

Article

Adsorption Studies of Pb(II) and Cd(II) Heavy Metal Ions from Aqueous Solutions Using a Magnetic Biochar Composite Material

Virendra Singh ¹, Nidhi Pant ¹, Rajat Kumar Sharma ² , Diwakar Padalia ^{3,*} , Pankaj Singh Rawat ⁴ , Rabina Goswami ¹, Praveen Singh ⁵, Akhilesh Kumar ⁵ , Prabhakar Bhandari ⁶ , Alam Tabish ⁷ and Ahmed Mohamed Deifalla ^{8,*}

- ¹ Department of Physics, G B Pant University of Agriculture & Technology, Pantnagar 263145, India; viren.pant@gmail.com (V.S.); pantnidhi99@gmail.com (N.P.); rabinagoswami2001@gmail.com (R.G.)
 - ² Department of Farm Machinery and Power Engineering, G B Pant University of Agriculture & Technology, Pantnagar 263145, India; rajat_sharma@hotmail.com
 - ³ Department of Physics, School of Basic and Applied Sciences, K R Mangalam University, Gurugram 122103, India
 - ⁴ Department of Physics, Uttarakhand University, Dehradun 248007, India; pankajsinghrawat1993@gmail.com
 - ⁵ Indian Veterinary Research Institute, Bareilly 243122, India; psingh67@yahoo.com (P.S.); dr_akhil2005@yahoo.co.in (A.K.)
 - ⁶ Department of Mechanical Engineering, School of Engineering & Technology, K R Mangalam University, Gurugram 122103, India; prabhakar.bhandari40@gmail.com
 - ⁷ Academy of Scientific and Innovative Research (ACSIR), Ghaziabad 201002, India; t.alam29300@gmail.com
 - ⁸ Structural Engineering and Construction Management Department, Future University of Egypt, New Cairo 111835, Egypt
- * Correspondence: padalia.diwakar@gmail.com (D.P.); ahmed.deifallah@gu.edu.eg (A.M.D.)



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Abstract: Heavy metal toxicity in water is a serious problem that may have harmful effects on human health and the ecosystem. Lead [Pb(II)] and cadmium [Cd(II)] are two such heavy metal ions, present in water, whose severity is well-known and well-studied. In the current research, magnetic biochar composite (MBC) is studied as an adsorbent material for the effective removal of lead and cadmium ions from water solutions. Magnetite (Fe₃O₄) nanoparticles and pine-needle-derived ultrasonicated magnetic biochar were used in different weight ratios to prepare APTES (3-aminopropyl triethoxysilane)-functionalized MBC (FMBC). An average crystalline size of ~10 nm for magnetite NPs was obtained via XRD analysis. The adsorption characteristics of both Pb(II) and Cd(II) ions were investigated in a batch experiment. The FTIR spectra of raw biochar, MBC, FMBC, and metal-loaded FMBC were obtained at different stages. The decrease in the intensity of the –NH₂ functional group in the FTIR spectra of the residue confirmed the successful adsorption of heavy metal ions. The SEM-EDX spectra of the residue showed the uniform adsorption of Pb(II) and Cd(II) heavy metal ions onto the surface of the adsorbent. Magnetic biochar composite (MBC) was found to be a very effective adsorbent at basic pH, as a maximum of 97% instantaneous heavy metal removal was observed for both ions in synthetic water solutions. The Langmuir isotherm model predicted the monolayer adsorption and good affinity between the metal ions and adsorbent. The prepared MBC is low-cost, environmentally friendly, and it has shown good adsorption performance. Therefore, our study suggests that the magnetic biochar composite under study is an effective adsorbent for lead and cadmium metal ion removal from aqueous solutions at normal room temperature. Only a few hundred milligrams of the adsorbent dose is sufficient to remove higher concentrations (~100 ppm) of lead and cadmium at basic pH conditions of aqueous solutions.

Keywords: Pb(II) and Cd(II) ions; magnetic biochar composite (MBC); adsorption; FTIR; Langmuir model

1. Introduction

According to studies, about 2.5% of the Earth's water is freshwater, but unfortunately this small portion of freshwater is being contaminated by various pollutants, such as dyes, antibiotics, toxic heavy metals, etc. [1,2]. More than 2.3 billion people worldwide are going through water-related diseases, mainly in developing countries [3]. These contaminants must be removed from water to make it safe for drinking and other purposes. Therefore, researchers have been developing different materials to eradicate the toxic contaminants from the eco-system [4–7]. The materials which are generally used in water purification mainly fall into two categories, i.e., adsorbents and filtration membranes. The most common membrane materials are synthetic polymers, porous ceramics, or composite materials [8]. Adsorption is one of the most widely used remediation methods because it is highly efficient, convenient, cost-effective, and eco-friendly [9,10]. Most common organic adsorbents are activated carbon derivatives [11]. Many inorganic adsorbents and metal oxide-based nanomaterials have been tried and tested by researchers in the past [12]. Biochar, a solid carbon-rich material, is a very suitable adsorbent for pollutant removal via the adsorption process. The carbon-richness, high porosity, availability of sites for various functional groups, and the large surface area of the biochar play an important role in toxic heavy metals' adsorption from the contaminated water [13]. There are different functional groups, including hydroxyl, carboxyl, alkyl, phenolic, and amino groups, situated on the surface of biochar which show strong attraction towards heavy metals like nickel (Ni), cobalt (Co), mercury (Hg), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), and lead (Pb) [14]. The challenges arise in terms of the difficult separation of biochar after treatment and how to improve the adsorption capacity. These problems may be greatly reduced by introducing some transition metal oxides into the biochar matrix to form magnetic bio-composites. Among all transition metal oxides, nano-sized iron oxide, in the form of magnetite, has been a primary choice because of its easy synthesis, low-cost production, superparamagnetism property, and high efficiency [15]. These iron-based nano-composite materials also offer a high surface area for better adsorption of pollutants. Magnetic biochar composite (MBC) materials have been studied in the past for the removal of heavy metals like lead, chromium, arsenic, cadmium, etc., from water and soil [16–20]. In spite of many useful available research outcomes, the formulation of magnetic biochar composite and its functionalization and adsorption mechanism must be studied and discussed further for better understanding. In the current research work, a functionalized magnetic biochar composite (FMBC) is studied as an adsorbent material for the removal of the lead (Pb) and cadmium (Cd) heavy metals from their aqueous solutions. Heavy metals, including Pb and Cd, are environmental pollutants which are resistant to biodegradation and pose a threat to animals, human health, and aquatic life due to their long-term perseverance in the environment [21]. The current study is unique in two ways. First, the biochar is derived from pine tree leaves, commonly known as pine needles. These pine needles are found in abundance in the hill region of Uttarakhand state in India, and considered to be a waste material. Moreover, they are highly inflammable, which causes damage to hills and carries the risk of landslides. Therefore, the eco-friendly utilization of hazardous pine needle waste is required. Second, the study is comprehensive that a model is presented to understand the composite formulation mechanism, its functionalization, and its heavy metal adsorption phenomenon. In addition, the adsorbent material is characterized well to investigate the structural and bonding properties. Dynamic and equilibrium adsorption studies were also conducted and modelled.

