PREPARATION AND CHARACTERIZATION OF MAGNETITE-ACTIVATED CARBON-CLAY COMPOSITE PELLETS FOR ADSORPTION IN WASTEWATER TREATMENT APPLICATIONS

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Abstract

In this research work, a magnetite-activated carbon-clay composite was prepared with a weight ratio of 2:1:1 (magnetite: activated carbon: clay) by the conventional immersion method. After preparing the composite, the samples were characterized by modern techniques such as ED XRF, XRD, SEM-EDX, and FT IR. To enhance usability, the composite was pelletized using a hydraulic automatic press (Cap-15 TON) under controlled conditions. Some physicochemical properties of the sample, such as moisture content and pH, were determined by the oven drying method and a digital pH meter. The diameter and thickness of the pellets were measured with the vernier caliper. Bulk density was measured to assess suitability for environmental applications such as adsorption and catalysis. Adsorption experiments were conducted under optimized conditions: pH 6, adsorbent dosage of 1.25 g, and a contact time of 160 minutes for an initial heavy metal concentration of 40 mg/L. The maximum removal efficiencies for Pb^{2+} and Cd^{2+} ions were 94.7 % and 96.5 %, respectively. Additionally, the magnetic properties of the composite allowed for easy separation from treated water and potential reuse, enhancing its practical applicability in wastewater treatment. This is the advantage for works water treatment in industries.

Keywords: Coconut shell activated carbon, magnetite, clay, composite, wastewater

Introduction

By synthesizing activated carbon from waste biomass, like wood, sawdust, and coconut shells, we may reduce a major environmental concern. Activated carbon is an amorphous carbon form with a porous structure and a high surface area, similar to graphite but not as refined. These factors have made activated carbon the best adsorbent for absorbing contaminants from contaminated water. Activated carbon can also be used for water purification systems (Iqbaldin *et al*., 2013).

On the other hand, magnetic nanoparticles are widely developed in various studies and application fields because of their magnetic properties. Fe_3O_4 can be synthesized by using various methods, including microemulsion, thermal decomposition, hydrothermal synthesis, and co-precipitation. The co-precipitation method is mostly used due to its low cost, high yield, and safe application without hazardous solvents or high temperatures (Jain, *et. al*., 2018). The magnetite production reaction is shown as follows in Equation 1:

$$2\,Fe^{3+}_{(aq)} + Fe^{2+}_{(aq)} + 8\,OH^-_{(aq)} \rightarrow Fe_3O_{4\,(s)} + 4\,H_2O_{(l)} \quad (1)$$

The stochiometric reaction of the equation showed that maximally by maintaining the mole ratio of 2:1 at pH conditions 9-4. In an environment that was not free of oxygen, the Fe(II) solution was easily oxidized to Fe(III), so it was not easy to maintain the mole ratio of 2:1 in the system. In the study performed under synthesis conditions, the mole ratio of Fe(III) and Fe(II)

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was 1.5:1 because it is possible to have an oxidation reaction of Fe(II) to Fe(III) during the reaction process. The stability of magnetite was studied at pH 10 to obtain the best yield percent and characteristics (Rahmayanti, 2020).

Some solid support materials, such as clay minerals that can be combined with magnetic properties, have received interest because clays also have a high adsorption capacity, which attracts and holds cations, such as heavy metals and cationic molecules. And clay, especially natural clays, are attractive materials due to their porosity, high specific surface area, and capacity to adsorb organic molecules and ions (Fadillah, *et. al*., 2020).

In the current study, was developed a new adsorbent, a magnetite-activated carbon-clay composite, that will be used to investigate the adsorption efficiency of Pb^{2+} ions and Cd^{2+} ions from industrial wastewater. Adsorption experiments have been carried out by varying solution pH, adsorbent dosages, contact time, and initial concentration.

Materials and Methods

Sample Collection

The coconut shell waste was chosen from Insein Market, Insein Township, Yangon, Myanmar. The local kaolinite clay samples were collected from Kyaukpataung Township, Mandalay Region, Myanmar.

(A) (B)

Figure 1(A) Raw coconut shells and (B) clay sample

Chemicals and Reagents

All the reagents and chemicals were of analytical grade and were used without any purification. For the preparation of magnetite, ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4.7H_2O$), and a 25 % ammonia solution were used. Hydrofluoric acid (HF 20 %), hydrochloride acid (HCl), and sodium hydroxide (NaOH) were used for the preparation of activated carbon.

