Composite of bentonite/CoFe₂O₄/hydroxyapatite for adsorption of Pb (II)

Yiene M Desalegn, Dinsefa M Andoshe and Temesgen D Desissa

Department of Materials Science and Engineering, School of Mechanical, Chemical and Materials Engineering (SoMCME), Adama Science and Technology University (ASTU), P.O.Box.1888, Adama, Ethiopia

E-mail: temesgen.debelo@astu.edu.et

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Abstract

In this contribution, a composite from bentonite (B), CoFe₂O₄ (CF), and hydroxyapatite (HAP) was developed by chemical synthesis route for adsorption of a lead ion, Pb (II) from wastewater. Initially, a composite of B/CF was synthesized by varying the weight ratio of CF, i.e., (1–x)B/(x)CF (x = 0.05, 0.15, 0.25, 0.50), followed by ternary composite synthesis, which was formulated from the sample of (0.85B/0.15CF) and different weight ratios of HAP, i.e., (1–y)(0.85B/0.15CF)/yHAP where y = 0.25, 0.35 and 0.45 weight ratios of HAP. The sample of 0.85B/0.15CF was found to be optimal in its adsorption capacity of about 20 mg g⁻¹ from the binary composite samples, while among the ternary composites, a sample with a composition of 0.65[(0.85B/0.15CF)]/0.35HAP revealed an optimum adsorption capacity of about 36 mg g⁻¹, which was then selected for further studies. The adsorption kinetics of Pb (II) by the optimum 0.65[(0.85B/0.15CF)]/0.35HAP sample was studied at different contact times from 30–120 min, where the equilibrium was reached at around 90 min of contact time and the kinetic behavior adopted Pseudo-second order adsorption mechanism. The initial concentration of Pb (II) was also varied from 50–200 mg l⁻¹ to study the adsorption isotherm, which resulted that adsorption capacity of 0.65[(0.85B/0.15CF)]/0.35HAP towards Pb (II) was increased to about 66 mg g⁻¹ and the adsorption isotherm data best fitted with Langmuir adsorption isotherm model. Therefore, the result of this study pinpoints that the present composite material is a potential candidate for the adsorption of Pb (II) ion.

1. Introduction

Access to clean water is very important for leading a healthy life for living organisms on earth, nevertheless, the contamination of water has become the most worrying environmental issue in recent years [1]. The presence of heavy and toxic metals in the water system is considered a major universal problem related to many harmful causes on the health of humans and other life forms. Heavy and toxic metals are generally considered to be those with a density greater than 5 g cm⁻³, which include lead (Pb), Chromium (Cr), Cadmium (Cd), Arsenide (As), Mercury (Hg), Copper (Cu), Zinc (Zn), and Nickel (Ni) [2, 3]. Among these toxic metals, lead ion (Pb (II)) can cause severe threats to human health including cancer, mental disorder, headache, and loss of memory as well as a major contributor to environmental pollutions as it can be easily incorporated into ecosystems and therefore to the food-chains [4, 5]. Pb (II) commonly contaminates water after it is discharged from processing and manufacturing industries such as steel plating facilities, oil processing, manufacturer of storage devices, paints, dyes, matches, photography and photographic products, and so on [6]. According to the World Health Organization (WHO), the maximum tolerable contaminant level of Pb (II) in drinking water should be kept well below 10 μg l⁻¹ [7, 8]. Therefore, it is indispensable to remove the contaminant from wastewater using several techniques: ion exchange mechanism, electrochemical, bio-remediation, membrane filtration, and adsorption on the catalyst (adsorbent). Among these techniques, the adsorption process has been widely used for the treatment of wastewater, as it is economically feasible and environmentally friendly [9–11]. The adsorption process is based on developing innovative adsorbent materials with properties such as high specific-surface-area...
(SSA) so that the material can efficiently and effectively remove toxic contaminants such as Pb (II) from wastewater. Bentonite clay and its composite-based materials have been used as an adsorbent to remove Pb (II) from wastewater due to the high surface porosity of the material. Studies have been conducted on using bentonite and metal oxides for possible adsorption of heavy metals. Irawan et al.\textsuperscript{[12]} studied the removal of Pb (II) and As (V) using montmorillonite coated by magnetic nanoparticles and reported a maximum adsorption capacity of about 38 and 19 mg g\(^{-1}\), respectively, towards Pb (II) and As (V). Jiang et al.\textsuperscript{[13]} also prepared bentonite/Fe\(_3\)O\(_4\)/MnO\(_2\) composite particles for Cd (II) removal from aqueous solutions, where they showed pH dependence of the adsorption capacity. In another work, Zhou et al.\textsuperscript{[14]} reported amino-functionalized bentonite/CoFe\(_2\)O\(_4\)/MnO\(_2\) magnetic recoverable nanoparticles for Cd (II) removal and reported that the maximum adsorption capacity of the composite was about 116 mg g\(^{-1}\). Moreover, Zou et al.\textsuperscript{[15]} investigated the adsorption of Hg (II) using Fe\(_3\)O\(_4\) and aluminum-pillared bentonite composite and has reported 26 mg g\(^{-1}\) adsorption capacity. The associated challenges with bentonite-based materials are separation difficulty and expansion of bentonite (swelling) upon hydration, which prevents its application for the adsorption process. The addition of controlled amounts of magnetic particles such as spinel-structured cobalt ferrite (CoFe\(_2\)O\(_4\)) to bentonite clay, i.e. a composite of bentonite and CoFe\(_2\)O\(_4\) could minimize the separation difficulty due to easy separation of magnetic CoFe\(_2\)O\(_4\) by applying a magnetic field. However, CoFe\(_2\)O\(_4\) has the potential of occupying active sites on the surface of bentonite, which may result in lower adsorption performance of the material over a long operational time \[16\]. We hypothesize that the active surface occupation challenge can be surpassed by the incorporation of hydroxyapatite (HAP) particles to the composites of bentonite and CoFe\(_2\)O\(_4\). The addition of controlled amounts of HAP could introduce the surface functionalization property, which could enhance the adsorption capacity of the composite of bentonite/CoFe\(_2\)O\(_4\)/HAP towards Pb (II) due to the easy availability of the HAP materials. The functional phosphate groups in HAP exhibit high affinity towards Pb (II) via electrostatic interaction, in addition to a possibility of ion exchange between Ca\(^{2+}\) present in the HAP sub-lattice and the Pb (II), which will enhance the overall adsorption of the Pb (II) by a composite material system. In this study, a composite of B/CF and B/CF/HAP was developed by a chemical synthesis method, followed by characterizations using x-ray diffraction (XRD), Scanning Electron Microscopy–Energy Dispersive Spectroscopy (SEM-EDX), Fourier Transform–Infrared spectroscopy (FTIR), and thermo-gravimetric analysis-differential thermal analysis (TGA-DTA). Atomic absorption spectroscopy (AAS) was used to determine the adsorption performance of the developed composite materials. Parameters such as initial Pb (II) concentration and effect of adsorption (contact) time on adsorption of Pb (II) by the composite materials were investigated. The adsorption mechanism was discussed using a combination of adsorption isotherm models and kinetic equations.