2. Materials and Methods

This section covers the procedures for the preparation of adsorbent and heavy metal solutions, techniques used in the study, adsorption models, and related formulae.

2.1. Synthesis of MBC and Preparation of Aqueous Solutions of Lead and Cadmium

2.1.1. Preparation of Magnetite and Biochar

Biochar (BC) was prepared through the pyrolysis of waste pine needles at 500 °C using a tubular batch reactor operating under inert atmospheric conditions to carry out the thermochemical conversion feedstocks. The reactor had a heating rate of typically 10 °C/min, which corresponds to conventional slow pyrolysis [22]. In the reactor, a quantity of 400 g of pine needles was placed. Before this, the removal of O₂ from the reactor was performed by introducing an inert gas (CO₂) at a flow rate of 3 L per minute, which was measured using a gas flow meter with a precision of 0.1 L per minute. After the residence time, the char was allowed to cool down in the reactor to reduce the chances of any oxidation. A 20 gm amount of such prepared BC was mixed in 1000 mL of deionised water and ultrasonicated for 2 min to generate extra pores on the surface of BC for easy adsorption. Further, it was filtered and dried overnight. The magnetite nanoparticles (MNPs) were prepared using the coprecipitation method, and the detailed synthesis procedure may be obtained from our previous work [23].

2.1.2. Synthesis of Magnetic Biochar Composite and Its Functionalization

Different weight ratios (1:1, 2:1, 3:1) of ultrasonicated biochar and magnetite nanoparticles were mixed with 500 mL of deionized water; then the mixture was stirred in an incubator shaker for 2 h at 45 °C to obtain Fe₃O₄-loaded magnetic biochar composite (MBC). The obtained magnetic biochar was filtered and dried. To stabilize the magnetic nanoparticle on the ultrasonicated biochar's surface, its functionalization is required with aminosilane compounds. The silanization prevents Fe-NP dissociation from the biochar and increases the quantity of nitrogen-containing functional groups, which enhances the adsorption of metal ions [24]. Dry MBC was mixed with 150 mL of deionized water and 10 mL of APTES (3-aminopropyl triethoxysilane) solution. The obtained mixture was stirred for 8 h at 50 °C in an incubator shaker to obtain the FMBC (adsorbent in final form), which was filtered and washed with deionized water to achieve a pH close to 7.

2.1.3. Preparation of Synthetic Solutions of Lead and Cadmium Metals

To conduct the adsorption study, synthetic solutions of the Pb and Cd were prepared via their compounds using the following approach:

Pb(NO₃)₂ was used to prepare a synthetic solution of lead heavy metal. To obtain the 100 ppm (100 mg/L) lead solution, 0.1598 gm of Pb(NO₃)₂ was dissolved in 1000 mL (1 L) of deionized water. The prepared samples were stored for further use. To prepare a synthetic solution of cadmium, CdCl₂·H₂O is used. To prepare 100 ppm (100 mg/L) cadmium solution, 0.17909 gm of CdCl₂·H₂O was dissolved in 1000 mL (1 L) of deionized water.

2.2. Adsorption Experiment

The 50 mL solutions of each of lead and cadmium were placed in the conical flask. Nitric acid and sodium hydroxide were used to make the pH of the solutions acidic and basic, respectively. Such prepared samples were stored for 24 h to attain equilibrium. Magnetic biochar composite (MBC) was added to solutions of lead and cadmium and shaken at 200 rpm for 5 min, 15 min, 30 min and 45 min to determine metal ion concentration. These solutions were further filtered using Whatman grade 1 filter paper. The filtrate solutions were used to determine metal ion concentration using atomic absorption spectroscopy (AAS) and the residue samples were collected for FTIR spectroscopic characterization to investigate the bonding mechanism.

2.3. Characterization Techniques

A Rikagu Smart Lab X-ray Diffractometer, equipped with Smart Lab Studio II software, was used to record X-Ray diffraction (XRD) patterns for the structural information, crystallite size, and crystallographic phase identification. To identify the functional group and corresponding bands in the prepared sample, Fourier Transform Infrared Spectroscopy

(FTIR) was used. In the present work, a Thermo scientific Nicolet FTIR spectrometer was used to record the spectrum in wave number region $500\text{--}4000\text{ cm}^{-1}$ with a resolution 8 cm^{-1} . This spectrometer is based on ATR. Atomic Absorption Spectroscopy (AAS) was employed to determine the concentration of heavy metals in the solution after treatment with functionalized MBC. The ECIC's Atomic Absorption Spectrophotometer Element AS was used in the present work. The SEM images and EDX mapping analysis of elements were obtained using the ZEISS EVO18 microscope.

2.4. Zero Point Charge pH (pH_{zpc})

Zero point charge pH (pH_{zpc}) was obtained using a slightly modified procedure [19]. Ten samples of varying pH (2.0–11.0) were prepared using a 0.01 M NaCl solution as the base electrolyte. The pH values were adjusted using 0.1 M HCl and 0.1 M NaOH solution. A 0.1 g quantity of FMBC was added to 50 mL of each of the as-prepared solutions of different pH values and thereafter kept on a shaker at room temperature for 24 h. The supernatant was decanted and pH values were measured again. The pH_{zpc} value was determined by plotting a graph of initial solution pH values and supernatant pH values.

2.5. Adsorption Isotherms and Kinetics

The MBC adsorption mechanism was investigated for different time durations (5 min, 15 min, 30 min and 45 min) and at different pHs (Acidic and basic). To predict the mechanisms of various adsorption systems, adsorption isotherms and adsorption kinetics were studied.

Removal% of metal ions:

This is defined as the percentage of that amount of metal ion which has been removed from the solution by the adsorbent [25]. It is calculated by the following formula:

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

here, C_i = initial metal ion concentration and C_e = final metal ion concentration.

Metal removal using MBC

The amount of metal ions (Q_e) which are adsorbed is determined by the equation given below:

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where m = weight of the adsorbent in gm; V = volume of the metal solution in lit.

Langmuir Adsorption Isotherm

This is a two-parameter isotherm which is used to quantify the adsorption capacity of different adsorbents. The Langmuir isotherm equation is expressed as the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (3)$$

Q_m = maximum adsorption capacity (mg/g); K_L = Langmuir adsorption equilibrium constant (L/mg).

