Efficient elimination of Pb(II) ions from aqueous solutions using magnetic Fe₃O₄-nanoparticles/activated carbon derived from agricultural waste

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Received 1 September 2021; Accepted 3 March 2022

ABSTRACT
Agricultural by-products are promising adsorbent materials for wastewater treatment, for example, removal of heavy metals. In this study activated carbons (AC) prepared from rice straw agricultural waste (treated with concentrated sulfuric acid) are used to remove lead ions (Pb²⁺) from aqueous solutions in batch mode. The calcination of AC at 500°C for 1 h shows improved removal efficiency. Synthesized magnetite nanoparticles (Fe₃O₄-NPs) are loaded on AC with different ratios (Fe₃O₄/AC(1)), (Fe₃O₄/AC(2)) using co-precipitation method. The chemical structure, surface composition and morphology are characterized by scanning electron microscopy–energy-dispersive X-ray, X-ray diffraction, Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller and Raman spectroscopic analyses. The adsorption process depends on the initial metal ion concentration, temperature, solution pH, the adsorbent dose and contact time. Fe₃O₄/AC(2) has the highest adsorption capacity (68 mg g⁻¹) at 100 mg L⁻¹ metal ion concentration, adsorbent dose of 1 g L⁻¹, room temperature (30°C ± 2°C), shaking speed = 200 rpm, contact time = 1 h and pH = 5. The thermodynamic studies show that the adsorption process fits Freundlich model (R² = 0.997) better than Langmuir and Temkin models. The adsorption/desorption kinetics of Pb²⁺ ions proceeds via pseudo-second-order kinetics. The temperature-dependent study (carried out in the range of 20°C–60°C) confirmed that the adsorption process was endothermic in nature.

Keywords: Rice straw; Magnetite nanoparticles; Active carbon; Calcination; Adsorption; Heavy metals; Isotherm; Kinetics

1. Introduction
Water is an important resource required for human life. Nowadays, water pollution has become a major environmental challenge and a hazard to the well-being of living organisms with various contaminants (mainly heavy metals). In nature, heavy metals are non-biodegradable, persistent, carcinogenic and toxic and are easily transported in the environment [1]. In living organisms, heavy metals are bio-accumulated (in what is called bio-magnification) through the food chain and their accumulation causes various diseases and malfunctions [2]. Naturally, heavy metals are present in low concentrations in the earth’s crust, but they have become concentrated because of human activity that leads to environmental pollution [3]. Pb²⁺ ions are considered among the most toxic metals, it is a highly dangerous and long-standing environmental pollutant. Various industries, such as the production of batteries, glass, metal plating and finishing, printing and tanning, produce enormous amounts of waste water polluted with

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lead ions [4]. For pregnant women, poisoning with Pb(II) ions causes liver, kidney and hemoglobin formation damage, mental retardation, infertility and abnormalities. Moreover, anemia, headache, chills, diarrhea and toxicity may be directly or indirectly induced, contributing to dysfunction of the kidneys, reproductive organs, liver, brain and central nervous system [5].

Numerous procedures have been studied to remove lead ions from water such as precipitation, coagulation, ion exchange, electro-coagulation, filtration and adsorption [6]. Adsorption is one of the best methods for heavy metal ion removal because of its easy, cost-effective method in addition to its operational simplicity [7]. As adsorbents, activated carbon (AC) is recognized as an effective candidate due to its high porosity, large surface area, and high catalytic activity [8]. Researchers, in both developed and developing countries, have extensively studied the use of agricultural waste to extract heavy metals [9]. One of the main significant obstacles for commercial producers is the high cost of AC manufacturing [10]. The use of a simple method for the production of activated carbon can also greatly reduce production costs. So the abundance and availability of agricultural by-products make them excellent sources of raw materials for activated carbon preparation [11]. Activated carbon produced from agricultural wastes has been investigated for pollutant removal from aqueous solution like rice straw (RS) [12].

Rice is the second largest cereal crop in the world after maize, staple food by more than 50% of the world’s population. In this context, rice straw (RS) has many structural and compositional features that enable its high absorbivity/adsorptivity of metals ions from aqueous solutions by the binding sites [13]. The chemical composition of RS predominantly contains cellulose (36%–40%), hemicellulose (15%–20%) and lignin (20%–23%) [14]. Rice husk (RH), RS and plastics are the primary solid waste in rice production [15], the burning of rice straw is a common practice after harvest which creates air pollution because of large amount of N₂O, SO₂, CH₄ and smoke are generated [16]. So it is crucial to reuse RS as a sorbent candidate.

Many of the activated carbons were generated through a two-steps, carbonization process then activation (chemical activation or physical activation). In physical activation, the precursor needs high temperatures (800°C–1,100°C) in the presence of oxidizing agents such as air, steam, CO₂ or a mixture of them [17]. Whereas, chemical activation takes place at much lower temperatures (400°C–600°C) [17]. The precursor is combined with a concentrated solution of an active agent which acts as dehydrating agent and oxidant [18], for example, H₃PO₄, ZnCl₂, H₂SO₃ and KOH allowing the formation of porous structures in the material [18]. The two steps are carried out simultaneously in the chemical activation process [19]. Chemical activation provides many advantages as it is carried out in a single stage, integrating carbonization and activation at lower temperatures and thereby contributing to the creation of a better porous structure [20]. Activation with acid breaks the covalent connection between components of lignocellulose, hemicellulose hydrolysis and lignin depolymerization, thus, increasing cellulose exposure, which further improves the adsorption properties of RS [21]. If we compare the surface area of the ACs prepared with H₂SO₃, H₃PO₄, ZnCl₂, the surface area of the AC treated with sulfuric acid was found to be the highest. The basic criteria for an effective adsorbent are high surface area and pore structure and these parameters are added by chemical activating agents such as H₂SO₄ [22]. This is due to the degradation of cellulosic content in plant materials and the aromatization of the carbon skeleton after H₂SO₄ treatment [23]. A review of literature on using rice residual waste for heavy metal removal is carried out by various researchers. Singh and Das [24] investigated the adsorption of Cu(II) by rice straw and rice bran with maximal adsorption capacities of 18.4 and 21.0 mg g⁻¹, respectively. Khan et al. [25] investigated the adsorption of hexavalent chromium [Cr(VI)] from aqueous solution by acidentally produced rice husk carbon (APRHC). Also the removal of Cr(VI) from water by carbon produced from the burning of rice straw is investigated by Hsu et al. [26]. The rapid adsorption of toxic Hg(II) from the liquid phase onto rice straw activated carbon (RSAC) manufactured employing microwave-assisted H₂SO₄ activation was thoroughly researched and explained by Mashhadi et al. [11]. Rocha et al. [27] modified rice straw by HNO₃ and NaOH and use it to remove Cu(II), Zn(II), Cd(II) and Hg(II) ions from aqueous solutions with maximum adsorptions at pH 5 and time less than 1.5 h.

In this paper rice straw treated with hot concentrated H₂SO₄ which acts as a strong dehydrating and oxidizing agent due to its ability to lose an oxygen atom to form SO₃, which quickly decomposes to SO₂ and H₂O. This will lead to carbonaceous material loaded with function groups such as –OH and –COOH on the surface [28]. Recent years have seen a greater interest in the use of nanoparticles as adsorbents in water treatment. Nanotechnology is the best possible method of treating both persistent and emerging contaminants [29]. It deals with nano-scale materials which often possess the novel size-dependent properties that differ from their larger counterparts. The small size and high surface area to volume ratio make nanomaterials detect highly sensitive contaminants [30].