2. Materials and methods

2.1. Materials

Analytical grade chemicals such as ferric chloride hexahydrate (FeCl\(_3\).6H\(_2\)O, 99%), cobalt nitrate hexahydrate (Co\((NO\_3)_2\).6H\(_2\)O, 97%), ortho-phosphoric acid (O-H\(_3\)PO\(_4\), 85%), sodium hydroxide (NaOH), ammonium hydroxide (NH\(_4\)OH), glutaraldehyde (C\(_5\)H\(_8\)O\(_2\), 25%), and lead nitrate (Pb\((NO\_3)_2\), 99%) were used in this work. Bentonite powder was purchased from Alkane Chemicals P.L.C (Addis Ababa, Ethiopia) while the eggshell for hydroxyapatite extraction was collected from students’ cafeteria of Addis Science and Technology University (ASTU), Adama, Ethiopia. Distilled water was used to prepare all the solutions required in this experimental work.

2.2. Materials synthesis methods

2.2.1. Hydroxyapatite (HAP) synthesis

The collected eggshell was subjected to pretreatments such as boiling for about 1 h and drying (at ambient temperature), followed by grinding to obtain a fine powder that contains CaCO\(_3\). The obtained powder sample was further transferred to an alumina crucible and was kept in a muffle furnace to calcine the powder in ambient conditions. The powder was calcined at a temperature of 900°C with a 10°C min\(^{-1}\) heating rate for 2 h, followed by cooling to room temperature with a cooling rate of 10°C min\(^{-1}\). After calcination, the CaCO\(_3\) was decomposed to calcium oxide (CaO), which was dissolved into distilled water to obtain 1 M calcium hydroxide (Ca(OH\(_2\))) solution. The solution was subjected to heating at a temperature of 40°C, followed by a dropwise addition of 0.6 M phosphoric acid (H\(_3\)PO\(_4\)) to the heated Ca(OH\(_2\)) solution. The pH of the resultant mixture was adjusted to a value of about 11 by drop-wise addition of ammonium hydroxide (NH\(_4\)OH) solution (25%, v/v), followed by stirring of the final mixture for about 2 h. The mixture was aged for 24 h at room temperature to obtain a precipitate, followed by washing and centrifuging of the precipitate. The separated precipitate was subjected to drying at a temperature of 100°C for about 12 h to remove solvents and finally, the obtained powder
was calcined at a temperature of about 900 °C with a 10 °C min⁻¹ heating rate for about 2 h calcination time to obtain hydroxyapatite [17].