3. Results and Discussion

3.1. Biochar Characterization

The proximate analysis was conducted to determine moisture content, volatile matter, and ash content, as per the American Society for Testing and Materials standard protocols ASTM D 3173, ASTM D 3175, and ASTM D 3174, respectively. Elemental analysis was performed using a CHN analyzer (Carlo Erba 1108, Carlo Erba Instruments, Cornaredo, Italy). The oxygen content was determined by calculating the difference in weight, assuming that

the entire biomass consisted of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and ash. For the determination of the high heating value, an isothermal bomb calorimeter with automatic micro-processor control (WISWO Instruments, New Delhi, India) was utilized, following the ASTM D240 protocols. The pH of the biochar derived from pine needles was measured using a digital pH meter (EUTECH Instruments pH 700). The electrical conductivity (EC) was measured using an ESICO-1615 microprocessor-controlled EC meter. To determine the biochar pH, a solution was created by adding 20 mL of distilled water to 1 g of biochar in a test tube, followed by manual shaking for 5 min. The pH measurement was then taken by immersing the meter probe into the solution. The same solution was left overnight to measure the electrical conductivity. Table 1 shows the elemental and proximate properties of pine needles as well as char.

Table 1. Proximate and elemental properties of pine needles and their char.

Properties	<i>Pinus roxburghii</i>	Pine Needles Char
Water content (% wb)	7.78	4.7
Volatile matter (% db)	71.58	21.1
Ash content (% db)	2.08	7.6
Fixed carbon (% db)	26.34	71.3
Elemental analysis (wt%)		
C	44.99	77.7
H	5.46	3.2
N	0.99	2.4
O	48.55	9.1
H/C	1.46	0.50
O/C	0.81	0.09
Empirical formula	$\text{CH}_{1.46}\text{N}_{0.02}\text{O}_{0.81}$	$\text{CH}_{0.50}\text{N}_{0.03}\text{O}_{0.09}$
HHV (MJ kg^{-1})	17.67	28.1
pH	-	8.4
EC (dSm^{-1})	-	2.15
Iodine Number	-	291

3.2. XRD Analysis of Magnetite Nanoparticles and Magnetic Biochar Composite

The XRD spectrum of prepared magnetite nanoparticles is presented in Figure 1. The magnetite sample exhibited sharp and strong peaks, which indicate the small crystallite size and ultrafine nature of the particle. Crystalline size, interplanar spacing, lattice parameter, and X-ray density were calculated using Lorentz fitting for the most intense peak (311) in the spectrum (Figure 2), and the values are presented in Table 2.

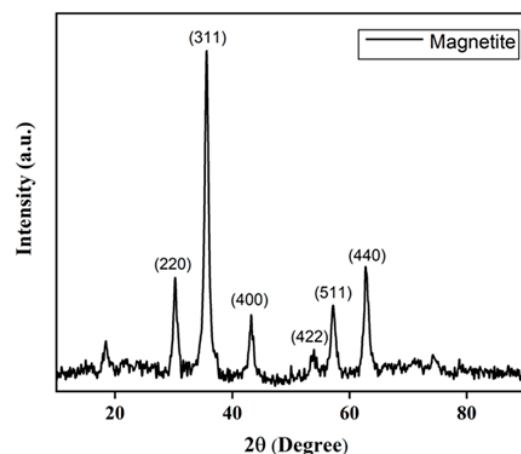


Figure 1. XRD pattern of Fe_3O_4 .

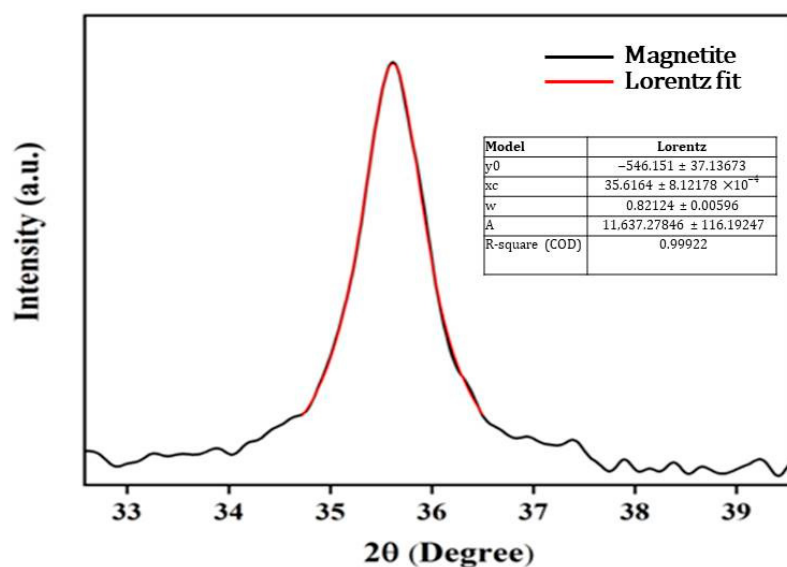


Figure 2. Lorentz fitting for the most intense peak (311) of magnetite.

Table 2. XRD parameters for magnetite NPs.

Crystallite Size	Interplanar Spacing	Lattice Parameter	X-ray Density
10.16 nm	2.51 Å	8.35 Å	5.27 g/cm ³

The XRD pattern of magnetic biochar, representing both the magnetite and biochar phases, is shown in Figure 3. Peaks (220), (311), (400), (422), (511) and (440) are visible in the pattern, along with the broad intense peaks of biochar (carbon) centred at $2\theta \sim 24$ and ~ 42 degrees [18].

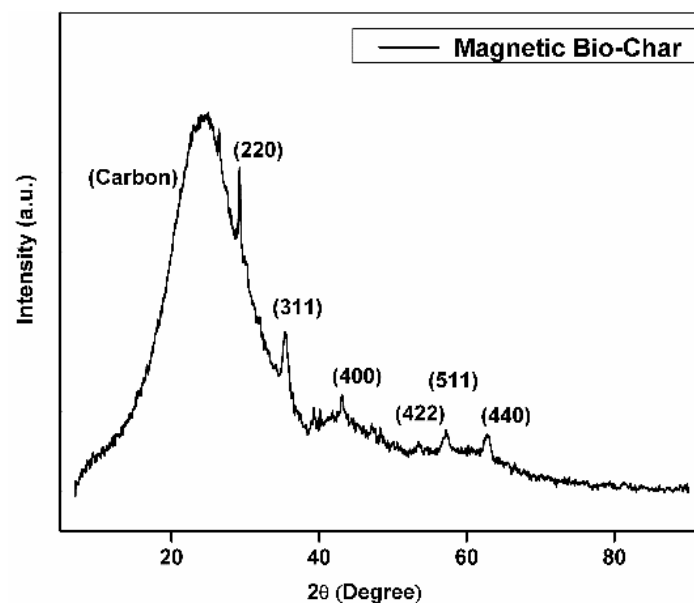


Figure 3. XRD pattern of magnetic biochar (MBC).