Preparation of Magnetite-Activated Carbon- Clay Composite

Fe_3O_4 was then loaded onto activated carbon and clay using the immersion method. Activated carbon and clay (2:1:1 ratio) were mixed with Fe_3O_4 solution and stirred at 60 ºC for 1

h. The composite was left to stand for 1 h, washed with distilled water, and dried at 110 ºC for 12 h. The synthesized magnetite-activated carbon-clay composite is shown in Figure 2.

Figure 2 Prepared magnetite-activated carbon-clay Composite

Characterization of Materials

The prepared magnetite-activated carbon-clay composite samples are characterized using various instruments, including X-ray diffraction analysis (XRD) performed using an X-ray diffractometer with a source of Cu-Kα radiation (λ = 1.54 Å) at 2θ 0˚ to 70˚ to obtain the crystalline phases. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) characterization was performed using the SEM-EDX instrument with the sample placed on the holder and then coated with Au-Pb to obtain the surface morphology and elemental percentage of the samples. FT IR spectroscopy was performed using an FT IR spectrophotometer within the range of 400-4000 cm^{-1} to identify functional groups in the samples.

Preparation of Magnetite-Activated Carbon-Clay Composite Pellets and Its Some Physicochemical Properties

The prepared composite samples were made by the process of compressing or molding a material into a pellet with different weights 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 g, respectively. The pellets of the prepared composite were pressed using a hydraulic automatic press cap of 15 tons at the Department of Chemistry, University of Yangon. The palletization process was implemented with a hydraulic automatic press, Cap-15 TON (Figure 6), pressed for 30 seconds with two times for each of the samples.

Some physicochemical properties of the sample, such as moisture content and pH, were determined by the oven drying method and a digital pH meter. The diameter and thickness of the pellets were measured with the vernier caliper. The bulk density of the prepared pellet was calculated by:

$$\rho = \frac{m}{v_w}$$

where ρ is the bulk density (kg/m^3) of pellet, m is the total sample mass (kg), and v_c is the cylinder volume of the pellet.

Adsorption Efficiency of Magnetite-Activated Carbon-Clay Composite

Pb^{2+} ions and Cd^{2+} ions solutions (1000 mg/L) are used to make two stock solutions from lead (II) nitrate $Pb(NO_3)_2$ and cadmium sulfate ($3CdSO_4.8H_2O$). Adsorption experiments were performed at room temperature and atmospheric pressure using the batch equilibration method to study the effect of various sorption process parameters (i.e., initial pH, adsorbent dosage, metal concentrations, and contact time). The pH of the solution was previously adjusted from 4 to 10 by using 0.01 M HNO_3 and 0.01 M NaOH. 0.5-1.75 g of magnetite-activated carbon-clay composite adsorbent was separately added to 100 mL of toxic Pb^{2+} ions and Cd^{2+} ions solutions, with the initial metal concentration (C_0) ranging from 20 to 100 ppm (mg/L). The effect of contact time was investigated at different contact times of 40-240 min. The following equation calculates the percentage removal of Pb^{2+} and Cd^{2+} (Alswat, *et. al*., 2022):

$$\text{percentage removal} = \frac{C^o - C^e}{C_o} \times 100\%$$

Where C_0 and C_e denote the initial lead and cadmium concentrations (mg/L) and equilibrium concentrations (mg/L), respectively.

Application of removal of Pb^{2+} ions and Cd^{2+} ions from Industrial Wastewater by Using Composite Pellet

The industrial wastewater was collected from Thilawa Industrial Zone and adjusted to pH 6 by using 0.01 M HNO_3 and 0.01 M NaOH. A 0.875 g magnetite-activated carbon-clay composite pellet was added to 100 mL of wastewater at pH 6, shaken for 30 min and left to stand for 130 min. The sample was then separated using a magnet. The concentrations of Pb^{2+} and Cd^{2+} in the filtrate were determined by atomic absorption spectroscopy (AAS). The percentage removal of lead and cadmium was calculated.

Results and Discussion

Characterization of Materials

EDXRF of the magnetite-activated carbon-clay composite sample

EDXRF analyses were carried out on the prepared magnetite-activated carbon-clay composite sample. The relative abundances of elemental compositions in the prepared sample are described in Table 1. The data indicated the highest values of magnetite (65.4 %) were presented in the prepared sample. SiO_2 (18.0 %) and Al_2O_3 (7.45 %) from the clay sample were also presented in the prepared composite. Some other impurities (Na_2O, MgO, P_2O_5, SO_3, Cl, K_2O, CaO, TiO_2, MnO, SrO, and ZrO_2) were also observed in the prepared composite sample.