2.2.2. Synthesis of bentonite/CoFe₂O₄ (B/CF) composites

Composites of bentonite/CoFe₂O₄ (B/CF) were prepared according to [18] with a slight modification. First, bentonite powder was subjected to pass through a 200-mesh sieve, followed by drying at ambient conditions. In a meantime, weighed amounts of Fe³⁺ and Co²⁺ with a molar ratio of 2:1 was dissolved in 150 ml of distilled water for about 30 min under constant stirring. Then, different amounts of air-dried bentonite powder were weighed and added to the solution, followed by stirring for another 2 h. The pH of the solution was adjusted to the value of 12 by drop-wise addition of 2 M NaOH, followed by ultra-sonication at a temperature of 70 °C for 3 h. The obtained precipitate was centrifuged until a neutral supernatant solution was obtained. The filtered precipitate was dried overnight at a temperature of 100 °C. For a comparison purpose, CoFe₂O₄ without the addition of bentonite was synthesized using the same method mentioned above.

2.2.3. Synthesis of bentonite/CoFe₂O₄/hydroxyapatite (B/CF/HAP) composite

As-synthesized B/CF composites and HAP have utilized for bentonite/CoFe₂O₄/hydroxyapatite (B/CF/HAP) composite preparations with different weight ratios of HAP. Initially, a weighed amount of B/CF composite with a composition of 0.85B/0.15CF and different weight ratios of HAP powders was dissolved by stirring in 50 ml of distilled water in separate beakers. After uniform mixing was obtained, HAP solutions were transferred into the B/CF composite solution under continuous stirring. Then to the mixtures, a drop-wise addition of 50 ml of glutaraldehyde was performed for crosslinking. The pH of the solution was adjusted to a value of 3 using 0.1 N HCl solutions and stirring overnight at room temperature. Then, the obtained precipitate was centrifuged and washed with distilled water. Finally, the prepared B/CF/HAP composite was dried at a temperature of 60 °C for 12 h.

2.3. Materials characterizations

The phase purity of adsorbents was examined using x-ray powder diffraction (XRD-700, Shimadzu, South Korea) using copper Kα radiation (λCuKα = 1.5418 Å), a scan speed of 4.0 deg/min, 40 kV, 30 mA, and a 2-θ scanning range from 4–80°. The surface morphology and elemental composition of the samples were analyzed using an SEM-EDX (COXIIEM-30, Shimadzu, South Korea). FTIR was used to identify functional groups from a wave number of 400–4000 cm⁻¹ (FT/IR-4000 series, JASCO). Thermal stabilities of the samples were investigated in a temperature range from 20°C–800°C using a TGA-DTA (DTG-60H, Shimadzu, South Korea) under an inert atmosphere maintained by injecting of N₂ flow at a flow rate of 50 ml min⁻¹. The adsorption capacity of the samples towards Pb (II) ion was examined using an AAS (ZEEnit 700P, Atomic Flame Mode, Analytik Jena).
Table 1. Summary of the investigated parameters with respect to adsorbent dosage.

| Adsorbent dosage | Investigated parameters |
|------------------|-------------------------|
| 25 mg of adsorbent in 30 ml of Pb (II) | Equilibrium adsorption capacity, \(q_e\), by changing the amount of CF in B/CF and HAP in B/CF/HAP composite |
| 25 mg of adsorbent in 30 ml of Pb (II) | Equilibrium adsorption capacity, \(q_e\), by changing the initial concentration of Pb (II) from 50–200 mg l\(^{-1}\) and thus adsorption isotherms |
| 100 mg of adsorbent (B, B/CF, B/CF/HAP) in 100 ml of 50 mg l\(^{-1}\) initial concentration of Pb (II) | Adsorption capacity, \(q_e\), at a time \(t\) by varying the contact time from 30–120 min and thus the adsorption kinetics |

Figure 2. XRD pattern of HAP (a) before calcination and (b) after calcination at a temperature of 900 °C.

2.4. Adsorption experiments

The standard Pb (II) solution (500 mg l\(^{-1}\)) was prepared by dissolving 799 mg of Pb(NO\(_3\))\(_2\) in distilled water. Then, a series of adsorption tests were conducted at typical equilibrium conditions for the optimization of adsorbents. For each adsorption test, about 25 mg of adsorbent was added to 50 mg l\(^{-1}\) concentration of 30 ml of Pb (II) solution, followed by stirring for about 5 h. The solution mixtures were filtered and the filtrates were analyzed by using AAS. Moreover, an adsorption isotherm study was conducted with 25 mg of adsorbent in 30 ml of Pb (II) solution at a contact time of 5 h by varying the initial concentration of Pb (II) solution from 50–200 mg l\(^{-1}\). To determine the kinetic performances, 100 mg of adsorbent was added to a 100 ml solution containing 50 mg l\(^{-1}\) initial concentration of Pb (II). Then, the mixture was stirred and the samples were taken at a different time interval from 30–120 min and then the filtrates were analyzed by AAS. The investigated parameters with respect to adsorbent dosage are summarized as in table 1 below.