3.3. FTIR Analysis of Biochar (Raw, Magnetised, and Functionalized) and Metal-Loaded MBC

The IR study was conducted for BC, MBC, FMBC, and metal-loaded MBC, and the peak positions and present functional groups are presented in Table 3. In the spectrum of raw biochar (BC), the broad band around 3322 cm^{-1} exhibited a hydrogen-bonded

hydroxyl group, i.e., -OH group, which was present due to the cellulose in the pine BC (Figure 4). The small peak at 1189 cm^{-1} shows the -C-O bending vibration [26].

Table 3. Band peaks' positions and assignments for FTIR spectra of BC, MBC, and FMBC.

FTIR SPECTRA	Band Peak Positions	Band Assignments
BC	3322 cm^{-1}	-OH group
	1189 cm^{-1}	C-O bending vibration
	1622 cm^{-1}	C=O carboxylic group.
	1333 cm^{-1}	CH_2 stretching vibration
Magnetic Biochar Composite (MBC)	3322 cm^{-1}	-OH group
	1189 cm^{-1}	C-O bending vibration
	1622 cm^{-1}	C=O carboxylic group.
	570 cm^{-1}	Fe-O stretching
	680 cm^{-1}	FeOOH stretching vibration
FMBC	741 cm^{-1}	Si-C vibration or SiO-C
	921 cm^{-1}	Si-O-C bond
	1354 cm^{-1}	Si-O-Fe
	1622 cm^{-1}	N-H bending of the -NH_2 group.

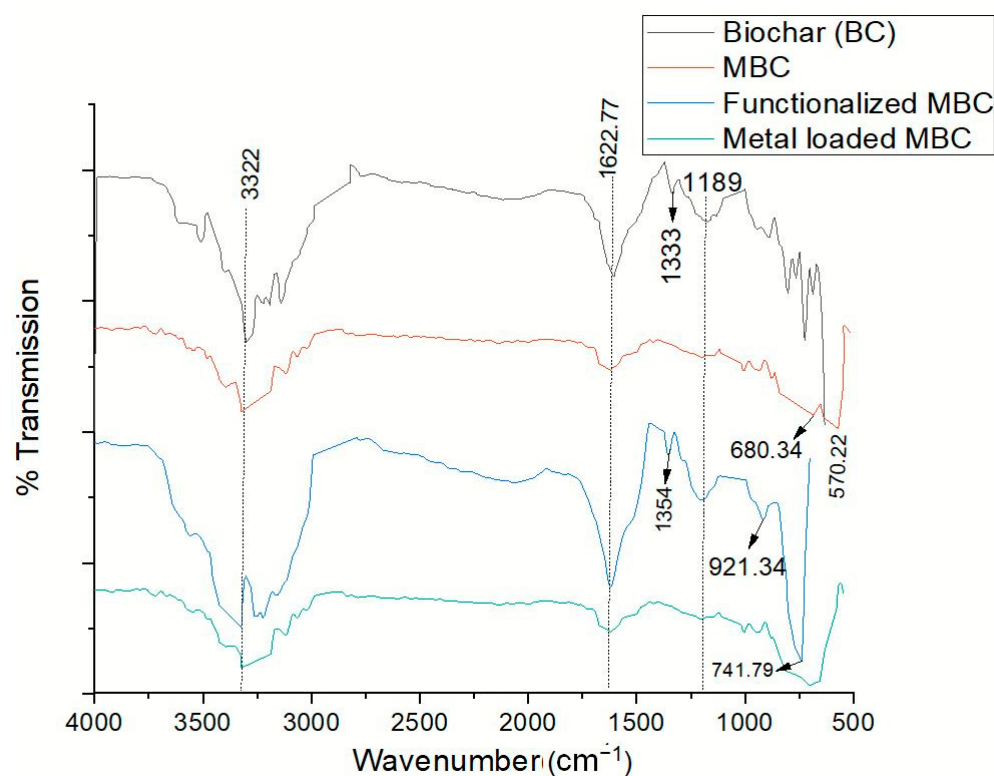


Figure 4. FTIR spectra of BC, MBC, FMBC, and Pb-loaded FMBC.

Further, the peak at 1622.77 cm^{-1} indicates the presence of the C=O carboxylic group. The small peak at 1333 cm^{-1} shows -CH_2 stretching vibration [27]. The IR spectrum of BC reveals that it contains hydroxyl, carboxylate, and alkane functional groups, which represent its hydrophilic nature. In the preparation of MBC, these groups act as anchoring sites for magnetite nanoparticles [28]. The magnetite nanoparticles attach to the surface of biochar by hydrogen bonding [29]. The presence of new peaks at 570 cm^{-1} and 680 cm^{-1} confirm the existence of magnetite in MBC. The high-frequency band at 570.22 cm^{-1} exhibits the Fe-O stretching mode of magnetite (Fe_3O_4) [30]. The sharp peak at 680.34 cm^{-1} may be due to the stretching vibration of FeOOH , which generally appeared for Fe^{3+} -modified

activated carbon [21]. These bands are common characteristics of inverse spinel ferrites [31]. The presence of these peaks in the IR spectrum of MBC suggests the attachment of magnetite nanoparticles to the BC. In the IR spectrum of MBC functionalized with APTES (FMBC), the characteristic peak at 741.79 cm^{-1} corresponds to Si-C vibration or SiO-C, which suggests that the organic alkyl chains are covalently bonded with Si-O-Si networks. The peaks at 921.34 cm^{-1} and 1354 cm^{-1} were assigned to Si-O-C bond and Si-O-Fe, respectively. These two peaks confirm the coating of the magnetite surface through the silanization reaction and verify the successful grafting of APTES on the magnetic biochar. The $-\text{NH}_2$ group overlaps the C=O stretching band, which can be clearly seen in the FTIR spectrum of FMBC [32]. Moreover, the intensity of a peak at 1622.77 cm^{-1} increased significantly in the IR spectrum of FMBC, which indicates the introduction of an electronegative atom containing a functional group, i.e., $-\text{NH}_2$ group [33]. After metal ion adsorption on MBC, a significant decrease was observed in the intensity of the $-\text{NH}_2$ functional group peak at 1622 cm^{-1} . This happens because the lone pair of electrons on nitrogen is no longer present in the $-\text{NH}_2$ group, i.e., electronegativity decreases. It suggested the complexation of metal ion Pb, with amine functional group of APTES. The decrease in the intensities of various functional groups of biochar is a result of the bonding of understudy metal ions with functional groups via the oxidation-reduction process. The heavy metals may also replace the Fe^{3+} in the host matrix via the cation exchange process.