Iron oxide is an ideal adsorbent since it has a high surface area to volume ratio. Excellent magnetic properties, great biocompatibility, ease of separation using external magnetic field, reusability, comparatively low cost and its surface can be modified. Also, because of variable oxidation states, it may coordinate with other components [22]. The use of magnetic nanoparticles in extracting heavy metals and dangerous materials from water has recently been studied by several researchers, demonstrating the efficiency of these materials. Among the magnetic materials, magnetite nanoparticles (Fe₃O₄-MNPs) are extremely effective and in recent years they have gained considerable attention and experimental emphasis [22]. These particles can be synthesized by various methods like sol-gel, chemical co-precipitation and hydrothermal methods. These nanoparticles have unique properties and a range of positive features in terms of their use, such as low cost and toxicity, strong magnetism, durability and biocompatibility, fast separation of water and their capacity for industrial applications [31]. It may be less efficient to use activated carbon alone, but when combined with a magnifying material, it may be
more effective in purification processes. Magnetic separation is a fast and efficient method of metal ion separation [32]. Another benefit is that the loaded adsorbents can be conveniently isolated by magnet instead of centrifugation from the aqueous solution, thereby saving energy [22]. This combination has transformed the rice straw waste into useful magnetic activated carbon sorbents for removing toxic ions from water. For the removal of Pb(II) ions from aqueous environments, several researchers have employed activated carbon as an adsorbent such as Ghasemi et al. [33] who synthesized Fig sawdust activated carbon (FSAC) by chemical activation with H3PO4 to remove Pb(II) ions from aqueous solution. The removal efficiency of Pb(II) ions via adsorption was reported to be highest (95.8%) at pH 4. Mouni et al. [5] also removed Pb(II) from dilute aqueous solution by AC produced from apricot stone with sulphuric acid with maximum adsorption capacity of 21.38 mg g⁻¹. Shekinal et al. [34] removed Pb(II) ions from aqueous solution using activated carbon from aquatic weed, Eichhornia with adsorption capacity 16.61 mg g⁻¹. The possibility of using raw rice straw to remove Pb(II) from water by biosorption was explored by Amer et al. [35]. At a pH of 5.5 and a dose of 4 g L⁻¹ at an initial Pb²⁺ concentration of 40 mg L⁻¹ maximum removal of 94% was achieved. Using the Langmuir isotherm, RS had a maximum adsorption capacity of 42.55 mg g⁻¹. In this section, we will discuss recent research findings on the use of active carbon supported with magnetite nanoparticles to remove heavy metals. Zarandi et al. [36] produced magnetic nanoparticles (Fe₃O₄) which immobilized on activated carbon (AC) and used as an effective adsorbent for Cu(II) ions removal from aqueous solution. Fatehi et al. [37] studied the ability of produced magnetic nanoparticles supported on activated carbon (AC-MNPs) to remove Pb(II) and Cr(VI) ions from single and binary component aqueous solutions in the presence of salinity in order to manufacture an efficient and low-cost adsorbent. Khandanlou et al. [38] synthesized and loaded porous carbons composite (MRH) from rice husk to precipitate the hydrated iron oxide under vigorous stirring at 80°C until pH reached 10–11. The suspension was reported to be highest (95.8%) at pH 4. Kakavandi et al. [39] synthesized the magnetic rice straw by chemical co-precipitation and magnetized powder activated carbon (M-PAC). (Fe₃O₄@C) was used as an adsorbent for lead ions (Pb²⁺) from aqueous solution with maximum monolayer adsorption capacity of 71.42 mg g⁻¹ at 50°C. Nethaji et al. [40] used activated carbon made from corn cob biomass and magnetized by magnetite nanoparticles (Fe₃O₄-NPs) in the absence of heat treatment on the surface of rice straw using the rapid precipitation method. Kakavandi et al. [39] synthesized the magnetic Fe₃O₄ nanoparticles using chemical co-precipitation and magnetized powder activated carbon (PAC). (Fe₃O₄@C) was used as an adsorbent for lead ions (Pb²⁺) from aqueous solution with maximum monolayer adsorption capacity of 71.42 mg g⁻¹ at 50°C. Nethaji et al. [40] used activated carbon made from corn cob biomass and magnetized by magnetite nanoparticles (MCCAC) to achieve the adsorption of Cr(VI) from aqueous solution with maximum monolayer adsorption capacity of 71.42 mg g⁻¹. Luo et al. [41] synthesized magnetic Fe₃O₄-loaded porous carbons composite (MRH) from rice husk for removal of arsenate As(V) with maximum absorption quantity (qₐ) of 4.33 mg g⁻¹. The adsorption of Cu(II) and Pb(II) ions onto magnetic-plum stone activated carbon (m-PSAC) is investigated by Parlayici and Pehlivan [32]. The maximum adsorption capacities of Cu(II) and Pb(II) ions calculated by the Langmuir model were 48.31 and 80.65 mg g⁻¹, respectively. In this work, the activated carbon was prepared from lignocellulosic agricultural by-product, rice straw by simple chemical activation without using inert gas or high temperature. The activated carbon was modified by loading its surface with the magnetite nanoparticles using a co-precipitation method in one step. This would make the process eco-friendly, effective and economically more attractive. This study also has another way for modification of the (AC) by thermal treatment (calcination at 500°C for 1 h in a muffle furnace in air) and compared with the synthesized magnetic rice straw activated carbon (Fe₃O₄/AC). All adsorbents used for the adsorption of lead ions (Pb²⁺) from aqueous solution. Characterization and batch-type removal experiments were carried under various operating process conditions.

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical grade (Sigma-Aldrich, Germany). Stock solution of 1,000 mg L⁻¹ concentration of Pb(NO₃)₂ was prepared in double distilled water acidified with nitric acid to prevent hydrolysis. All the working solutions were made by proper dilution of the stock solution. The pH of each working solution was adjusted to the required value by using 0.1 M NaOH or 0.1 M HCl and measured using an electronic pH meter (WTW inoLab pH 730, Germany). The concentrations of the heavy metals in the solutions were determined by GBC Atomic Absorption Reader (Model SavantAA AAS with GF 5000 Graphite Furnace).

2.2. Preparation of activated carbon from rice straw (chemical activation) [28]

Rice straw (RS) was cut into small pieces and washed with water then allowed drying at room temperature. The above dried rice straw was crushed into fine powder in a steel mill. Crushed powder was boiled in distilled water for 2 h to remove dust and other soluble materials and dried in hot air oven at 60°C for 24 h. The washed powdered material was sieved in the size range of 250 µm; 200 g of it was added to 1,000 mL of 13 M sulfuric acid. The mixture was heated at 180°C for 3 h using a magnetic hot plate stirrer. The resulting black mixture was cooled and then filtered under vacuum using a Buchner funnel; it was washed several times with distilled water to a neutral pH and dried at 105°C in a hot air oven for 24 h. The dried activated carbon (AC) was crushed in a mortar and sieved in the size range of 63 µm and stored in a desiccator for further use.