3. Results and discussions

3.1. Phase purity analysis

Figure 1 shows XRD patterns of bentonite, CoFe\(_2\)O\(_4\), and bentonite/CoFe\(_2\)O\(_4\) composites with the latter having compositions of (100–\(x\))B/(\(x\))CF (\(x = 0.05, 0.15, 0.25, 0.50\)). The XRD pattern of bentonite exhibited that of the sodium-montmorillonite diffraction peaks at 2θ of 6.6°, 20.1°, 35.7°, 54.1°, and 61.8°, which correspond, respectively, to the (001), (100), (105), (210), and (300) crystallographic planes and agrees to the Joint Committee on Powder Diffraction Standards (JCPDS) database of (JCPDS No. 12-0204) [19, 20]. The diffraction peaks for CoFe\(_2\)O\(_4\) appeared at a 2θ of 18.3°, 30°, 35.5°, 37.1°, 43.2°, 53.6°, 57.1°, 62.5°, and 74.5° corresponding, respectively, to the (111), (220), (311), (222), (400), (422), (511), (440), and (533) crystallographic planes (JCPD No. 22-1086) [21]. The CoFe\(_2\)O\(_4\) synthesized in this work showed high crystallinity with a space group of Fd-3m and a crystallographic density of 5.27 g · cm\(^{-3}\), which is in agreement to the theoretical density of about 5.29 g · cm\(^{-3}\) [22]. The characteristic peaks of the XRD patterns of the composite materials are also shown in figure 1, with varying percentages of the CF from 5%–50% in the bentonite matrix. With increasing the percentages of CF in the matrix, the diffraction intensities of the clay in the composite samples decreased, which suggests that the layered structure of the sodium-montmorillonite clay has changed to a certain extent. This can be attributed to the intercalation of CF particles in between the layers and/
or adsorption of the CF particles on the surface of the clay [23, 24]. With increasing the percentage weight ratios of CF from 0.05, 0.15, 0.25, and 0.50, the (001) peak intensity of the sodium-montmorillonite clay decreased, suggesting the effective formation of the composites between the bentonite and the CF particles. The d-spacing of bentonite after interaction with CF showed a negligible shift and this may indicate that CF particles could be mostly attached on the surface of the bentonite clay [25].

Figure 2 presents the XRD spectrum (in the 2-θ range from 10–80°) of hydroxyapatite (HAP) before and after subjected to calcination at a temperature of 900 °C. Single-phase of HAP was obtained after the calcination process which removed unwanted and secondary phases presented in the dried powder. The single-phase synthesized HAP powder in this work has a space group of R-3C and a crystallographic density of 3.07 g·cm⁻³ which is comparable to the theoretical density of about 3.16 g·cm⁻³ [26]. Details of the crystallographic planes and the corresponding (hkl) of the planes are reported elsewhere [27, 28].

The XRD pattern of the composite of bentonite/CoFe₂O₄/HAP (B/CF/HAP) is exhibited in figure 3 below. In the pattern, sharp and major peaks related to bentonite powder were observed at a 2θ of 6.6°, 20.1°, 35.7°, 54.1°, and 61.8°, which indicate the existence of sodium-montmorillonite (JCPDS No. 13-0135) [29]. The CoFe₂O₄ diffraction peaks were also observed at a 2θ of 35.5°, 43.2°, 53.6°, and 57.1°, 62.7° indexed to (311), (400), (422), (511), and (422) crystallographic planes, respectively, according to the JCPDS, No.22-1086 [30]. Moreover, the presence of HAP with all the peaks was confirmed in the B/CF/HAP composites.

3.2. Microstructural and elemental analysis

Figures 4(a)–(c) presents the surface morphology and microstructure of bentonite, CoFe₂O₄, HAP, bentonite/CoFe₂O₄, bentonite/CoFe₂O₄/HAP, respectively. In figure 4(a), bentonite exhibited a microstructure with variable particle size in which the surface morphology exhibited slightly rough and porous. Figure 4(b) is the microstructure of CoFe₂O₄ with irregular aggregates of platelets and flaky-like structures that may be related to either the magnetic dipole interactions among the CoFe₂O₄ nanoparticles [31] or their instability because of their high surface energy. Figure 4(c) is the microstructure of HAP, which revealed spherical particle morphology with relatively high porosity of the microstructure. The morphology showed a cluster of very fine particles with a slight agglomeration. Moreover, the overall particle size is slightly smaller than HAP and CoFe₂O₄. In figure 4(d), the surface morphology of bentonite/CoFe₂O₄ is relatively rougher and slightly porous compared to the surface morphology of bentonite alone suggesting that bentonite/CoFe₂O₄ has a large surface area that could lead to higher adsorption capacity [18]. Figure 4(e) is the microstructure of the ternary composite, i.e., 0.65[(0.85B/0.15CF)]/0.35HAP, showing a large number of fine particles covering or enveloping the plate or flaky-like structure of the composite surface that could be related to the effective loading of HAP particles.