3.4. Effect of pH and Contact Time on the Adsorption Process

Kinetic studies were conducted by determining the amount of adsorbed metal ions Q_t , the final metal concentration in solution C_t , and the % removal for 5 min, 15 min, 30 min, and 45 min contact times of the adsorbent with the target metal ion. The samples were prepared in triplicate and the experiments were conducted for basic and acidic media (Tables 4 and 5). The initial pH values of prepared samples were adjusted to 3 and 11, respectively, for acidic and basic media treatments, using HCl and NaOH solutions. At a low pH, the functional group present on the surface of MBC became protonated and positively charged. Therefore, the metal ions which existed as cations resisted adsorption on the surface of the adsorbent. In the acidic solution, due to the presence of large amounts of H^+ ion and H_3O^+ ion, the cationic adsorption sites on biochar were also hindered and the adsorption process was affected adversely at low pH values because of the electrostatic repulsion [34]. At a basic pH, the surface of the adsorbent became negatively charged and so the metal ions were easily adsorbed on the surface of the adsorbent [35]. At a low pH (acidic medium), the removal efficiency was less in comparison to the high pH (basic medium). We studied the three biochar–magnetite composite ratios, i.e., 1:1, 2:1, and 3:1, although for different composite ratios of biochar to magnetite no significant difference was observed in the adsorption capacities. This indicates that the mechanism of adsorption does not differ significantly even after enhancing the biochar in the composite material. Therefore, the results of only a 1:1 biochar–magnetite composite are presented here in this kinetic study. Initially, the adsorption rate was observed to be very fast and gradually it became slow. The reason behind this is that there were so many vacant sites at the beginning, which gradually decreased with time as the pores were filled by metal ions.

Table 4. Kinetic study of adsorption of lead (Pb) by 1:1 biochar–magnetite ratio FMBC.

Contact Time (min)	Acidic			Basic		
	C_t (mg/L)	Q_t (mg/g)	% Removal	C_t (mg/L)	Q_t (mg/g)	% Removal
5	41.30 ± 0.3000	19.56 ± 0.0800	58.70	5.42 ± 0.0153	32.86 ± 0.0100	94.58
15	40.90 ± 0.3477	19.70 ± 0.0208	59.10	4.37 ± 0.0173	32.87 ± 0.0321	95.63
30	40.60 ± 0.2443	19.80 ± 0.0458	59.40	4.17 ± 0.0404	32.90 ± 0.1216	95.83
45	39.90 ± 0.2570	20.03 ± 0.0808	60.10	3.75 ± 0.0252	33.08 ± 0.0513	96.25

Table 5. Kinetic study of adsorption of cadmium (Cd) by 1:1 biochar–magnetite ratio FMBC.

Contact Time (min)	Acidic			Basic		
	C_t (mg/L)	Q_t (mg/g)	% Removal	C_t (mg/L)	Q_t (mg/g)	% Removal
5	48.50 ± 0.0721	17.10 ± 0.0252	51.50	4.88 ± 0.0404	33.23 ± 0.0473	95.12
15	47.70 ± 0.0265	17.43 ± 0.0173	52.30	4.12 ± 0.0321	33.31 ± 0.0300	95.88
30	47.50 ± 0.0493	17.50 ± 0.0529	52.50	3.72 ± 0.0600	33.33 ± 0.0462	96.28
45	46.20 ± 0.0404	17.93 ± 0.0153	53.80	2.82 ± 0.0321	33.33 ± 0.0321	97.12

The removal of Pb and Cd heavy metals was higher and instantaneous in a basic pH medium. For both metals, the removal percentage was as high as 97% for an initial contact time of 5 min only. The adsorption capacity and % removal both increased with increasing contact time (Figures 5 and 6). In an acidic pH medium, the values of adsorption capacity and % removal for Pb and Cd were much slower and did not increase much even after 45 min contact time.

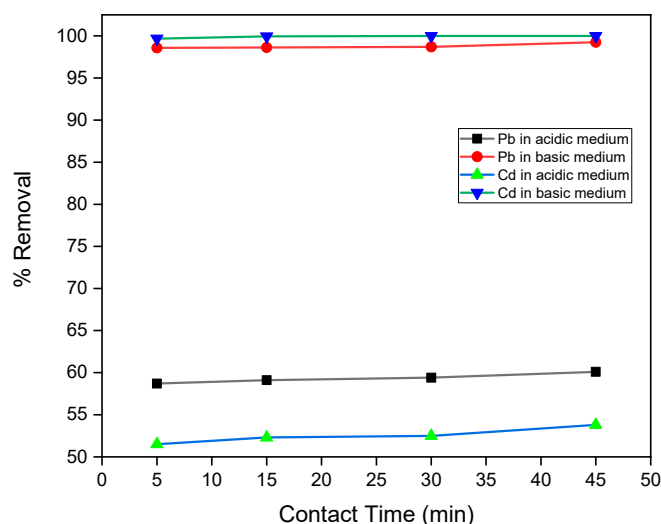


Figure 5. Removal (%) of Pb and Cd by FMBC in acidic (3 pH) and basic (11 pH) media.

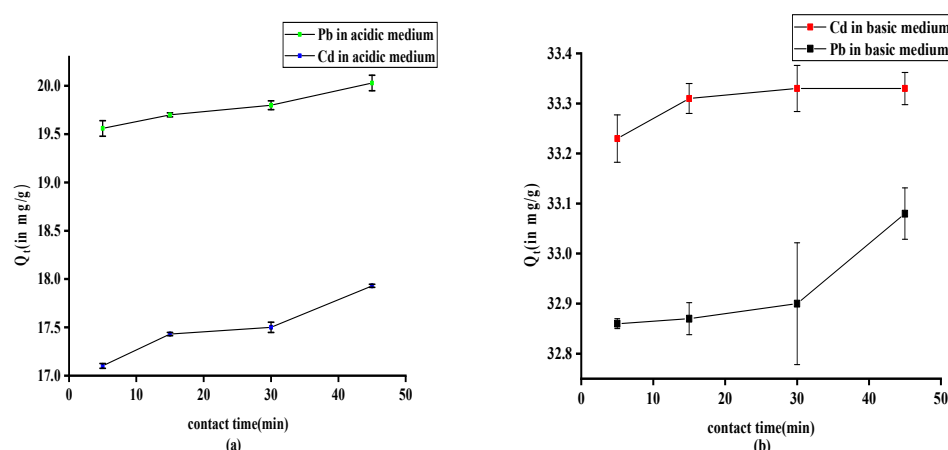


Figure 6. Kinetic study of adsorption of Cd and Pb onto 1:1 ratio magnetic biochar FMBC in (a) acidic medium and (b) basic medium.

3.5. pH_{zpc} Determination

A pH_{zpc} value of nearly 4.85 (Figure 7) was obtained for the FMBC by using the procedure discussed in Section 2.4. This pH_{zpc} value clearly explains why this adsorbent worked better under basic pH conditions. The surface charge of the adsorbent will be

positive at pH values below pH_{ZPC} and anions will be adsorbed. Conversely, cations will be adsorbed if the pH is above the pH_{ZPC} value, as the surface charge will be negative in such cases. The adsorption condition will be favourable at basic pH conditions for understudy pollutant ions Cd(II) and Pb(II), well in agreement with the discussion in the previous section.

