(II) and Pb(II) solutions with concentrations of 9.47 and 5.63 mg/L, respectively. In addition, another set of experiments was performed in which 4 g/L of ABn was used to treat the Cu(II) and Pb(II) solutions with concentrations of 23.40 and 21.83 mg/L, respectively. The percentage removal of the two metal ions after various contact times are shown in **Fig. 8**. It was observed that an increase in the contact time favored the uptake of Cu(II) and Pb(II) from the aqueous solutions. The adsorption rates obtained for a 2 g/L solid dose were different from that of a 4 g/L solid dose for the two metal ions. When the adsorbent dose was maintained at 2 g/L, the percentage uptake of Cu(II) and Pb(II) steadily increased with time and an apparent equilibrium at the

solid/solution interface was achieved within 5 h. However, a very fast adsorption rate was observed within the initial 30 min using 4 g/L of ABn solid, and a further increase in the contact time slowly increased the percentage removal of the two metal ions. Similar effects of the contact time in the removal of Cu(II) and Pb(II) ions were previously observed using activated carbon and manganese immobilized activated carbon adsorbents [6]. In addition, sorption kinetic data collected were analyzed with pseudo-first order kinetic and pseudo-second order kinetic models in order to clarify the adsorption kinetics of the Cu(II) and Pb(II) onto the ABn surfaces. The equations were taken in their linear forms as follows [57]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \quad (4) \text{ and}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5),$$

where q_e is the maximum adsorption capacity (mg/g) and q_t (mg/g) is the amount of the metal ions adsorbed at time t . The values of k_1 (min^{-1}) and k_2 ($\text{g/mg}/\text{min}$) are the adsorption rate constants of the pseudo-first order and pseudo-second order models, respectively. The plot of the $\ln(q_e - q_t)$ versus t and the plots of $\frac{t}{q_t}$ against t for the pseudo-first order kinetic and pseudo-second order kinetic models, respectively, are shown in **Fig. 9 (a&b)**. The unknown values, such as the adsorption capacity (q_e) and the rate constants (k_1 and k_2), were calculated from the slope of the plot and the values obtained are shown in **Table 6**. The kinetic data showed a better fit to the pseudo-second order kinetic model with the R^2 values of 0.988 and 0.980 for Cu(II) and Pb(II), respectively.

Intra-particle diffusion

The time-dependent intra-particle diffusion rates of the Cu(II) and Pb(II) from the surface adsorption sites onto the interior sites of the material were evaluated using the kinetic-based model developed by Weber and Morris [58]. According to this theory, intra-particle diffusion is the rate-limiting step, assuming the plots of the amount of metal adsorbed

per unit mass of adsorbent (q_t) against the square root of time ($t^{1/2}$) are linear and pass through the origin. The intra-particle diffusion model (Eq. 6) was expressed as follows:

$$q_t = k_{id}t^{\frac{1}{2}} + Z, \quad (6)$$

where k_{id} is the intra-particle diffusion rate constant ($\text{g/mg/min}^{1/2}$) and Z is the intercept. The intra-particle diffusion plots of Cu(II) and Pb(II) at various concentrations and the different doses of the ABn are shown in Fig. 9(c). The time dependent adsorption data fit well to the intra-particle diffusion model and this result suggested that intra-particle diffusion plays a significant role in the removal of Cu(II) and Pb(II) from aqueous solutions using ABn [59]. However, the plot of q_t versus $t^{1/2}$ showed a deviation from the origin, especially in the removal of Pb(II) using 4g/L of ABn. This result might have been due to the difference in the mass transfer during the initial and final stages of the sorption process [60]. The intra-particle diffusion constants along with the R^2 values are given in **Table 6**.