2.3. Preparation of (Fe₃O₄/AC) nanoparticles

The co-precipitation method was used to prepare two distinct ratios of (Fe₃O₄/AC) NPs as reported by [22] with some modification. 2.5 g of AC for ((Fe₃O₄/AC(1)) and 1.25 g of AC for (Fe₃O₄/AC(2)) were dispersed in 250 mL solution of 28 mM FeCl₂·6H₂O and 14 mM of FeSO₄·7H₂O with vigorous stirring at 700 rpm at 70°C–80°C. 100 mL of NaOH (5 M) solution was added drop wise into the above mixture to precipitate the hydrated iron oxide under vigorous stirring at 80°C until pH reached 10–11. The suspension was stored in a desiccator until use.
was further stirred for 1 h on a magnetic stirrer at 80°C. Next, it was aged at room temperature for 24 h. The FeO/AC NPs were separated by a magnet and washed continuously with distilled water and ethanol up to neutral pH then dried in a hot air oven at 80°C for 12 h. After drying, the nanoparticles were crushed in a mortar and placed in airtight plastic containers for further use.

### 2.4. Calcination of the active carbon

The activated carbon (AC) prepared from RS by concentrated sulfuric acid was further modified by thermal treatment at 500°C for 1 h in a muffle furnace without inert gas. After that the calcined AC was cooled and placed in airight plastic containers for further use. This method resulted in a substantial increase in the porosity of the material so surface area, pore volume and pore size increased.

### 2.5. Characterizations

#### 2.5.1. Surface area analysis

The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore diameter were determined by Barrett–Joyner–Halenda desorption method in N₂ atmosphere at 77 K using Quantachrome Nova 3200 instrument (Boynton Beach, FL, USA). The samples before measurement were degassed at 200°C for 24 h to remove moisture.

#### 2.5.2. Fourier-transform infrared analysis

Fourier-transform infrared (FTIR) spectra of the samples were recorded using Fourier-transform infrared spectrometer (FTIR, 4100 JASCO, Japan) in the wavelength range of 4,000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

#### 2.5.3. X-ray diffraction analysis

The crystalline structure of the nanoparticles and the amorphous nature of active carbon were checked using a Bruker AXS-D8 Advance X-ray diffraction (XRD) spectrometer (Karlsruhe, Germany). The scan was collected in the 20 range from 4° to 80° with a step size of 0.02° and scan step time of 0.6 s using Cu-Kα (K = 1.5406 Å) operated at 40 kV and current of 40 mA.

#### 2.5.4. Field-emission scanning electron microscopy and energy-dispersive X-ray analysis

The elemental analysis and morphology of surface of FeO/AC NPs were determined via Field-emission scanning electron microscopic (FE-SEM) technique (Zeiss Sigma 300 VP) coupled with energy-dispersive X-ray (EDX) Oxford X-MAX.

#### 2.5.5. Raman spectroscopic analysis

Due to its sensitivity to various carbon structures, Raman spectroscopy is specifically used to classify carbon-based materials. Raman spectra were achieved in SENTERRA dispersive Raman microscope (Bruker, Billerica, MA, USA).

### 3. Batch adsorption experiments

Batch adsorption experiments were performed to determine the elimination of (Pb²⁺) from aqueous solution. In each experiment, 25 mL of Pb²⁺ ions solution of known initial concentration (ranging from 10 to 100 mg L⁻¹) was treated with a specified known amount (by wt.) of adsorbents (0.25–4 g L⁻¹) and at known pH. The solution pH was adjusted to the desired value by adding 0.1 M HCl or 0.1 M NaOH. Then, shaker flasks were agitated in a mechanical shaker at a constant speed of 200 rpm at room temperature (30°C ± 2°C) for a prescribed time to attain the equilibrium. Then the solutions were filtered and the final concentrations of metal ions were analyzed by using GBC atomic absorption reader (Model SavantAA AAS with GF 5000 Graphite Furnace). The effects of initial concentration of Pb²⁺ ions (10–100 mg L⁻¹), contact time (2–120 min), solution pH (3–5) and adsorbent dose (0.25–4.0 g L⁻¹) were studied. Blank solutions were treated similarly (without adsorbent) and the concentration at the end of each operation was taken as the initial one. The percent metal removal (R%) was calculated using Eq. (1):

\[
R(\%) = \frac{C_i - C_e}{C_i} \times 100
\]

where \( C_i \) and \( C_e \) represented initial and equilibrium concentrations of metals in the solution respectively. The adsorption capacity (\( q_e \)) at equilibrium time was calculated using Eq. (2):

\[
q_e (\text{mg/g}) = \frac{(C_i - C_e) \times V}{m}
\]

where \( V \) is the volume of metal ion solution (L) and \( m \) is the mass of the adsorbent (g).

### 4. Results and discussion

#### 4.1. Characterizations of adsorbents

The data in Table 1 indicates that the surface area and pore volume increased when magnetite nanoparticles loaded on AC obtained from rice straw FeO/AC(1,2) and also when AC calcined at 500°C for 1 h.

The FTIR technique is an important tool for the identification of the characteristic functional groups involved in metal ion adsorption. Adsorbents have the ability to bind with metal ions with different kinds of chemical groups such as carboxyl, hydroxyl, ester, aldehyde, ketone etc. Their metal uptake affinity depends on variables such as the number of sites, their availability, chemical structure, affinity between binding sites and metal ions, etc [42]. FTIR spectra of AC, CAC and FeO/AC(1) and (2) are shown in Fig. 1. Activation of RS with sulfuric acid indicated the presence of the acidic groups on the active carbon surface, which increases metal adsorption.

The FTIR spectrum of AC shows a broad peak at 3,397.96 cm⁻¹ is due to –OH stretching of the H-bond which confirms the presence of the hydroxyl group [43]. Bands at 2,923.56 and 2,857.02 cm⁻¹ are ascribed to the asymmetric
Table 1
Surface area, total pore volume and average pore diameter of AC, CAC and Fe\textsubscript{3}O\textsubscript{4}/AC(1,2)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Average pore diameter (nm)</th>
<th>Total pore volume (cm\textsuperscript{3} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>22.75</td>
<td>3.4</td>
<td>0.04</td>
</tr>
<tr>
<td>CAC</td>
<td>204.69</td>
<td>10.3</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}/AC(1)</td>
<td>38.03</td>
<td>15.3</td>
<td>0.16</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}/AC(2)</td>
<td>109.89</td>
<td>10.5</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Fig. 1. FTIR spectra of: (A) AC, (B) CAC, (C) Fe\textsubscript{3}O\textsubscript{4}/AC(1), and (D) Fe\textsubscript{3}O\textsubscript{4}/AC(2).