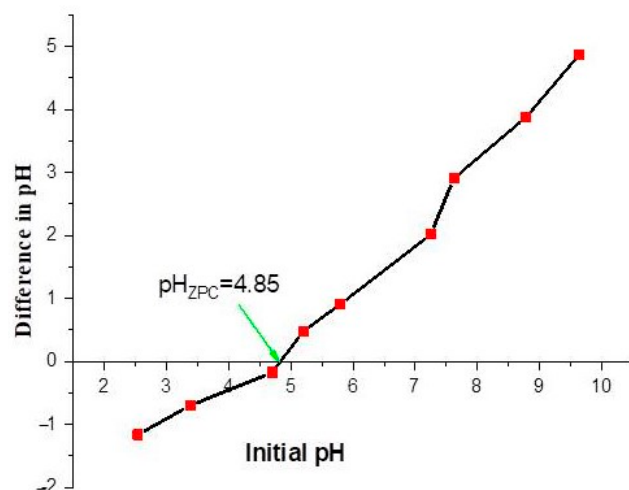


Figure 7. Determination of pH_{ZPC} value of FMBC.

3.6. Langmuir Adsorption Isotherms

Two isotherm models, viz., the Freundlich adsorption isotherm and the Langmuir adsorption isotherm, were studied and it was observed that the Langmuir adsorption isotherm was best fitted to the experimental data of lead and cadmium. Therefore, only the Langmuir adsorption isotherm is considered here in the study. The equilibrium values of Q_e (mg/g) and C_e (mg/L) were obtained for a contact time of 120 min. The graphs of C_e/Q_e versus C_e were plotted to determine the values of Q_m and R^2 (Figures 8 and 9). The maximum adsorption capacities for Pb and Cd using the FMBC adsorbent is presented in Table 6. The Q_m values were better for basic medium. The Q_m was compared with other studied adsorbents, and the results are presented in Table 7. A comparative study shows that our FMBC material was very efficient in the removal of Pb and Cd from aqueous solutions.

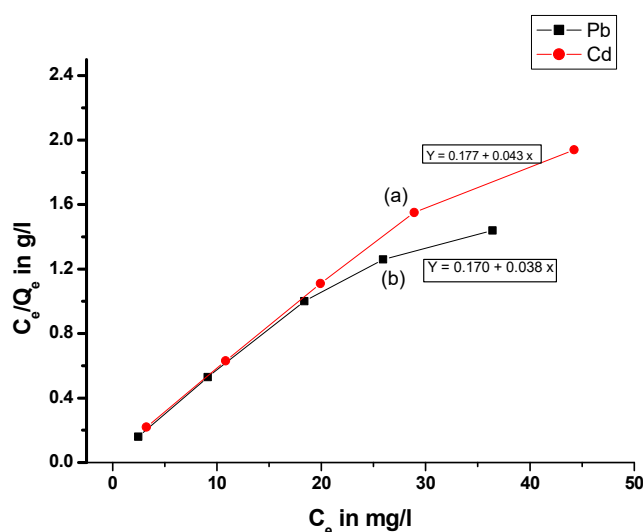


Figure 8. Langmuir adsorption isotherm model for the sorption of (a) Cd and (b) Pb onto FMBC (1:1 ratio of biochar-magnetite) at 3 pH value.

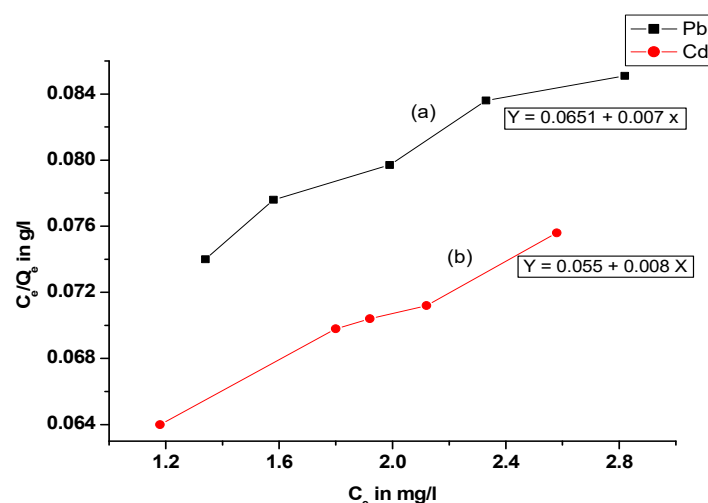


Figure 9. Langmuir adsorption isotherm model for the sorption of (a) Pb and (b) Cd, onto FMBC (1:1 ratio of biochar-magnetite) at 11 pH value.

Table 6. Maximum adsorption capacity Q_m and R^2 value for Pb and Cd in two media.

Medium	Pb		Cd	
	Q_m (mg/g)	R^2	Q_m (mg/g)	R^2
Acidic (3 pH)	26.32	0.95	23.26	0.97
Basic (11 pH)	142.86	0.95	125.00	0.99

Table 7. Comparative study of various adsorbents for the removal of Pb(II) and Cd(II) heavy metals.

Feedstock	Pyrolysis Temperature (°C)	Modification Reagent	Target Contaminant	Removal Capacity	Reference
White tea residue	450	Fe ₃ O ₄	Pb(II) and Cd(II)	Pb(II):81.6 mg/g and Cd(II):38.6 mg/g	Zhang et al. [36]
Coconut skin fibre	600	Ce(NO ₃) ₃ /Fe(NO ₃) ₃	Pb(II)	Pb(II): 140.83 mg/g	Yang et al. [37]
Coconut peel	600	Fe(NO ₃) ₃ and KMnO ₄	Pb(II)	Pb(II):170.668 mg/g	Xu et al. [38]
Rice straw	500	Fe ₃ O ₄	Cd(II) and As(III)	Cd(II): 25.04 mg/g and As(III): 4.58 mg/g	Wang et al. [39]
Pine bark	800	Fe ₃ O ₄ @/APTES	Pb(II) and Cr(VI)	Pb(II): 64.92 mg/g and Cr(VI): 48.86 mg/g	Nnadozie and Ajibade [24]
Egg white, corn straw	500	Fe(NO ₃) ₃ ·9H ₂ O, Mn(NO ₃) ₂	Pb(II) and Cr(VI)	Pb(II): 154.94 mg/g and Cd(II): 127.83 mg/g	Zhang et al. [40]
Rice husk	600	Fe(NO ₃) ₃ ·9H ₂ O, KMnO ₄	Pb(II) and Cd(II)	Pb(II): 148 mg/g and Cd(II): 79 mg/g	Sun et al. [41]
Wetland plant reed	500	NaBH ₄ , FeSO ₄	Pb(II), Cd(II), Cr(VI), Cu(II), Ni(II), and Zn(II)	Pb(II): 38.31 mg/g; Cu(II): 30.37 mg/g; Cr(VI): 23.09 mg/g; Cd(II): 39.53 mg/g; Ni(II): 47.85 mg/g and Zn(II): 111.11 mg/g	Zhu et al. [42]

Table 7. Cont.