The elemental distribution of the samples was investigated using an energy dispersive x-ray (EDX) and figures 5(a)–(c) exhibits the elemental analysis of bentonite, B/CF, and B/CF/HAP samples, respectively.
Figure 5 (a) is an elemental analysis of bentonite, which is the sodium-montmorillonite with a composition of Na$_{0.3}$(Al, Mg)$_2$(Si$_4$O$_{10}$)(OH)$_2$$_{32}$. The elemental analysis confirmed the presence of all the expected elements in the sodium-montmorillonite, i.e., sodium (Na), aluminum (Al), magnesium (Mg), and silicon (Si). Figure 5 (b) is the elemental analysis of the B/CF composite. The analysis exhibited the elemental composition of the bentonite and the cobalt ferrite (CoFe$_2$O$_4$), i.e., presence of cobalt (Co) and iron (Fe). In the EDX elemental analysis, all expected elements from bentonite, CoFe$_2$O$_4$ such as Co and Fe as well as calcium (Ca) and phosphorous (P) from HAP were present.

3.3. FTIR analysis

The presence of functional groups in the samples of HAP, B, B/CF, and B/CF/HAP was examined by using FTIR as shown below, figure 6. The band around a wave number of 3440 cm$^{-1}$ and 1640 cm$^{-1}$ are attributed to the stretching of the hydroxyl groups (OH$^-$) from adsorbed water molecules [33]. The sharpness of the peaks could determine the amount of water (H$_2$O) molecule adsorbed on the surface of the samples [34], which in turn can be used to estimate the amount of the hydroxyl functional groups present in the sample.

Relatively, reduced band sharpness is observed for the bentonite/CoFe$_2$O$_4$ composite sample, which may indicate that the composite possesses fewer bonded H$_2$O molecules. This could be due to the stirring and sonication effect at 70 °C during composite sample synthesis. On the other hand, the peaks of the band for bentonite/CoFe$_2$O$_4$/HAP composite exhibited an increment which may be attributed to the presence of more water molecules adsorbed on the surface. Therefore, the presence of a large number of hydroxyl groups (–OH$^-$) on bentonite/CoFe$_2$O$_4$/HAP composite can be hypothesized that the sample is favorable for the adsorption of...
Pb (II). The occurrence of $\text{PO}_4^{3-}$ from the HAP is observed at a band of 1037 cm$^{-1}$ confirming the loading of HAP on the bentonite surface. Moreover, the characteristic peaks of the phosphate group of the HAP can be observed at a band spectra of 561 and 608 cm$^{-1}$ due to P–O bending and vibrations. The bentonite displays Si–O–Si stretching bond at around a band of 1037 cm$^{-1}$ where the peak intensity was pronounced for a sample of bentonite/CoFe$_2$O$_4$/HAP composite due to the band overlapping from $\text{PO}_4^{3-}$ of HAP. Typical bentonite peak at 570 cm$^{-1}$, displayed the Al–O–Si deformational vibration [35]. The peaks at a band of 565 cm$^{-1}$ and 472 cm$^{-1}$ correspond to the vibration of Co–O and Fe–O peaks from the CF sample [34].

Figure 5. EDX spectra of (a) bentonite, (b) B/CF (0.85B/0.15CF), and (c) B/CF/HAP (0.65[(0.85B/0.15CF)]/0.35HAP).
3.4. Thermal property analysis

Figures 7(a)–(d) exhibit thermal properties of bentonite (B), CoFe$_2$O$_4$ (CF), B/CF, and B/CF/HAP composite samples from room temperature up to 800 °C.

All samples exhibited different stages of weight loss as can be observed from the TGA and the corresponding DTA curves. The first stage of weight loss which is about 8.82%, 8.41%, 9.61%, and 7.87%, respectively, for
bentonite, CF, B/CF, and B/CF/HAP, corresponds to the evaporation of weakly attached water molecules to the surface crystal structures. The second weight losses are related to dehydration of coordinated water molecules (dehydroxylation) and the decomposition process of the clay such as the decomposition of the organic content present in the material in the B, B/CF, and B/CF/HAP composite samples, followed by crystallization process [36–40]. It is highly likely that when bentonite is subjected to thermal treatment, pore volume may have decreased, and therefore its surface area may be reduced, which gives rise to distortion of the crystal lattice to a certain extent [41, 42]. The onset temperature ($T_{\text{onset}}$) during the second stage weight loss is about 136 °C, 159 °C, and 191 °C, respectively, for bentonite, B/CF, and B/CF/HAP samples. Similarly, the corresponding finishing temperature ($T_{\text{finish}}$) during the second stage of weight loss is about 457 °C, 471 °C, and 508 °C, for bentonite, B/CF, and B/CF/HAP samples, respectively. Moreover, based on weight loss, the B/CF/HAP showed an overall weight loss of about 11% while that of the B/CF was about 16%. These suggest that the thermal stability of B/CF/HAP is enhanced compared to the B/CF composite and the individual materials.