Table 1. Relative Abundance of Elemental Compositions in the Prepared Magnetite-Activated Carbon-Clay Composite Sample by EDXRF

No	Elemental Compositions	Relative Abundance (%)
1.	Na_2O	0.77
2.	MgO	1.04
3.	Al_2O_3	7.45
4.	SiO_2	18.0
5.	P_2O_5	0.21
6.	SO_3	1.33
7.	Cl	0.17
8.	K_2O	0.82
9.	CaO	4.56
10.	TiO_2	0.54
11.	MnO	0.67
12.	Fe_3O_4	65.4
13.	SrO	0.06

XRD data of the magnetite-activated carbon-clay composite sample

The XRD pattern of the magnetite-activated carbon-clay composite indicates a higher iron oxide content (Figure 3). The average particle size of the magnetite-activated carbon-clay composite was estimated to be around 14.91 nm in the cubic crystal system. The prepared composite sample found five characteristic peaks at 2θ of 30.15, 43.15, 57.15, and 62.74, which corresponded to Miller indices of (220), (400), (511), and (440) due to the crystal planes of Fe_3O_4 (JCPD card number: 00-065-0731). The elemental peak is shown by element C (graphite) at 2θ of 43.5716, which corresponds to Miller indices of (0015) and shows the presence of activated carbon in the prepared composite. The other characteristic peaks at 2θ of 35.54 corresponded to Miller indices of (111), which indicated the presence of a clay sample in the prepared composite (Table 2). The well-preserved crystallinity of the magnetite and clay phases, combined with the amorphous carbon, suggests that the composite retains the individual characteristics of each component while potentially benefiting from their combined properties in various applications such as adsorption, catalysis, or environmental remediation (Yang, *et. al.*, 2007).

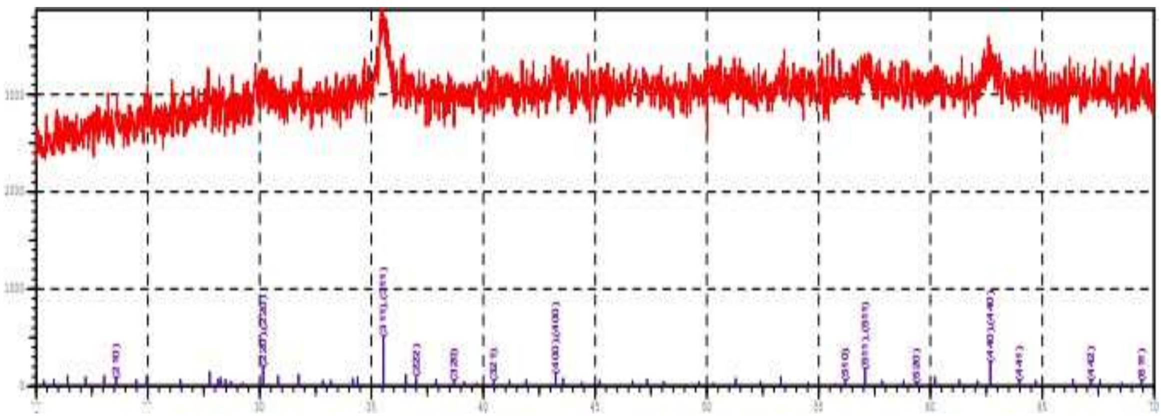

Figure 3 XRD diffractogram of the prepared magnetite-activated carbon-clay composite sample

Table 2 XRD data of the Prepared Magnetite-Activated Carbon-Clay Composite Sample

Diffraction Angle (2θ) (degree)	Interplanar Spacing (Å)	Miller Indices			Crystallite Sizes (nm)	Average Crystallite Sizes (nm)	Crystal System
		h	k	l			
30.16	2.96	2	2	0	10.20		
35.56	2.52	1	1	1	14.19		
43.24	2.09	4	0	0	14.41	14.86	Cubic*
43.57	2.07	0	0	15	16.78		
57.07	1.61	5	1	1	20.66		
62.68	1.48	4	4	0	12.95		

SEM-EDX data of the prepared magnetite-activated carbon-clay composite sample

The SEM image and EDX spectra for magnetite-activated carbon-clay composites are presented in Figure 4. The SEM image reveals a cluster of spherical shape due the aggregative nature of magnetite nanoparticles. An analysis of the EDX data obtained for magnetite-activated carbon-clay composites showed that four elements, namely carbon (C), aluminum (AL), silicon (Si), and iron (Fe), had values of 1.33, 0.36, 0.29, and 98.01 %, respectively (Table 3). The weight percentages for C, Al, Si, and Fe in magnetite-activated carbon-clay composite depend on the specific proportions of activated carbon, magnetite, and clay used in the synthesis. SEM-EDX effectively quantifies these elements, confirming the successful integration of the composite components.