Feedstock	Pyrolysis Temperature (°C)	Modification Reagent	Target Contaminant	Removal Capacity	Reference
Pine bark		$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Pb(II) and Cd(II)	Pb(II): 25.294 mg/g and Cd(II): 14.960 mg/g	Reddy and Lee [31]
Pine bark		APTES functionalized nano Fe_3O_4 -Biochar composite	Pb(II) and Cd(II)	Pb(II): 26.23 mg/g in acidic aqua medium and 142.86 mg/g in basic aqua medium Cd(II): 23.26 mg/g in acidic aqua medium and 125.00 mg/g in basic aqua medium	Present work

3.7. SEM-EDX Study

Figure 10 shows the elemental mapping and morphology of the residue after the adsorption of Cd(II) in a basic medium. The EDX spectra of the same sample, along with the elemental composition values, are presented in Figure 11 and Table 8, respectively. The biochar had a flake like structure, as shown in the SEM image in Figure 10a. The iron, in the form of magnetite, was uniformly attached to biochar to form MBC, as evident from the mapping image in Figure 10f. Cadmium was found to be adsorbed throughout the surface of FMBC (Figure 10g). SEM images indicated the adsorption of cadmium on the MNP sites and the sites of biochar functional groups. However, some coagulation of the magnetite NPs was observed in SEM images. A 10 μm scale image of MBC (Figure 10h) shows the porous structure of biochar material, and this structure plays a key role in the heavy metals adsorption process. The EDX spectrum of this particular MBC residue sample shows the presence of adsorbed cadmium. The SEM-EDX results clearly illustrate the successful adsorption of Cd(II) heavy metal ions on the surface of FMBC. Similar results were obtained for lead adsorption by FMBC in a basic medium. However, the adsorption was moderately adversely affected in an acidic medium.

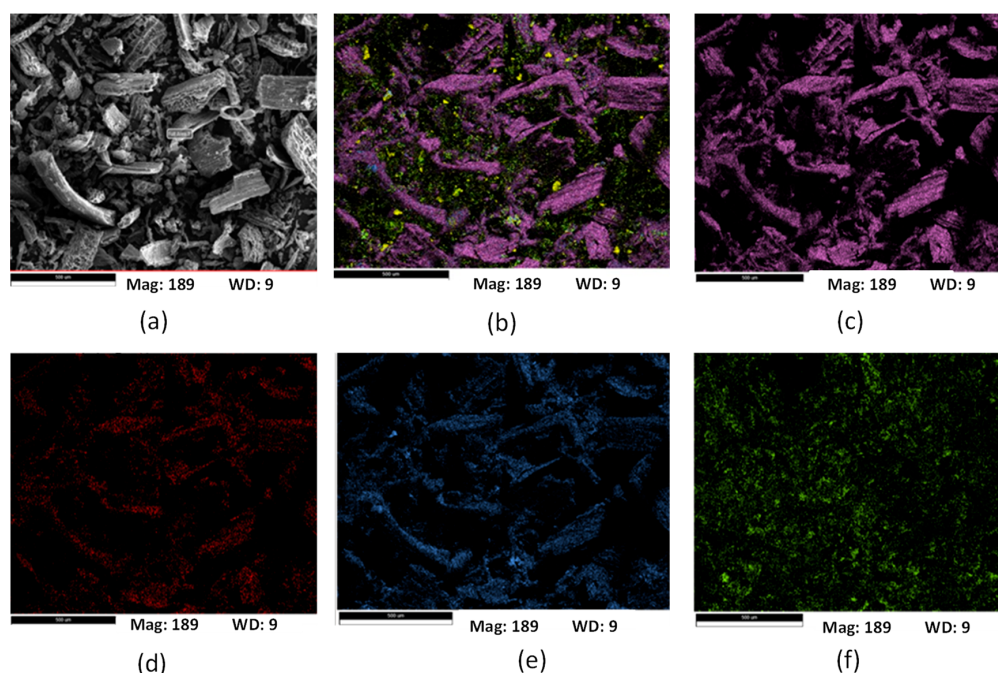


Figure 10. Cont.

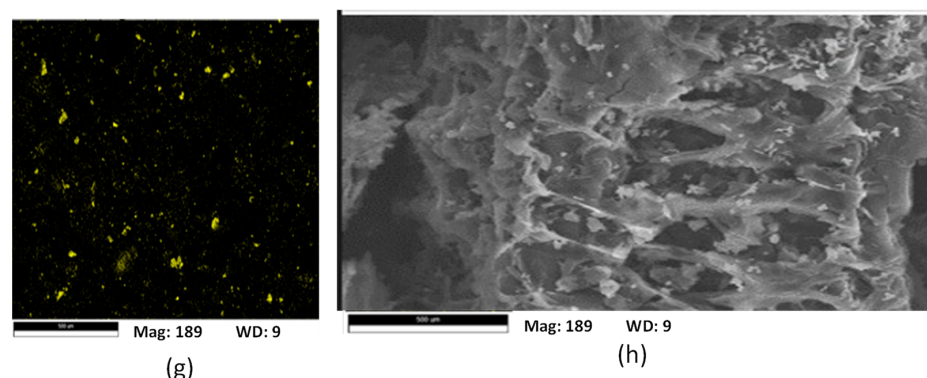


Figure 10. (a) SEM image of FMBC residue after cadmium adsorption (for basic medium) at 500 μm scale; (b) mapping image of all present elements; (c–g) mapping images of carbon, nitrogen, oxygen, iron, and cadmium, respectively; and (h) SEM image of MBC residue at 10 μm scale.