Effects of the doses of adsorbents

In order to optimize the effects of the dose of the adsorbents on the removal of Cu(II) and Pb(II), batch experiments were performed in which the dose of the ABn was increased from 0.5 g/L to 5.0 g/L, and the initial sorptive concentration and pH of the sorptive solution were maintained at approximately 10 mg/L and 5.0, respectively. The percentage removal of the metal ions versus the dose of the adsorbents is plotted in **Fig. 10**. With an increase in the amount of adsorbents, the surface area or the number of active sites were naturally increased for the sorption reaction. Therefore, the percentage uptake of the Cu(II) and Pb(II) increased with an increase in the adsorbent dosage [61]. The percentage removal of both of the metal ions promptly increased, while the dose of the adsorbents was increased from 0.5 to 2.0 g/L. However, a further increase in the sorbent amount beyond 2.0 g/L was found to be less significant especially in the removal of Pb(II). Therefore, a 2.0 g/L dosage was applied in this study.

Competition with other metal ions

The removal of these two metal ions was studied in the presence of several co-existing cations with the initial Cu(II)/Pb(II) concentration of approximately 10.0 mg/L at pH 5.0. The concentration of the co-existing ions was maintained at about 50.0 mg/L. The heavy metal ions, such as Cd(II), Fe(II), and Mn(II), and the alkali and alkaline earth metals, such as Na, K, Ca, and Mg, were selected as the competing ions and the results are given in **Fig. 11**. The uptake of Cu(II) was slightly decreased by the presence of Cd(II), Fe(II), and Mn(II); although the removal of Pb(II) was not significantly affected by the presence of these three heavy metal ions. On the other hand, the presence of Na, K, Ca, and Mg notably decreased the uptake of Cu(II) and Pb(II) from the aqueous solutions using ABn. In addition, the removal of Pb(II) was more affected by the presence of alkali or alkaline earth metal ions. However, it could be observed that more than 40% of Cu(II) was removed in the presence of these cations except in the presence of Ca in which 35% of the Cu(II) was removed. Therefore, these results showed that ABn could be effectively applied for the removal of Cu(II) in the presence of other heavy metal ions, or alkali or alkaline earth metal ions; whereas Pb(II) could be selectively removed in the presence of other heavy metal ions using ABn [62].

Fixed-bed column reactor studies

The fixed-bed column experiments were performed at a relatively higher concentration of the metal ions, i.e., about 25 mg/L for Cu(II) and Pb(II), and with a pH of 5.0 as a constant. The results are presented graphically in **Fig. 12**. The complete breakthrough occurred at the throughput volumes of 0.5 L and 1.3 L for Cu(II) and Pb(II), respectively. These results inferred that the ABn possessed a significantly higher loading capacity for these metal ions, even under these dynamic conditions. The data obtained were further utilized to optimize the loading capacity of these solids under the dynamic conditions using the non-linear Thomas

equation (7) as follows [63]:

$$\frac{C_e}{C_o} = \frac{1}{1 + e^{(K_T(q_o m - C_o V))/Q}}, \quad (7)$$

where C_e is metal concentration in the effluent (mg/L), C_o is the metal concentration in the feed (mg/L), K_T is the Thomas rate constant (L/min/mg), q_o is the maximum amount of Cu(II)/Pb(II) that could be loaded (mg/g) under the specified column conditions, m is the mass of the adsorbent loaded (g), V is the throughput volume (L), and Q is the flow rate of the pumped sorptive solution (L/min). The Thomas equation was successfully used to fit the column data, and the unknown parameters, q_o and K_T , were evaluated. The values obtained are given in **Table 7**. The results showed that relatively higher amounts of Cu(II) and Pb(II) were loaded into the column packed with ABn, and the loading capacity of Pb(II) was higher than that obtained for Cu(II), which was in accordance with the results obtained from batch reactor studies.

Conclusions

In summary, we developed a novel protocol to obtain a low cost adsorbent from naturally abundant bentonite clay by simple acid activation under mild synthetic conditions. The solid materials were fully characterized with the help of XRD, XRF, FT-IR, SEM, and BET analyses. The parent clay composition was considerably changed after the acid treatment. The specific surface area and pore volume of the 6 N H₂SO₄ treated clay were found to increase by 3.3 and 2.75 times, respectively. The activated material was then efficiently utilized for the removal of Cu(II) and Pb(II) from aqueous solutions.