and symmetric C–H stretching vibration models of aliphatic molecules, respectively [44]. The small band at 2,334.41 cm\textsuperscript{-1} is corresponding to the carboxyl group [43]. The smaller shoulder peaks at 1,710.55 and 1,616.06 cm\textsuperscript{-1} are attributed to unionized C=O stretching of carboxylic acid and C=O stretching of carboxylic acid with intermolecular hydrogen bond, respectively [21]. The peaks at 1,510.9 and 1,458.89 cm\textsuperscript{-1} are indicative of the aromatic C=C stretching vibration in lignin aromatic groups [45]. The strong peak at 1,103 cm\textsuperscript{-1} is attributed to C–O stretching vibration and O–H bending modes of alcoholic, phenolic, and carboxylic groups. The C–H out-of-plane bending vibrations in aromatic structures cause the band at 802.242 cm\textsuperscript{-1} [46]. So, it can be concluded that there exists hydroxyl, carboxyl and carboxyl groups on the AC surface. After calcination of AC small peaks at 3,900 and 3,840 cm\textsuperscript{-1} may be ascribed to isolated OH groups and the strong broad peak centered at 3,443.2 cm\textsuperscript{-1} can be assigned to O–H stretching vibration of hydroxyl functional groups [46]. After calcination, great changes occurred to AC chemical composition and the peaks shifted as compared to AC. At high temperature silica content increased and this confirmed by the strong peaks at 1,097.3 and 804.2 cm\textsuperscript{-1} which play a vital role in the adsorbent development [37], the peak at 1,097.3 cm\textsuperscript{-1} is very strong due to asymmetric stretching of Si–O and Si–O–Si stretching in silica at 465.7 cm\textsuperscript{-1}. The weak band of aliphatic groups stretching vibration at 2,930.3 cm\textsuperscript{-1} its intensity was lower than the spectrum of AC, leading to the decrease in aliphaticity in the activated carbon by increasing temperature. Bands at 1,510.9 and 1,458.89 cm\textsuperscript{-1} which are indicative of the aromatic C=C stretching vibration in lignin aromatic groups disappeared because of the removal of most of the lignin. Residual lignin ascribed at the smaller shoulder peak at 1,632.5 cm\textsuperscript{-1}. At the same time two bands of carboxyl groups appeared at 2,360.4 and 2,334.4 cm\textsuperscript{-1}. On the other hand, in Fe\textsubscript{3}O\textsubscript{4}/AC(1) and (2), the presence of Fe\textsubscript{3}O\textsubscript{4}-NPs on the surface of AC is evidenced by the new adsorption bands observed at 666.3 and 558.3 cm\textsuperscript{-1} for Fe\textsubscript{3}O\textsubscript{4}/AC(1) and at 787.8, 574.7 cm\textsuperscript{-1} for Fe\textsubscript{3}O\textsubscript{4}/AC(2), respectively, which corresponds to Fe–O stretching in Fe\textsubscript{3}O\textsubscript{4} [36,41]. Absorption peaks at 3,365.2 and 3,370.9 cm\textsuperscript{-1} in Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2), respectively, are characterized by OH groups, indicating the presence of AC [38]. The shifting of those peaks and other peaks of the function groups of AC is due to the binding of Fe\textsubscript{3}O\textsubscript{4}-NPs with AC and confirm (Fe\textsubscript{3}O\textsubscript{4}/AC) preparation.

The comparison of XRD patterns of the four samples (Fig. 2) indicates that the iron oxide nanoparticles in Fe\textsubscript{3}O\textsubscript{4}/AC samples are crystalline in nature and have the cubic structure of magnetite. The XRD pattern (Fig. 2C) of Fe\textsubscript{3}O\textsubscript{4}/AC(1) shows four characteristic diffraction peaks (with corresponding Miller indices) at 20 of 33.14° (220), 35.55° (311), 54.15° (422) and 62.41° (440) respectively. Also (Fig. 2D) of Fe\textsubscript{3}O\textsubscript{4}/AC(2) shows four characteristic diffraction peaks (with corresponding Miller indices) at 20 of 35.69° (311), 43.25° (400), 57.22° (511) and 62.86° (440) respectively. These observations were in line with previous research [22,31,41,44–52]. The XRD pattern (Fig. 2C) of Fe\textsubscript{3}O\textsubscript{4}/AC(1) shows four characteristic diffraction peaks (with corresponding Miller indices) at 20 of 33.14° (220), 35.55° (311), 54.15° (422) and 62.41° (440) respectively. Also (Fig. 2D) of Fe\textsubscript{3}O\textsubscript{4}/AC(2) shows four characteristic diffraction peaks (with corresponding Miller indices) at 20 of 35.69° (311), 43.25° (400), 57.22° (511) and 62.86° (440) respectively. These observations were in line with previous research [22,31,41,44–52].
area of Fe$_3$O$_4$/AC(2) than Fe$_3$O$_4$/AC(1) because it had more Fe$_3$O$_4$-NPs agglomerated and attached to each other making the surface rough and coarse. EDX gives the elemental composition of the four adsorbents as shown in Fig. 4.

As can be seen in the EDX spectra of AC samples (Fig. 4A and B), they contain carbon, Oxygen and silicon which originated from silica present in rice straw. Fig. 4C and D show the presence of Fe along with C and O in Fe$_3$O$_4$/AC(1) and (2) samples, which confirmed the infusion of Fe$_3$O$_4$-NPs on the AC surface. This analysis also illustrated that the weight fraction of carbon is 50.24% and iron content is only 8.88% in Fe$_3$O$_4$/AC(1), indicating that the activated carbon content was significantly higher than Fe$_3$O$_4$ NPs. On the other hand, the weight fraction of carbon is only 28.15% but iron content is 32.86% in Fe$_3$O$_4$/AC(2), confirming that Fe$_3$O$_4$ NPs were more than AC. Moreover, the EDX spectrum of Fe$_3$O$_4$/AC(1) and (2) samples showed an additional peak which was assigned to Na that might have originated during Fe$_3$O$_4$ NPs preparation.

Raman spectroscopy is primarily applied to the characterization of carbon-based materials. The G band refers to the presence of sp$^2$ carbon in graphite-like structures and the D band is referred to as disorders/defects in graphitic
Fig. 4. EDX spectra of: (A) AC, (B) CAC, (C) Fe₃O₄/AC(1), and (D) Fe₃O₄/AC(2).
structures. The Raman spectrum of the AC exhibits G, and D bands, at 1,148.30 and 1,089.99 cm⁻¹, respectively. As shown in Fig. 5 shifting occurred to (G, D) bands values in CAC and also in Fe₃O₄/AC(1) and (2).

In the graphitic structure of the activated carbon, the intensity ratio (I_D/I_G) of the D and G bands is the ratio of sp³ hybridized carbon atoms (amorphous/disordered carbon) to sp²-bonded carbon atoms (graphitic carbon) which is attributed to defects; the higher the intensity ratio, the higher degree of graphitic defects. A greater I_D/I_G quantity demonstrates a higher surface area and a higher amount of covalent reactions exist on the adsorbent surface [1,54]. It was calculated as indicated in (Table 2); Fe₃O₄/AC(1) and CAC have the highest I_D/I_G then Fe₃O₄/AC(2) and AC has the lowest ratios.

4.2. Batch studies

4.2.1. Effect of pH

The solution pH has an important impact on the adsorption of the metal ions by the adsorbents because its effect on the solubility of adsorbates, chemical status of the functional groups responsible for adsorption and the degree of ionization of the adsorbate during reaction [33]. Maximum adsorption has been found to occur at a particular pH value [55]. To determine the optimum adsorption pH, Fig. 6 shows the influence of pH on the adsorption of Pb²⁺. While screening the pH values, all the other process variables such as initial metal ion concentration (10 mg L⁻¹), (AC, CAC and Fe₃O₄/AC(1)) dose (2 g L⁻¹) and Fe₃O₄/AC(2) dose (1 g L⁻¹), at room temperature (30°C ± 2°C), shaking speed (200 rpm) and contact time (1 h) were maintained constant.

Fig. 6 shows the maximum removal efficiency percentage of Pb²⁺ from aqueous solution by using AC, CAC, Fe₃O₄/AC(1) and Fe₃O₄/AC(2) was found to be 70.6%, 97%, 98% and 95%, respectively, at solution pH 5. The charge of active sites accessible on the surface of an adsorbent, which is usually influenced by the pH of the solution, affects the adsorption of lead ions onto the surface of an adsorbent. This is due to the fact that the H⁺ is a strong competing adsorbate, and the chemical speciation of metal ions as the pH of the solution changes. At low pH, lower adsorption of metal ions onto the adsorbents due to the presence of excess H⁺ ions competing with the metal ions for the active sites. The abundance of hydronium ions (H₃O⁺) in the solution, causing competition for adsorption onto adsorbent surface between hydronium ions and Pb²⁺ ions (Lead ions is present as Pb²⁺ and Pb (OH)⁺ at lower pH), lowering the overall adsorption efficiency of these metal ions at lower pH. On the other hand, at higher pH levels the functional groups present on the surface of nanoparticles, such as carboxylic acid, hydroxyls, and phenol, are deprotonated, resulting in negative sites on the adsorbent surface. As a result of the electrostatic interaction between these negatively charged adsorption sites and positively charged Pb²⁺ ions, the adsorption is increased [56]. As a result, the formation of hydroxide precipitation (Pb(OH)OH) at pH higher than 5 can be linked to a portion of metal ion elimination and the decrease in adsorption of metal ions at higher pH is mainly due to the formation of soluble hydroxyl complexes [57]. To prevent the formation of these complexes, all the experiments were carried at optimum solution pH 5.