The color coding for different elements in Figure 10b is as follows:

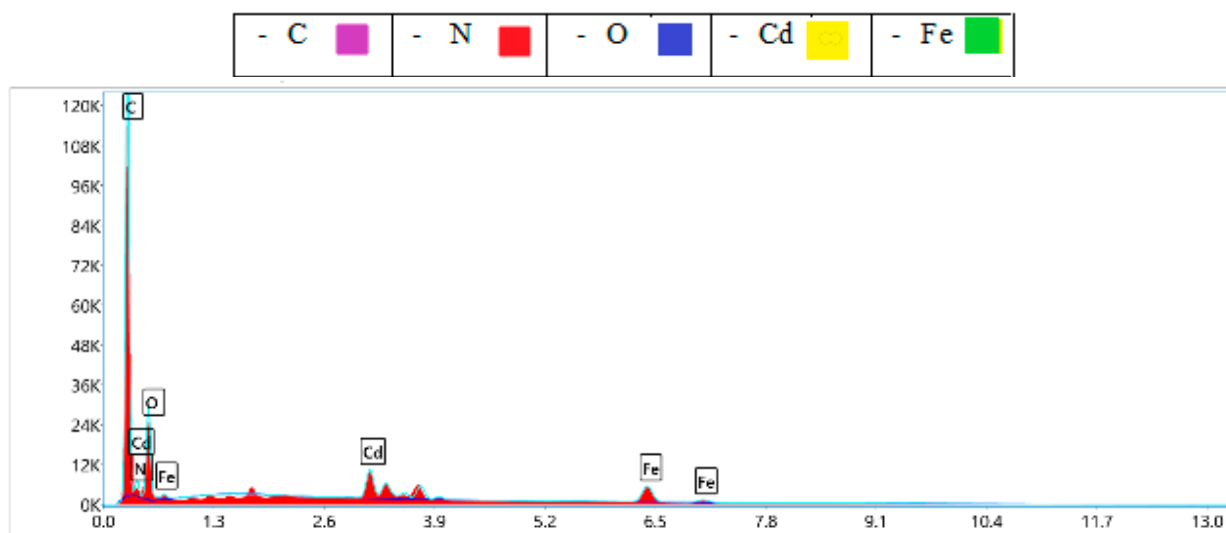


Figure 11. EDX spectra of MBC residue sample after cadmium adsorption.

Table 8. Elemental composition of MBC residue after cadmium adsorption, obtained with the EDX technique.

Element	Weight%	Atomic%
C	67.5	76.8
N	7.0	6.8
O	17.5	15.0
Fe	3.7	0.9

3.8. FMBC Bonding Model and Adsorption Mechanism

Based on the outcomes of IR analysis, SEM micrographs, XRD analysis, and kinetic and isotherm study, a graphical model was constructed; see Figure 12. The various functional groups in biochar materials are shown in the Figure. The magnetite nanoparticles were attached to biochar via hydrogen bonding. In the functionalization process of MBC, the silane group of APTES was attached to the reduced oxygen in biochar functional groups and to MNPs via Si-O-Fe bonding. The complexation of the heavy metal cation (Pb^{2+} in the Figure) with amine groups of silane would have occurred via lone pair donation. Heavy

metal ions were bonded to the functional group of biochar via reduced oxygen and to MNPs via cation exchange in the host matrix.

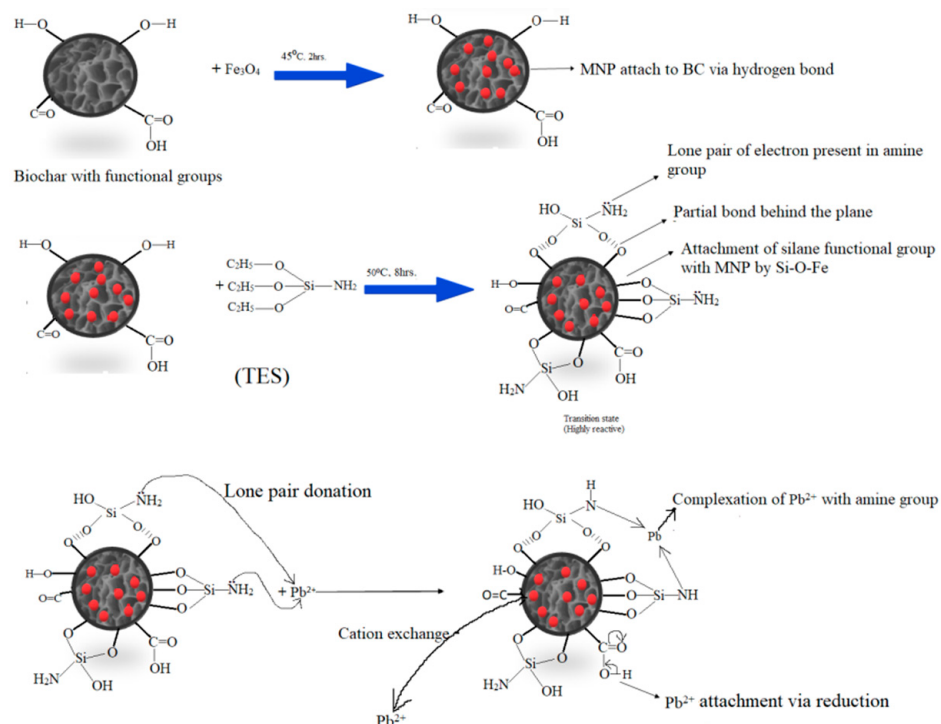


Figure 12. Binding model of magnetite onto biochar, its functionalization process, and the bonding mechanism with heavy metal ions.

4. Conclusions

In the present study, the magnetic biochar composite (MBC) material was synthesized and further applied for the removal of Pb(II) and Cd(II) heavy metal ions from aqueous solutions. The prepared MBC was functionalized with APTES (3-aminopropyl triethoxysilane) to incorporate the amine groups for the better adsorption of heavy metals. The FTIR and XRD analysis revealed the bonding mechanism of biochar with magnetite nanoparticles and APTES. Under study, the functionalized magnetic biochar composite (FMBC) material was found to be very efficient in the removal of lead and cadmium heavy metals, which was confirmed by the decrease in the intensity of the -NH₂ functional group peak in the FTIR spectra of metal-loaded FMBC residue. Kinetic adsorption studies have shown that the process of adsorption was instantaneous for both heavy metals. The zero point charge pH of the material was found to be 4.85. The adsorption capacities of FMBC were higher at a basic pH value than at acidic pH due to the negatively charged surface of the adsorbent at basic pH. Only a small amount of adsorbent (~150 mg) was found to be sufficient for as high as ~97% removal of the studied heavy metals for ~100 ppm initial metal concentration at basic pH values. The Langmuir adsorption isotherm predicted the monolayer adsorption with a maximum adsorption capacity of 125 mg/g and 142 mg/g, respectively, for Cd(II) and Pb(II) heavy metal ions. The SEM study showed the uniform adsorption of heavy metal ions onto the surface of porous FMBC. The EDX spectroscopy results of residues confirmed the binding of heavy metals with the FMBC adsorbent. Ultimately, a graphical FMBC binding model and adsorption mechanism were also presented to explain the possible bonding mechanisms. The current work concludes that the functionalized magnetic biochar composite can effectively remove the Pb(II) and Cd(II) heavy metal ions from aqueous solutions. However, further research is required to enhance the efficacy of the MBC material under study for heavy metal removal in an acidic medium. The composite material may also be investigated for the removal of other pollutants such as dyes, pesticides, etc.

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