FT IR spectrum data of prepared magnetite-activated carbon-clay composite sample

Figure 5 shows the FT IR spectra of the prepared magnetite-activated carbon-clay composite. According to the spectra, the peak observed at 1618 cm^{-1} and 1037 cm^{-1} indicated the presence of C=C and C-O stretching vibrations from the activated carbon. The Si-O-Si stretching was presented by the peak observed at 795 cm^{-1} from the kaolinite. Finally, the peak observed at 897 cm^{-1} and 555 cm^{-1} indicates the presence of a Fe-O stretching and bending vibration in the magnetite-activated carbon- clay composite. The data is tubulated in Table 4.

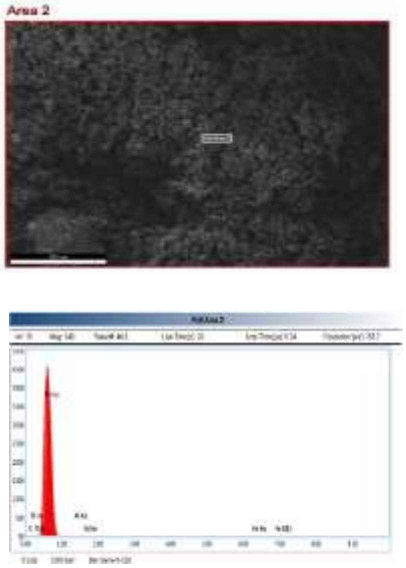

Figure 4 SEM-EDX spectrum of the prepared magnetite-activated carbon-clay composite sample

Table 3 Weight Percentage of C, Al, Si,and O in the Prepared Magnetite-Activated Carbon- Clay Composite Sample by SEM-EDX

No	Element	Weight (%) of the Prepared Composite
1	C	1.33
2	Al	0.36
3	Si	0.29
4	Fe	98.01

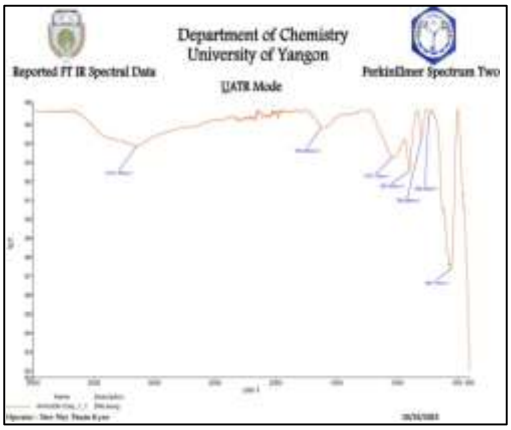

Figure 5 FT IR spectrum of the prepared magnetite- activated carbon-clay composite sample

Table 4. FT IR Spectrum Data of the Prepared Magnetite-Activated Carbon-Clay Composite Sample

Observed wavenumber (cm^{-1})	Literature wavenumber $*(cm^{-1})$	Band Assignments
3141	3270	O-H stretching-vibration
1618	1632	C=C stretching vibration
1037	1120	C-O-C stretching vibration
897	875	Fe-O stretching vibration
795	790	Si-O bending vibration
555	553	Fe-O bending vibration

(*Jozanikohan *et al*., 2022; Hakim et al., 2020)

Magnetite-Activated Carbon-Clay Composites Pellet

The pellets of the prepared composite were pressed using a hydraulic automatic press cap of 15 tons with a difference weight of 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 g to use the adsorption process. The prepared composite pellets were applied as an adsorbent for the removal of heavy metals such as cadmium and lead. The photograph of the hydraulic automatic press cap of 15 tons is presented in Figure 6 and Figure 7 show the photograph of measurement of composite pellet by using vernier caliper.