The batch experiments showed that the removal of Cu(II) and Pb(II) were favored by an increase in the pH of the solution. High percentage removals of Cu(II) and Pb(II) were obtained at lower initial metal concentrations. However, the extent of removal significantly increased with an increase in the initial metal concentrations. The equilibrium data obtained at various initial concentrations fit well to both the Langmuir and Freundlich adsorption

isotherms. The adsorption processes were found to be fast and the kinetic data showed a better fit to the pseudo-second order kinetic model. It was observed that intra-particle diffusion played an important role in the removal of these two metal ions. The presence of other heavy metal ions did not significantly suppress the removal of both Cu(II) and Pb(II), whereas the other alkali or alkaline earth metal cations, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺, showed a notable decrease, particularly in Pb(II) removal. In addition, the fixed bed column experiment was performed and the breakthrough data reasonably fit well to the non-linear Thomas equation. The loading capacities were estimated and found to be 9.793 and 21.359 mg/g for Cu(II) and Pb(II), respectively. Therefore, the results of this study suggested that the ABn obtained from naturally abundant bentonite clay could be adequately used for the treatment of aqueous waste contaminated with Cu(II) and Pb(II).

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Figures Legend

Fig. 1. Powder X-Ray diffraction patterns of the bentonite samples before and after the acid treatments (M: Montmorillonite, K: Kaolin, Q: Quartz).

Fig. 2. FT-IR spectra of the natural bentonite (BnR) and acid activated bentonite (ABn).

Fig. 3. (A) N₂ adsorption-desorption isotherm of the pristine raw and acid activated bentonite samples. (B) BJH pore diameter distribution patterns of the bentonite samples before and after the acid treatments.

Fig. 4. SEM image of the bentonite samples before and after the acid treatments: (A) BnR and (B) ABn.

Fig. 5. Pyridine adsorption FT-IR spectra of acid treated ABn.

Fig. 6. Effects of the pH on the removal of Cu(II) and Pb(II) using ABn.

Fig. 7. Percentage removal of the Cu(II) and Pb(II) at various initial concentrations using two different doses of ABn.

Fig. 8. Effects of the contact time on the removal of the Cd(II) and Pb(II) using two different doses of ABn.

Fig. 9. Plots of the (a) pseudo-first order and (b) pseudo-second order kinetic models for the Cu(II) and Pb(II).

Fig. 10. Effects of the dose of the adsorbents on the removal of the Cu(II) and Pb(II).

Fig. 11. Percentage removal of the Cu(II) and Pb(II) in the presence of other cations.

Fig. 12. Breakthrough curve obtained for the Cu(II) and Pb(II).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Table 1. Characteristics and properties of the natural bentonite (BnR).

Properties	Swelling ¹	LOI ²	CEC ³	pH ⁴	WI ⁵	Bulk Density ⁶	
						cc/g	
						Loose	Packed
BnR	26	20.3	75	9.09	23	0.80	1.22

¹ Method from the specification for bentonite, published by the Bureau of Indian Standard publications, BIS IS 6186:1986 (R2003). ² Loss of ignition was determined gravimetrically at 1,000 °C (2 h). ³ The cation exchange capacity (CEC) was measured with the standard ammonium acetate method. ⁴ pH of the aqueous clay suspensions (1 wt%), measured with a Toshniwal digital pH meter at 30 °C. ⁵ Whiteness index with respect to the standard MgO. ⁶ Weight of clay of the known volume before and after packing.

Table 2. Experimental conditions and textural properties of the bentonite clay samples before and after acid treatment. (Activation temperature of 65 °C and activation time of 10 h).