4.2.2. Effect of initial metal ion concentration

Fig. 7 reveals the effect of the initial concentrations (10, 25, 50 and 100 mg L⁻¹) on the removal of Pb²⁺ aqueous
solution using (2 g L\(^{-1}\)) from (AC, CAC and Fe\(_3\)O\(_4\)/AC(1)) and (1 g L\(^{-1}\)) from Fe\(_3\)O\(_4\)/AC(2) adsorbent materials at room temperature (30°C ± 2°C), 1 h contact time with a 200 rpm rotating shaking and pH = 5. It is indicated that the metal removal by both the sorbent materials employed decreased as the metal ion concentration in the solution was increased from 10 to 100 mg L\(^{-1}\) in the solution. Also the maximum Pb\(^{2+}\) removal percent obtained was achieved 70.6%, 97%, 98% and 95% at concentration 10 mg L\(^{-1}\) by using AC, CAC, Fe\(_3\)O\(_4\)/AC(1) and Fe\(_3\)O\(_4\)/AC(2), respectively. However, as the concentration of the metal ion increased, the adsorption capacity of the metal ion increased on all adsorbents. It increased from 3.53 to 7.35 mg g\(^{-1}\) for AC, 4.85 to 30 mg g\(^{-1}\) for CAC, 4.9 to 33 mg g\(^{-1}\) for Fe\(_3\)O\(_4\)/AC(1) and 9.5 to 68 mg g\(^{-1}\) for Fe\(_3\)O\(_4\)/AC(2). The increase in adsorption capacity (as shown in Fig. 8) can be explained on the basis that, an increase in initial metal ion concentration led to an increase in diffusion of Pb\(^{2+}\) ions from the solution phase to the surface of the adsorbents due to an increase in the driving force of metal ions causes collisions between metal ions and the surface of nanoparticles, resulting in an increase in adsorption capacity [58]. Similarly, Ibrahim et al. [59] used modified soda lignin (MSL) extracted from oil palm empty fruit bunches (EFB) for the removal of lead(II) ions from aqueous solutions. They found that the adsorption capacity of lead(II) ions increased from 2.47 to 21.54 mg g\(^{-1}\) as the initial concentration was increased from 5 to 100 ppm. The decrease in removal efficiency with an increase in metal ion concentration may be due to the restriction of adsorption sites present on the surface of adsorbent materials. This is attributed to the availability of more adsorption sites at low metal ion concentrations for the sorption of Pb\(^{2+}\) ions. At higher metal ion concentrations, the available active sites for the adsorption of metal ions become less and the percentage removal of metal ions depends on the initial metal ion concentration [4,50,60]. Therefore, to determine the effect of contact time and adsorbent dose, a metal ion concentration of 10 mg L\(^{-1}\) was used.

**4.2.3. Effect of adsorbent dosage**

The adsorbent dose is another important parameter, which influences the adsorption of metal ions onto the different adsorbents. The metal adsorption efficiency of the adsorbent materials with varying amounts for Pb\(^{2+}\) ions is shown in Fig. 9. The adsorbent dosage is 0.00625, 0.0125, 0.025, 0.0375, 0.05 and 0.1 g/25 mL of AC, CAC, Fe\(_3\)O\(_4\)/AC(1) and Fe\(_3\)O\(_4\)/AC(2) separately; for 10 mg L\(^{-1}\) of Pb\(^{2+}\) solution at 1 h contact time with a rotating shaker at 200 rpm, room temperature (30°C ± 2°C) and shaking speed (200 rpm).

Fig. 7. Effect of initial metal ion concentration on the removal of Pb\(^{2+}\) by the different adsorbents at pH 5, 1 h, dose (2 g L\(^{-1}\)) of (AC, CAC and Fe\(_3\)O\(_4\)/AC(1)) and (1 g L\(^{-1}\)) of Fe\(_3\)O\(_4\)/AC(2), at room temperature (30°C ± 2°C) and shaking speed (200 rpm).

Fig. 8. Effect of initial metal ion concentration on the adsorption capacity of Pb\(^{2+}\) by the different adsorbents at pH 5, 1 h, dose (2 g L\(^{-1}\)) of (AC, CAC and Fe\(_3\)O\(_4\)/AC(1)) and (1 g L\(^{-1}\)) of Fe\(_3\)O\(_4\)/AC(2), at room temperature (30°C ± 2°C) and shaking speed (200 rpm).

Fig. 9. The adsorbent dosage is 0.00625, 0.0125, 0.025, 0.0375, 0.05 and 0.1 g/25 mL of AC, CAC, Fe\(_3\)O\(_4\)/AC(1) and Fe\(_3\)O\(_4\)/AC(2) separately; for 10 mg L\(^{-1}\) of Pb\(^{2+}\) solution at 1 h contact time with a rotating shaker at 200 rpm, room temperature (30°C ± 2°C) and pH = 5.

Fig. 8 demonstrates that the percentage removal of metal ions increases with increase of adsorbent dose. This is due to the increase of surface area and the number of adsorption sites, which may be the reason for the removal of more ions at their surfaces [61]. At higher adsorbent doses, the adsorption capacity was lower (Fig. 10). At first all the adsorbent sites are available and later the adsorption rate was lowered that may be due to the lack of available active sites required for further uptake after reaching the equilibrium. The decrease in adsorption capacity as the adsorbent dose is increased may be due to particle interactions, such as aggregation, caused by high adsorbent concentrations, which reduce the active surface area of the adsorbent [39,62]. The removal percent of Pb\(^{2+}\) ions reached 79%, 100%, and 100% when using 4 g L\(^{-1}\) dose of AC, CAC and Fe\(_3\)O\(_4\)/AC(1), respectively, and 100% when using 1.5 g L\(^{-1}\) of Fe\(_3\)O\(_4\)/AC(2). The optimum dosages of AC, CAC and Fe\(_3\)O\(_4\)/AC(1) were used for the removal of lead is 2 and 1 g L\(^{-1}\) of Fe\(_3\)O\(_4\)/AC(2).