Figure 6. The photograph of the hydraulic automatic press cap of 15 TON

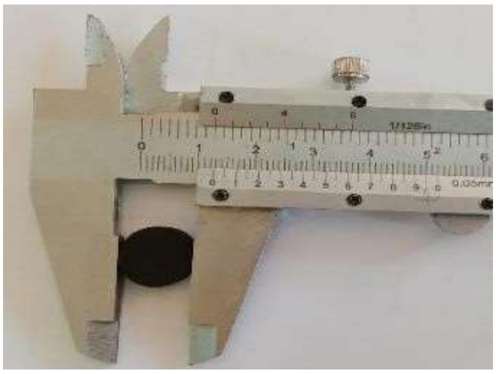

Figure7. The photograph of measurements of magnetite-activated carbon-clay composite pellet using vernier caliper

Physicochemical Properties of Magnetite-Activated Carbon-Clay Composites Pellet

The moisture content of the sample was 0.35 % and the pH value was 7. The diameter, thickness, and bulk density of the pellets are listed in Table 6. These physicochemical properties are crucial for assessing the performance of the magnetite- activated carbon-clay composite pellets in various industrial applications. Moisture content affects stability, pH impacts adsorption capacity, diameter and thickness influence the surface area, and bulk density determines the material's packing and porosity. The proper characterization of these properties ensures that the composite material is well-suited for specific applications such as environmental remediation, adsorption, and catalysis.

Table 5 Some Physiochemical Properties of Magnetite-Activated Carbon-Clay Composite Pellet

Physiochemical Properties	Magnetite-Activated Carbon-Clay Composite					
	0.50 g	**0.75 g**	**1.00 g**	**1.25 g**	**1.50 g**	**1.75 g**
Moisture (%)	0.35	0.36	0.35	0.37	0.35	0.35
pH	7.00	7.00	7.00	7.00	7.00	7.00
Diameter (mm)	14.90	14.90	14.90	14.90	14.90	14.90
Thickness (mm)	3.40	5.20	6.80	8.20	10.20	11.60
Bulk density (g/cm^3)	0.84	0.83	0.84	0.87	0.84	0.86

Adsorption Efficiency of Magnetite-Activated Carbon-Clay Composite

Adsorption experiments were performed to study the effect of various sorption process parameters (i.e., initial pH, adsorbent dosage, metal concentrations, and contact time). The highest adsorption of the Pb^{2+} and Cd^{2+} ions occurred at pH 6, as shown in Figure 6 (a), which was chosen at the optimum pH. he pH of the solution is an essential parameter in cadmium ion adsorption processes. This behavior may be due to the fact that, at a low pH, the competition between hydronium ions (H^{+}) and Cd^{2+} for active sites causes the adsorption efficiency of these metal ions to be low. On the other hand, at high pH, changes in cationic metal speciation and ion precipitation could occur (Izman, *et. al*., 2020). The ~~amount~~ removal percentage of Pb^{2+} and Cd^{2+} ion increased with higher adsorbent dosages, as in Figure 6 (b), due to the increase in available active sites. The adsorption efficiency was initially increased as a result of the variety of adsorption sites and the larger surface area incorporated by increasing the frequency of adsorbent particles (Alswat, *et. al*., 2022). The effect of contact time on the removal of cadmium by the magnetite-activated carbon-clay composite was investigated to determine the optimum duration. Figure 6 (c) depicts that the removal percentage increased with increasing contact time. The experiments were carried out by varying the contact time between 40 and 240 minutes. Similarly, the effect of initial metal concentration on the magnetite-activated carbon-clay composite at various concentrations (20, 40, 60, 80, and 100 mg/L) is shown in Figure 6 (d). The results showed the decrease in removal efficiency with an increase in metal concentration may be due to the fact that the concentration of metal ions increases. And hence, at higher metal ion concentrations, the adsorption capacity of the adsorbent gets exhausted due to the non-availability of free binding sites. So, the optimal pH 6 was found to be suitable for both Pb and Cd removal, and the composite dosage of 1.25 g/100 mL was efficient until saturation. Content time typically achieving equilibrium in 4 h.