Conditions/Properties	Samples		
	BnR	ABn	ABn ⁵
Acid: Clay ¹	---	1	1
BET Surface Area (m ² /g)	92.0	294	291
BJH des Pore Diameter (nm) ²	2.80	4.40	4.40
Average Pore Diameter(nm) ³	2.29	4.40	4.60
Total Pore Volume (cc/g)	0.10	0.32	0.34
% Wt. Loss ⁴	---	18.0	20.0
% Yield of Activated Product	---	82.0	80.0
pH ⁶	9.09	3.30	3.20
Acidity (mg KOH/g clay)	6.00	30.0	29.0

¹ Ratio of normality of acid to % concentration of clay in suspension (w/v); ² BJH desorption average pore diameter (4V/A); ³ Adsorption average pore diameter = 4Vt/BET (nm); ⁴ % weight loss in the yield of product after acid treatment; ⁵ Experiment for reproducibility scale up to a bulk batch size of 200 gram experiment. ⁶ pH of the aqueous clay suspensions (1 wt. %), measured with a Toshniwal digital pH meter at 30 °C.

Table 3. Chemical composition of natural and acid activated bentonite samples.

Metal Oxide (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	LOI	Total
BnR	47.68	15.37	12.21	1.29	1.08	1.00	0.01	1.11	20.26	100.00
ABn	55.21	14.50	7.68	0.87	0.01	0.01	0.01	1.65	20.06	100.00

Table 4 Langmuir and Freundlich constants along with the least square sum (s^2) values obtained for Cu(II) and Pb(II).

Sample	Dose of ABn	Langmuir			Freundlich		
		q_o	K_L	R^2	$1/n$	K_F	R^2
		(mg/g)	(L/g)			(mg/g)	
Cu(II)	2 g/L	3.787	1.287	0.992	0.434	1.492	0.876
Pb(II)	2 g/L	6.535	1.514	0.993	0.517	2.904	0.888
Cu(II)	4 g/L	2.88	2.077	0.991	0.189	1.823	0.993
Pb(II)	4 g/L	4.831	12.937	0.992	0.236	3.935	0.978

Table 5. Maximum adsorption capacity (based on the Langmuir adsorption isotherm) of the various adsorbents for Cu(II) and Pb(II).

Materials	Langmuir Adsorption Capacity (mg/g)		Reference
	Cu(II)	Pb(II)	
Sericite	1.674	4.697	[37]
Activated Carbon from Rice Hulls	0.684	5.348	[6]
Mg-oxide Immobilized Sand	0.938	2.843	[6]
Iron-oxide Immobilized Sand	1.264	2.087	[35]
Act-Carbon from Hazelnut Husks	6.645	13.05	[46]
Marula Seed Husks	10.20	20.00	[47]
Coconut Residue	2.76	9.74	[48]
ABn	3.787	6.535	Present Study

Table 6: Rate constants (k_1 and k_2), sorption capacity (q_e), and least square sum (s^2) values obtained from the pseudo-first order and pseudo-second order kinetic models along with the intra-particle diffusion constants obtained for the Cu(II) and Pb(II).

Sample	Dose of ABn	Pseudo-First Order Model			Pseudo-Second Order Model			Intra-particle Diffusion		
		k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2	K_{id} (mg/g.min ^{1/2})	Z	R^2
Cu(II)	2 g/L	1.15×10^{-2}	1.546	0.979	1.08×10^{-2}	3.703	0.988	0.176	0.831	0.953
Pb(II)	2 g/L	1.15×10^{-2}	1.349	0.955	7.60×10^{-3}	2.463	0.980	0.122	0.130	0.993
Cu(II)	4g/L	2.30×10^{-3}	2.033	0.952	2.79×10^{-3}	6.250	0.960	0.190	1.433	0.965
Pb(II)	4 g/L	2.30×10^{-3}	1.803	0.962	5.28×10^{-3}	9.901	0.994	0.145	6.224	0.980

Table 7: Thomas constants (K_T) and sorption capacity (q_0) obtained for Cu(II) and Pb(II) under dynamic conditions.

	q_0	K_T	Least
Sample	(mg/g)	(L/min.mg)	Square Sum
Cu(II)	9.793	4.943×10^{-4}	3.1×10^{-1}
Pb(II)	21.359	1.83×10^{-4}	1.8×10^{-1}