### 3.5. Adsorption performance analysis

A series of adsorption tests have been carried out at an equilibrium condition to determine adsorption capacity ($q_e$) of the adsorbents with a compositions $(1-x)B/(x)CF (x = 0, 0.05, 0.15, 0.25$, weight ratios of CF) and $(1-y) [(0.85B/0.15CF)]/yHAP with y = 0.25, 0.35 and 0.45 weight ratios of HAP. The adsorption capacity of the materials can be calculated according to equation (1) below [25]:

$$q_e = V \left( \frac{C_0 - C_e}{m_s} \right)$$

where $q_e$ (mg g$^{-1}$) is the equilibrium adsorption capacity, $C_0$ is the initial concentration of heavy-metal ion (mg/l), $C_e$ (mg/l) is the concentration of Pb (II) ion at equilibrium time, $V$ is the solution volume (L), and $m_s$ is the

![Figure 8. Equilibrium adsorption capacity of (a) B/CF composites with different CF loading and (b) B/CF/HAP composites with different loading of HAP on (0.85B/0.15CF) composite.](image-url)
mass of the adsorbent (g). Figures 8(a) and (b) present the adsorption capacity of \((1-x)B/(x)CF\) with \(x = 0, 0.05, 0.15, 0.25\) weight ratios of CF and \((1-y)\left(0.85B/0.15CF\right)/yHAP\) with \(y = 0.25, 0.35\) and 0.45 weight ratios of HAP, respectively.

The adsorption capacity of B/CF towards Pb (II) increased from about 17 mg g\(^{-1}\) and reached an optimum. The sample with a composition of 0.85B/0.15CF showed an optimum adsorption capacity of about 20 mg g\(^{-1}\). Further increase in the weight percentage of CF resulted in lower adsorption capacity, which could be attributed to the fact that CF may have occupied some of the active sites on the bentonite surface [16]. Due to its optimum adsorption capacity towards Pb (II), 0.85B/0.15CF composite was selected for the synthesis of ternary composites. Then, three different ternary composites were prepared from 0.85B/0.15CF and different amounts of HAP, designated as \((1-y)\left(0.85B/0.15CF\right)/yHAP\) with \(y = 0.25, 0.35\), and 0.45 weight ratios of HAP and their adsorption capacity was evaluated. Figure 8(b) presents the adsorption capacity and the composite with a composition of 0.65\((0.85B/0.15CF)/0.35HAP\) was found to be the sample with an optimum adsorption capacity of about 36 mg g\(^{-1}\). Therefore, this sample was used for further studies such as determination of the effect of contact time and variation of the initial Pb (II) concentrations on the adsorption capacity of the composite sample. Comparing the adsorption capacity of the present work of the ternary composite to that of the literature values of HAP reported by Wei et al [43], the adsorption capacity of the B/CF/HAP requires further optimizations. The adsorption capacity of the composite can be optimized through several material synthesis methods such as hydro(solvo)thermal techniques as this provides control over surface morphology and particle size, which would further increase the adsorption capacity of the materials.

3.5.1. Effect of contact time and Pb (II) initial concentration

Figure 9(a) presents the effect of the variation of contact time between the composite and the Pb (II) on adsorption capacity. The adsorption of Pb (II) was very fast in the first 30 min for all samples, because of the availability of a large number of vacant active-sites on the surface of the composite materials. Then, the
adsorption capacity of the materials showed a slight increase and eventually reached an equilibrium point. For comparisons, the adsorption capacity of B and B/CF under different contact time is also included in the plot of figure 9(a). The sample of 0.65[(0.85B/0.15CF)]/0.35HAP or B/CF/HAP showed an optimum adsorption capacity of about 36 mg g\(^{-1}\) at a contact time of about 90 min, followed by a slight decrease in adsorption capacity with a further increment of contact time. The presence of a large number of active sites on the surface (surface diffusion) and pores could result in a rapid adsorption process. For instance, \(~73\%\) of the adsorption capacity of B/CF/HAP was completed within the first 30 min, followed by the gradual occupation of sites with Pb (II) ion and reached equilibrium within about 90 min of adsorption (contact) time.

Figure 10. A plot showing (a) Freundlich isotherm, (b) Langmuir isotherm, and (c) Sips isotherm model for 0.65[(0.85B/0.15CF)]/0.35HAP composite material.
Table 2. Parameters extracted from the two isotherm models for the sample of 0.65[(0.85B/0.15CF)]/0.35HAP composite material.

| Isotherm models | Parameters | Values         | \( R^2 \) |
|-----------------|------------|----------------|-----------|
| Freundlich      | \( n \)    | 3.2 ± 0.1      | 0.86 ± 0.03|
|                 | \( K_F(I_g)^{-1} \) | 12.5 ± 0.5   |           |
| Langmuir        | \( q_{max} (mg \cdot g^{-1}) \) | 80.0 ± 13    | 0.95 ± 0.02|
|                 | \( b (mg^{-1}) \) | 0.03 ± 0.01   |           |
|                 | \( R_L \) | 0.4 ± 0.02     |           |
| Sips            | \( q_{max} (mg \cdot g^{-1}) \) | 4.0 ± 0.2    | 0.77 ± 0.02|
|                 | \( n \)    | 2.8 ± 0.5      |           |
|                 | \( K_L(I_g)^{-1} \) | 2.4 ± 0.3    |           |