**4.2.4. Effect of contact time**

One of the most critical parameters that regulate adsorption processes is contact time. The effect of contact time on the removal of Pb\(^{2+}\) by the different adsorbent materials was then investigated in order to determine the optimum time taken to attain the equilibrium. Fig. 11 shows the adsorption of Pb\(^{2+}\) at pH 5 by using 2 g L\(^{-1}\) dose of AC, CAC, and Fe\(_3\)O\(_4\)/AC(1) and 1 g L\(^{-1}\) dose of Fe\(_3\)O\(_4\)/AC(2) at room temperature (30°C ± 2) and 10 mg L\(^{-1}\) metal ion concentration for the different time points; 2, 5, 10, 20, 40, 60, 90 and 120 min. Fig. 11 depicts that the rate of Pb\(^{2+}\) ion removal increased over time, reaching saturation in about 2 h. Due to a rapid saturation of adsorption sites, lead showed a quick rate of adsorption within the first hour of adsorption, and the rate of removal percent became almost insignificant. The rapid adsorption may be due to the adsorption sites being more readily available at the start of the process. The adsorption sites were steadily occupied and began to saturate over time.
due to a decline in the number of binding sites available suggesting monolayer coverage of the surface, resulting in a slower adsorption rate in the later stages [54,63,64]. After 5 min, about 51.45%, 65.17%, 72.9%, and 75% of Pb\textsuperscript{2+} were removed from the solutions by using AC, CAC, Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2), respectively. Within 120 min of operation about 78.75%, 99%, 99.9% and 99% of Pb\textsuperscript{2+} were removed from the solutions by using AC, CAC, Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2), respectively. Taking into account that Fe\textsubscript{3}O\textsubscript{4}/AC(2) optimum dose used in all adsorption tests is 1 g L\textsuperscript{–1}. On the other hand, 2 g L\textsuperscript{–1} is the optimum dose used in AC, CAC and Fe\textsubscript{3}O\textsubscript{4}/AC(1) adsorbents.

4.2.5. Effect of temperature

The effect of temperature on the removal of Pb\textsuperscript{2+} by the different adsorbent materials was studied by varying the temperature in the range of 20°C–60°C again keeping all other process variables constant. Fig. 12 shows the removal of Pb\textsuperscript{2+} at pH 5 for 10 mg L\textsuperscript{–1} of Pb\textsuperscript{2+} solution at 1 h contact time with a rotating shaker at 200 rpm by using 2 g L\textsuperscript{–1} dose of AC, CAC and Fe\textsubscript{3}O\textsubscript{4}/AC(1) and 1 g L\textsuperscript{–1} dose of Fe\textsubscript{3}O\textsubscript{4}/AC(2) and 10 mg L\textsuperscript{–1} metal ion concentration for the different temperature points; 20°C, 30°C, 40°C, 50°C, and 60°C. The figure reveals that the adsorption of ions increased with an increase in temperature. The adsorption efficiency for Pb\textsuperscript{2+} increased from 59.12% to 74.2%, from 85.8% to 99%, from 96.3% to 100% and from 94% to 100% for AC, CAC, Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2), respectively.

The results indicated that the adsorption process was endothermic in nature. This may be due to the fact that as the temperature rises, the mobility of the ions rises, increasing the interaction between the ions and the surface of the nanoparticles [22,37]. 30°C was chosen as the optimum temperature for all of the experiments because it is appropriate for practical application under field conditions. On the basis of the obtained data from section 4.2.1 to 4.2.5, a table (Table 3) has been prepared showing the optimum conditions needed for the highest removal efficiency of AC, CAC, Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2) for removal of Pb\textsuperscript{2+} ions.

4.2.6. Pb\textsuperscript{2+} adsorption mechanism

By combining isothermal modelling of adsorption equilibrium data with surface characterization and pH studies, it is clear that the surface of Fe\textsubscript{3}O\textsubscript{4}/AC has a various functional groups which effectively chelate Pb\textsuperscript{2+} ions from water as indicated by FTIR analysis and the surface become rough and porous after activation of rice straw by the acid and addition of magnetic nanoparticles (Fe\textsubscript{3}O\textsubscript{4}–NPs) as shown by FE-SEM technique. pH studies also explained the adsorption process, Pb\textsuperscript{2+} adsorption was lower at lower pH but increased as pH increased. This behavior is due to the lower pH causes an abundance of hydronium ions (H\textsubscript{3}O\textsuperscript{+}) in the solution, causing competition for adsorption onto adsorbent surface between hydronium ions and Pb\textsuperscript{2+} ions (Lead ions is present as Pb\textsuperscript{2+} and Pb(OH)\textsubscript{4}– at lower pH), lowering the overall adsorption efficiency of these metal ions at lower pH. On the other hand, at higher pH levels the functional groups present on the surface of nanoparticles, such as carboxylic acid, hydroxyls, and phenol, are deprotonated, resulting in negative sites on the adsorbent surface. As a result of the electrostatic interaction between these negatively charged adsorption sites and positively charged Pb\textsuperscript{2+} ions, the adsorption is increased [56]. As a result, the formation of hydroxide precipitation (Pb(OH)\textsubscript{2}) at pH higher than 5 can be linked to a portion of metal ion elimination [65]. Pb\textsuperscript{2+} adsorption was maximum at pH 5, hence that was chosen as the optimal pH [57,66]. The regression coefficient (R\textsuperscript{2})
values of the Langmuir, Freundlich, and Temkin isotherm models also support this mechanism. The Freundlich isotherm model was shown to be more applicable than the other two, indicating that multi-layered physiosorption is the most common mechanism of Pb(II) ions adsorption heterogeneous adsorbent surfaces [67]. Fig. 13 represents the adsorption mechanism in graphical form.

4.2.7. Thermodynamic studies

Thermodynamic investigations can be used to determine if the adsorption mechanism is physical or chemical. The thermodynamic parameters for the removal of Pb²⁺ by the studied adsorbents were estimated using the following equations: standard Gibb’s free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°).

\[
\Delta G^0 = -RT \ln K \\
\Delta G^0 = \Delta H^0 - T \Delta S^0 \\
\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \\
K = \left( \frac{q_e}{C_e} \right)
\]

where \( R \) (8.314 J mol⁻¹ K⁻¹) is the universal gas constant, \( q_e \) is the amount of ion adsorbed on the surface of adsorbent (mg g⁻¹), \( C_e \) is equilibrium concentration (mg L⁻¹), \( T \) is temperature in Kelvins. Table 4 displays the thermodynamic parameters for adsorption of Pb²⁺ ions adsorbed on the surface of the studied adsorbents at different temperatures.

The negative value of ΔG in Table 4 indicates that the adsorption process is viable and spontaneous in nature. This is consistent with the Langmuir separation factor \( R_L \) results, which showed that the \( R_L \) values were between 0 and 1, that is, \( 0 < R_L < 1 \), and the Freundlich exponent \( n \) was likewise bigger than 1. The value of ΔG reduced as the temperature increased, showing that the increased temperature was beneficial to the adsorption process. The positive ΔH indicates that the adsorption process is endothermic and irreversible. The adsorption process is a mixture of two simple processes, Gibb’s free energy (ΔG°) and standard enthalpy (ΔH°), with a positive value of (ΔS°). Furthermore, positive ΔS° values suggested that the adsorbent surface was affine to Pb²⁺ ions and that the degrees of disorder and randomness at the solid-liquid interface were significant [33,68,69].