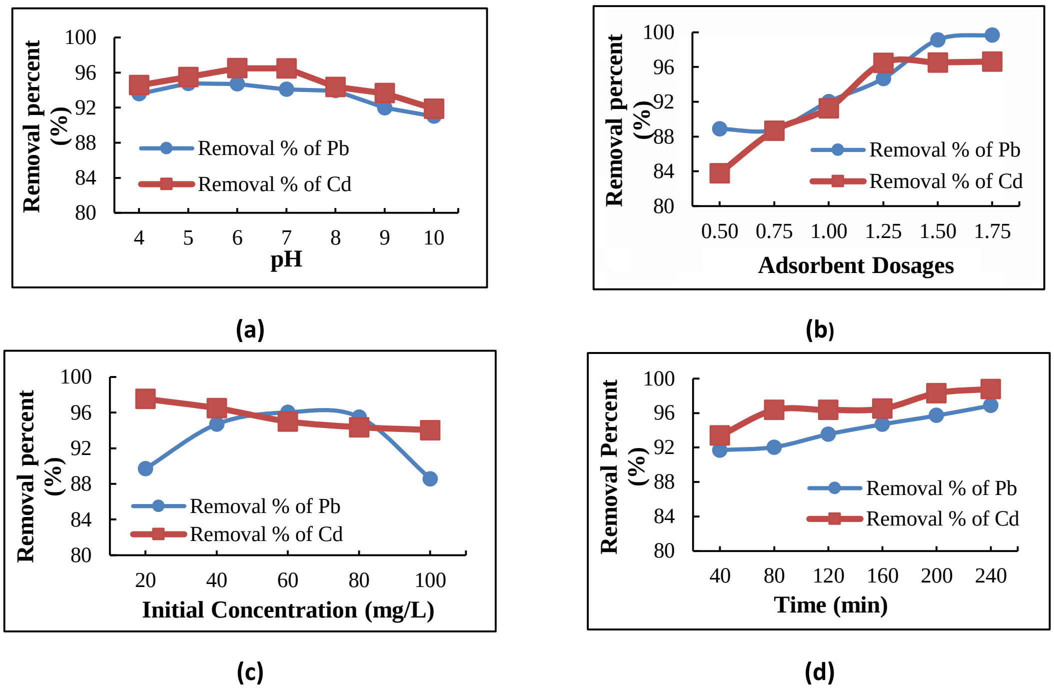

Figure 6. Removal percent of Pb^{2+} and Cd^{2+} ions by a magnetite-activated carbon- clay composite as an effect of (a) pH (b) adsorbent dosages (c) initial concentration, and (d) content time

Effect of Magnetite-Activated Carbon-Clay Composite Dosage on the Removal of Lead and Cadmium from Wastewater

In this research, an initial concentration of lead ions in the collected wastewater sample was 8.18 mg/L, and cadmium ions in wastewater were 2.85 mg/L. The experiment was carried out with three dosages (0.500, 0.750, and 0.875 g) of magnetite-activated carbon-clay composite. It was found that lead and cadmium ions removal percents increased with weight of the composite. Table 6 described lead and cadmium ion removal percents were found to be 100 % for 0.875 g of the composite in wastewater.

Figure 7. Removal of Pb^{2+} and Cd^{2+} ions from wastewater by using composite pellet

Table 6 **Pb^{2+} and Cd^{2+} ions Removal Percents from Industrial Wastewater by Using Composite Pellet**

Sr No.	Dosages (g)	Removal percent of Pb^{2+} ions (%)	Removal percent Cd ions (%)
1.	0.500	86.18	83.67
2.	0.750	98.04	98.62
3.	0.875	100	100

Conclusion

In this work, activated carbon was prepared by pyrolysis method and chemical activation process. Magnetite was synthesized by the co-precipitation method using ferric chloride, a ferrous sulfate solution, and ammonium hydroxide. The clay sample was collected from Kyaukpadaung Township. And then a magnetite-activated carbon-clay composite was prepared by the conventional immersion method with a specific weight ratio of 2:1:1 (magnetite: activated carbon: clay). The prepared composite was estimated to be around 14.91 nm in a cubic crystal system by XRD analysis and FT IR also provide an effective way to quantify these percentages and confirm the successful integration of the composite's components. The composite was tested at different dosages and characterized some physiochemical properties of composite to use the adsorption process. The proper characterization of these properties ensures that the composite material is well-suited for specific applications of wastewater treatment. According to the adsorption efficiency of composite, the optimal pH 6 is appropriate for both Pb and Cd, and the dosage of composite 1.25 g/100 mL was efficient until saturation. Finally, the composite was applied for the removal of Pb^{2+} ions and Cd^{2+} ions from industrial wastewater. It was found that lead and cadmium ions removal percents were found to be 100 % for 0.875 g of the composite in wastewater.

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