Figure 9(b) is a plot showing the effect of the initial concentration of Pb (II) from 50–200 mg \( l^{-1} \) on the adsorption capacity of the composite sample of 0.65[(0.85B/0.15CF)]/0.35HAP. At a Pb (II) concentration of 50 mg \( l^{-1} \), the adsorption capacity was about 36 mg \( g^{-1} \) and further increment of the initial concentration to 100 mg \( l^{-1} \) resulted in an adsorption capacity of about 44 mg \( g^{-1} \). Increasing the concentration of Pb (II) to about 150 mg \( l^{-1} \) resulted in adsorption capacity of about 60 mg \( g^{-1} \) while that of 200 mg \( l^{-1} \) provided an adsorption capacity of about 66 mg \( g^{-1} \), suggesting the leveling out of the adsorption capacity with a further increment of the Pb (II) initial concentration. It can be theorized that for 50 mg \( l^{-1} \) of Pb (II) initial concentration, the active binding sites remain unsaturated, offering a large surface area for Pb (II) adsorption. As the concentrations of Pb (II) ion increased, the adsorption capacity slightly increased and showed a tendency of saturation with a further increment of lead ion concentration.

3.5.2. Adsorption isotherm analysis

The adsorption capacity of the ternary composite material i.e., 0.65[(0.85B/0.15CF)]/0.35HAP or B/CF/HAP was evaluated using Freundlich, Langmuir, and Sips isotherm models [44–48]. The Freundlich isotherm is a non-linear sorption model that assumes a monolayer adsorption process with heterogeneous surfaces so that there is no over-loading even at high concentrations [49] and this process further assumes that there is an interaction of adsorbed species [44]. The equation describing this model can be given as in equation (2) below [44]:

\[
q_e = K_F C_e^n/n
\]  

(2)

Equation (2) can be linearized and rewritten as in equation (3) below:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  

(3)

where \( K_F \) is the Freundlich constant which represents binding energy of the adsorbents (sorption capacity) and \( 1/n \) is an adsorption intensity that varies with the heterogeneity of the adsorbed monolayer on adsorbing surfaces. A plot of \( \ln(q_e) \) against \( \ln(C_e) \) would yield a linear plot, figure 10(a), from which the values of \( K_F \) and \( n \) can be calculated, as given in table 2.

Moreover, the Langmuir isotherm model is a non-linear theoretical treatment of the adsorption process, which assumes that the adsorption occurs on homogeneous surfaces without interaction between adsorbed Pb (II) [50], and can be expressed according to the following equation (4) below [44].

\[
q_e = \frac{q_{max} b C_e}{1 + b C_e}
\]  

(4)

Equation (4) above can be linearized as follows, equation (5):

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} \frac{C_e}{q_e}
\]  

(5)

where \( b \) (\( 1/mg \)) is the Langmuir adsorption constant related to adsorption energy and \( q_{max} \) is the maximum adsorption capacity of the adsorbent (\( mg \cdot g^{-1} \)) for complete monolayer. According to equation (5), a plot of \( C_e/q_e \) against \( C_e \) would provide a linear plot from which the values of \( b \) and \( q_{max} \) can be obtained, figure 10(b) and table 2.

Furthermore, the Sips model is a non-linear model equation containing three parameters. The model is the combination of Freundlich and Langmuir isotherm models [51] and the equation can be expressed as in the following equation (6):

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} \frac{C_e}{q_e}
\]  

(6)
where $K_s (L/g)$ is the Sips adsorption isotherm model constant and $n$ is the dimensionless heterogeneity factor, when its value is in between 0 and 1. A plot of the value of $q_e$ against $C_e$, (figure 10(c)), is useful to determine the three parameters of the Sips isotherm model, i.e., $K_s$, $n$, and $q_{max}$ where the parameters are presented in table 2.

Table 2 presents the parameters extracted from the three isotherm models. The Freundlich isotherm model resulted in an $n$ value of about 3.2 and $K_F$ value of about 12.5, while the parameters extracted from the Langmuir model yielded a value of about 80, 0.03, and 0.4, respectively, for $q_{max}$, $b$, and $R_L$. Moreover, the three parameters extracted from the Sips model resulted in a value of about 4, 2.8, and 2.4, respectively, for $q_{max}$, $n$, and $K_s$. From the extracted parameters of the isotherm models and experimental data fittings, the Langmuir isotherm model showed the best fit with $R^2$ of about 0.95 compared to that of the Freundlich and Sips isotherm models with $R^2$ of 0.86 and 0.77, respectively.