Table 3

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Dose (g L⁻¹)</th>
<th>Initial concentration (mg L⁻¹)</th>
<th>Contact time (min)</th>
<th>Temperature (°C)</th>
<th>Removal efficiency</th>
</tr>
</thead>
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<td>AC</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>60</td>
<td>30</td>
<td>70.6%</td>
</tr>
<tr>
<td>CAC</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>60</td>
<td>30</td>
<td>97%</td>
</tr>
<tr>
<td>Fe₃O₄/AC(1)</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>60</td>
<td>30</td>
<td>98%</td>
</tr>
<tr>
<td>Fe₃O₄/AC(2)</td>
<td>5</td>
<td>1</td>
<td>10</td>
<td>60</td>
<td>30</td>
<td>95%</td>
</tr>
</tbody>
</table>
### 4.2.8. Adsorption isotherms

The aim of adsorption isotherms is to find a relationship between the adsorbate concentration in the bulk and the amount adsorbed at the interface [62]. Batch adsorption data was described using Langmuir, Freundlich and Temkin models [70]. Monolayer adsorption is defined by the Langmuir isotherm, which assumes homogeneous sorption sites and sorption energies on the surface of adsorbents [35]. It is also believed that once a metal ion has occupied a site, no further sorption will take place [71]. Both the Langmuir and Freundlich isotherm models have been shown to be adequate for explaining short-term and mono component metal ion adsorption by various sorbent materials. The linear form of Langmuir model and its dimensionless constant separation factor $R_L$ is expressed in Eqs. (7) and (8) [72].

\[
\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \\
R_L = \frac{1}{1 + bC_e} \tag{7}
\]

\[
R_L = \frac{1}{1 + bC_e} \tag{8}
\]

where $Q_o$ (mg g$^{-1}$) is the maximum Langmuir adsorption capacity and $b$ (L mg$^{-1}$) is the Langmuir constant related to free energy. A plot of $C_e$ vs. $C_e/Q_e$ for using AC, CAC, Fe$_3$O$_4$/AC(1) and Fe$_3$O$_4$/AC(2) for Pb$^{2+}$ is shown in Fig. 14. The Langmuir constants $Q_o$ and $b$ were calculated from the

#### Table 4

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$T$ (K)</th>
<th>$\Delta G$</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$R^2$</th>
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<td>AC</td>
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<td>12.334</td>
<td>40.731</td>
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<td></td>
<td>313</td>
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<td>119.628</td>
<td>423.55</td>
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<td>-18.558</td>
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<tr>
<td>Fe$_3$O$_4$/AC(1)</td>
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<td>-23.386</td>
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<td></td>
<td>323</td>
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<td>Fe$_3$O$_4$/AC(2)</td>
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<td>-29.364</td>
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</tr>
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</table>

Fig. 14. Langmuir isotherm model plots for removal of Pb$^{2+}$ ions using different adsorbents.
slope and intercept of the Langmuir plot of $C_e$ vs. $C/Q$, is represented in Table 5.

The Langmuir treatment is based on the idea that total adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, with constant adsorption energy and no adsorbate migrate into the plane of the surface. The Langmuir constant $b$ quantifies the affinity between the adsorbent and the adsorbate, and the lower the value obtained, the greater the metal’s affinity for the adsorbent material. Furthermore, the adsorption capacity can imply a relationship between the adsorbent’s surface area and porosity, that is, the higher the surface area and pore volume, the greater the metal ion adsorption capacity [73]. The value of area and pore volume, the greater the metal ion adsorption capacity, whereas values between 1 and 2 indicate a moderately difficult adsorption characteristic, and values less than 1 indicate a poor adsorption characteristic [78]. A plot of $\log Q_e$ vs. $\log C_e$ for using AC, CAC, Fe$_3$O$_4$/AC(1) and Fe$_3$O$_4$/AC(2) for Pb$^{2+}$ ions is shown in Fig. 15. The values obtained for the slopes and intercepts of these plots are presented in Table 5. The adsorption intensity ($n$) values were between 2 and 10 for all adsorbent materials, which indicates a favorable process and the surface of sorbent materials was heterogeneous. The values of ($R^2$) in Freundlich model for Pb$^{2+}$ using AC; (0.972), CAC; (0.972), Fe$_3$O$_4$/AC(1); (0.966), and Fe$_3$O$_4$/AC(2); (0.997), respectively were higher as compared to Langmuir model thus, indicating that Freundlich model fitted the data well confirming multilayer adsorption. Except in the case of Pb$^{2+}$ by AC in Langmuir $R^2$ value (0.972) is higher than that of Freundlich (0.915).

The Temkin isotherm model predicts that adsorption energy decreases linearly with surface coverage because of adsorbent-adsorbate interactions. The Temkin isotherm model’s linear form is as follows [40]:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

where $T$ is the absolute temperature (Kelvin) and $R$ is the universal gas constant (J mol$^{-1}$ K$^{-1}$). $b$ is the Temkin constant related to the heat of adsorption and $K_T$ is the equilibrium constant.

Table 6
Comparison of monolayer adsorption capacity of different adsorbents reported in literature used for Pb(II) removal

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>7.56</td>
<td>[74]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>6.68</td>
<td>[74]</td>
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<tr>
<td>Blast furnace slag</td>
<td>5.52</td>
<td>[74]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>0.948</td>
<td>[74]</td>
</tr>
<tr>
<td>Kaolin</td>
<td>0.500</td>
<td>[74]</td>
</tr>
<tr>
<td>Bagasse fly ash</td>
<td>2.5</td>
<td>[65]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>3</td>
<td>[75]</td>
</tr>
<tr>
<td>Tea waste</td>
<td>2</td>
<td>[75]</td>
</tr>
<tr>
<td>Peach stone</td>
<td>0.0023</td>
<td>[75]</td>
</tr>
<tr>
<td>Apricot stone</td>
<td>0.0013</td>
<td>[75]</td>
</tr>
<tr>
<td>Magnetic oak wood char</td>
<td>10.13</td>
<td>[76]</td>
</tr>
<tr>
<td>Rice husk biochar</td>
<td>1.84</td>
<td>[76]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/AC(2)</td>
<td>10.225</td>
<td>This study</td>
</tr>
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Table 5
Freundlich, Langmuir and Temkin isotherms’ constants for Pb$^{2+}$ adsorption onto the studied adsorbents

<table>
<thead>
<tr>
<th>Metal</th>
<th>Adsorbent</th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
<th>Temkin isotherm model</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{max}$</td>
<td>$K_L$</td>
<td>$R_L$</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>AC</td>
<td>0.938</td>
<td>8.234</td>
<td>0.012</td>
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<td></td>
<td>CAC</td>
<td>4.525</td>
<td>7.621</td>
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<td>Fe$_3$O$_4$/AC(2)</td>
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<td>0.095</td>
</tr>
</tbody>
</table>
Fig. 15. Freundlich isotherm model plots for removal of Pb^{2+} ions using different adsorbents.

Fig. 16. Temkin isotherm model plots for removal of Pb^{2+} using different adsorbents.
binding constant (L mg⁻¹) corresponding to the maximum binding energy. The values of these parameters are calculated and presented in Table 5. A plot of q_e vs. lnC_e enables the determination of the isotherm constant K_T and RT/b as shown in Fig. 16.

4.2.9. Adsorption kinetics

Adsorption kinetics, which is dependent on the physical and chemical properties of the adsorbent, describes the rate of reaction and reaction pathways. Three separate kinetic models, the pseudo-first-order, pseudo-second-order equations and intraparticle diffusion, were used to test the experimental results. Pseudo-first-order kinetic model was used to explain adsorption in a solid–liquid system Eq. (11) [77]. One metal ion is sorbed onto one sorption site on the adsorbent’s surface, according to this model:

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \]  

where q_e is the adsorption capacity at equilibrium time and q_t (mg g⁻¹) is the adsorption capacity at time t (min), and k_1 (min⁻¹) is the equilibrium rate constant for pseudo-first-order model. The value of k_1 is derived from the slope of the linear plots of log (q_e – q_t) vs. time (min) as shown in Fig. 17. The values of q_e (experimental) (mg g⁻¹), q_e (calculated) (mg g⁻¹), k_1 (min⁻¹) and R² for Pb²⁺ by AC, calcined AC, Fe₃O₄/AC(1) and Fe₃O₄/AC(2) are given in Table 7. The table shows that the regression coefficient (R²) values for the pseudo-first-order model are poor, and the calculated q_e values are not close to experimental q_e values, suggesting that this model does not match our data well. Therefore, the adsorption of Pb²⁺ ions by AC, CAC, Fe₃O₄/AC(1) and Fe₃O₄/AC(2) was examined using a pseudo-second-order model.