The adsorption intensity ($R_L$), which is the evaluation of the favorability of Langmuir isotherm can be determined by the following expression, as in equation (7):

$$R_L = \frac{1}{1 + bC_0}$$

(7)

If the value of $R_L$ is $> 1$, the Langmuir isotherm is unfavorable for the adsorption process. However, the Langmuir isotherm model is a linear adsorption process if $R_L$ is equivalent to unity (1) and it is a favorable condition for adsorption if the value of $R_L$ is between 0 and 1 [52]. Therefore, in the present material system, the value of $R_L$ was found to be about 0.4, which is between 0 and 1, as reported in table 2. This indicates that the adsorption of Pb (II) on the present composite material system obeys the favorability condition of the adsorption of the Langmuir isotherm model.
Table 3. Calculated parameters from Pseudo-first and Pseudo-second-order kinetic models for the sample of 0.65(0.85B/0.15CF)/0.35HAP composite material.

| Model               | Parameters         | Values      | $R^2$ |
|---------------------|--------------------|-------------|-------|
| Pseudo-first-order  | $q_{e,\text{exp}}$ (mg g$^{-1}$) | $\approx36$ | 0.91 ± 0.04 |
|                     | $q_{e,\text{calc}}$ (mg g$^{-1}$) | 27         |       |
|                     | $K_1$ (min$^{-1}$) | 0.0405      |       |
| Pseudo-second-order| $q_{e,\text{exp}}$ (mg g$^{-1}$) | 36         | 0.99 ± 0.02 |
|                     | $q_{e,\text{calc}}$ (mg g$^{-1}$) | 41         |       |
|                     | $K_2$ (min$^{-1}$) | 0.00174     |       |

3.5.3. Adsorption kinetics

During the design of adsorption experiments, i.e., formulating innovative composite materials with specific stoichiometric compositions, it is useful to determine the rate at which adsorption of the metals takes place. As a result, it is imperative to establish the time dependency of such a process under different conditions [45]. In adsorption studies, two kinetic models are commonly used. These are Lagergren pseudo-first and pseudo-second-order adsorption kinetics [53]. These models for the present composite materials can be calculated using equations (8) and (9), respectively, as given below [25, 45, 47, 54]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$  

(8)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e}$$  

(9)

where, $q_e$ (mg g$^{-1}$) is the adsorption capacity at an adsorption time of $t$, and $K_1$ (1 min$^{-1}$) and $K_2$ (g/(mg · min)) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively. Based on equation (8), the plot of $\log(q_e - q_t)$ against the adsorption time $t$ would yield a linear plot, from which $K_1$ can be determined, figure 11(a) and table 3. Moreover, from equation (9), a plot of $\frac{t}{q_t}$ against the adsorption time $t$ would provide a linear plot from which $K_2$ can be evaluated as presented in figure 11(b) and table 3, together with their corresponding $R^2$ value.

The parameters extracted from the pseudo-first and pseudo-second-order kinetic models are presented in table 3, together with the experimental adsorption capacity ($q_{e,\text{exp}}$) and calculated adsorption capacity ($q_{e,\text{calc}}$) from the two kinetic models.

Comparing the $q_{e,\text{exp}}$ to $q_{e,\text{calc}}$ from the pseudo-first-order kinetic model, the difference is around 9 mg g$^{-1}$, while the difference is about 5 mg g$^{-1}$ from the pseudo-second-order kinetic model, suggesting that the pseudo-second-order kinetic model is valid for the present experimental activity. Moreover, the pseudo-second-order kinetic model showed a good fit for the experimental data having a higher correlation coefficient $R^2$ of about 0.99 compared to that obtained by pseudo-first-model $R^2$ of about 0.91. These pinpoint that the adsorption of Pb(II) onto 0.65(0.85B/0.15CF)/0.35HAP obeys the pseudo-second-order kinetic model.

4. Conclusions

In this study, a composite of B/CF was synthesized by changing the weight ratios of CF, i.e., (1−$x$)B/(x)CF ($x = 0, 0.05, 0.15, 0.25$) where the sample with a composition of 0.85B/0.15CF showed an optimum adsorption capacity of about 20.0 mg g$^{-1}$. Then, three different ternary composites were prepared from an optimized sample of 0.85B/15CF and different weight ratios of HAP, i.e., (1−$y$)((0.85B/0.15CF))/yHAP where $y = 0.25, 0.35$, and 0.45 weight ratios of HAP. The composite with a composition of 0.65((0.85B/0.15CF))/0.35HAP showed an optimum adsorption capacity of about 36 mg g$^{-1}$ towards Pb(II). FTIR data showed the presence of a large amount of −OH functional groups in the composite of B/CF/HAP, which enhanced the adsorption through the formation of surface complexation with Pb(II). With a variation of the initial concentration of Pb(II) from 50–200 mg l$^{-1}$, the adsorption capacity of 0.65((0.85B/0.15CF))/0.35HAP composite was increased to about 66 mg g$^{-1}$ under a concentration of 200 mg l$^{-1}$ of Pb(II) initial concentration, which may be attributed to the complexion of Pb(II) with −OH functional groups. It is highly likely that the Pb(II) can also be exchanged with the mobile Ca$^{2+}$ component of HAP and could result in a formation of lead-hydroxyapatite complexes.

The experimental data obeyed the Langmuir isotherm model, while the adsorption kinetics was best fitted with the pseudo-second-order kinetic model. In summary, the experimental results of this study suggest that B/CF/HAP which is cost-effective and environmentally friendly could be potential candidate material systems for adsorption of Pb(II).
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ORCID iDs

Dinsesa M Andoshe @ https://orcid.org/0000-0001-9664-1344
Temesgen D Desissa @ https://orcid.org/0000-0003-3612-7153

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