The pseudo-second-order model (Eq. 12) assumes that, on the surface of the adsorbent, one metal ion is sorbed into two sorption sites. The chemisorption kinetics of liquid solutions has been studied using this model. k_2 (g mg⁻¹ min⁻¹) is the equilibrium rate constant and q_e(0) is the initial adsorption rate (mg g⁻¹ min⁻¹) for pseudo-second-order model [79]. The values of 1/k_2q_e(0) and 1/q_e are derived from the intercept and slope of the linear plots of t/q_e vs. time (min) as shown in Fig. 18, which leads to calculation of the values of k_2 and q_e(calculated) [59]:

\[ \frac{t}{q_e} = \frac{1}{k_2q_e(0)} + \frac{1}{q_e} \]  

The values of q_e (experimental) (mg g⁻¹), q_e (calculated) (mg g⁻¹); k_2 (g mg⁻¹ min⁻¹) and R² of Pb²⁺ removal by AC, CAC, Fe₃O₄/AC(1) and Fe₃O₄/AC(2) are given in Table 7. Investigations of the use of AC, CAC, Fe₃O₄/AC(1) and Fe₃O₄/AC(2) as sorbent for removal of Pb²⁺ ions from
Fig. 18. The pseudo-second-order rate for adsorption of Pb\textsuperscript{2+} by different adsorbents.

Table 7
Pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models for the removal of Pb\textsuperscript{2+} by the studied adsorbents

<table>
<thead>
<tr>
<th>Metal</th>
<th>Adsorbent</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{exp}$</td>
<td>$q_{cal}$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>Pb</td>
<td>AC</td>
<td>3.938</td>
<td>1.468</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>CAC</td>
<td>4.95</td>
<td>1.740</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{3}O\textsubscript{4}/AC(1)</td>
<td>4.995</td>
<td>1.560</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{3}O\textsubscript{4}/AC(2)</td>
<td>9.9</td>
<td>2.969</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 8
Comparison of adsorption capacity of Fe\textsubscript{3}O\textsubscript{4}/AC(1) and Fe\textsubscript{3}O\textsubscript{4}/AC(2) with other adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg g\textsuperscript{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4} magnetite activated carbon composite</td>
<td>2.19</td>
<td>[81]</td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>18.59</td>
<td>[82]</td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>17.6</td>
<td>[83]</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O/SC</td>
<td>15</td>
<td>[84]</td>
</tr>
<tr>
<td>RHC-mag-CN</td>
<td>16</td>
<td>[85]</td>
</tr>
<tr>
<td>Iron oxide NPs embedded in orange peel pith</td>
<td>5.37</td>
<td>[86]</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O/AC</td>
<td>4.4</td>
<td>[22]</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O/AC(1)</td>
<td>33</td>
<td>This study</td>
</tr>
<tr>
<td>Fe\textsubscript{3}O/AC(2)</td>
<td>68</td>
<td>This study</td>
</tr>
</tbody>
</table>
solution indicated that the process was a second-order process due to high regression value of $R^2$ are (0.995, 0.995, 0.996 and 0.999), in case of using AC, CAC, Fe$_3$O$_4$/AC(1) and Fe$_3$O$_4$/AC(2), respectively. In addition, values of $q_e$ (experimental) and $q_e$ (calculated) are close to each other, indicating that the pseudo-second-order model better fits the data than the pseudo-first-order model.

The Weber–Morris model (1963) is used to investigate the adsorption kinetics and determine the role of diffusion in the adsorption process. The transport of ions from bulk solution to solid phase is described by this model (Eq. 13) [80]. It is assumed that the adsorption process takes place in two stages. The first straight segment illustrates macro-pore diffusion (i.e., diffusion of heavy metals from the solution to the nano-sorbent’s exterior surface, also known as external diffusion), whereas the second depicts micro-pore diffusion (diffusion of heavy metals from the nano-sorbent’s surface into the pores):

$$q_t = K_{id} \frac{t^{1/2}}{g^{1/2}} + C$$

where $q_t$ is the metal ion adsorbed (mg g$^{-1}$) at time $t$ (min), $K_{id}$ (mg g$^{-1}$ min$^{-1/2}$) is the rate constant for intraparticle diffusion which can be obtained from the slope of the straight line (slope of the plots between $q_t$ and $t^{1/2}$) and $C$ is the thickness of the boundary layer obtained from the intercept of the plots between $q_t$ and time (min). The values of $K_{id}$ and $C$ are given in Table 7. Greater the value of $C$, greater is the effect of the boundary layer. If intraparticle diffusion occurs, the relationship between $q_t$ and $t^{1/2}$ will be linear as shown in Fig. 19, with the line passing through the origin. However, because the line did not pass through the origin in our case, it is likely that another process is involved in the adsorption. The calculated intraparticle diffusion rate constants are not zero, implying that the adsorption process may not be controlled by the intraparticle diffusion model [33,41].

4.2.10. Comparison of adsorption capacity with other adsorbents

The maximum adsorption capacity of Fe$_3$O$_4$/AC adsorbent for the removal of Pb$^{2+}$ was compared with other adsorbents reported in the literature and the values are given in Table 8. It is clear that the adsorption capacity of Fe$_3$O$_4$/AC is comparable with other nanomaterials suggesting that, it is effective in removing Pb$^{2+}$ from aqueous solutions [22,81–86].

5. Conclusion

In this study, the adsorption potential of AC, CAC, Fe$_3$O$_4$/AC(1) and Fe$_3$O$_4$/AC(2) adsorbent materials was investigated for the removal of Pb$^{2+}$ ions. The XRD analysis of Fe$_3$O$_4$/AC(1,2) confirmed the presence of magnetite phase which is crystalline in nature and has the cubic structure, on the other hand, activated carbon didn’t show any specific peak confirming that the AC is amorphous in nature in AC and CAC samples. The optimum adsorption pH was
found to be 5 for Pb\(^{2+}\). The removal efficiency of the adsorbents decreased with an increase in the concentration, that is, 70.6%–14.69%, 97%–60%, 98%–66% and 95%–68% for Pb\(^{2+}\) by AC, CAC, Fe\(_2\)O\(_3\)/AC(1) and Fe\(_2\)O\(_3\)/AC(2), respectively. The adsorption efficiency for Pb\(^{2+}\) by Fe\(_2\)O\(_3\)/AC(2) was high in the beginning of the experiments as indicated by 75% removal in the first 5 min. The optimum conditions for the highest removal efficiency of AC, CAC, Fe\(_2\)O\(_3\)/AC(1) and Fe\(_2\)O\(_3\)/AC(2) for removal of heavy metal Pb\(^{2+}\) was pH = 5, room temperature (30°C ± 2°C), initial metal ion concentration = 10 mg L\(^{-1}\), contact time = 60 min and dose of 2 g L\(^{-1}\) by AC, CAC and Fe\(_2\)O\(_3\)/AC(1) and 1 g L\(^{-1}\) by Fe\(_2\)O\(_3\)/AC(2). The maximum Freundlich adsorption capacity for Pb\(^{2+}\) ions was 2.820, 6.979, 8.058 and 12.715 mg g\(^{-1}\) by AC, CAC, Fe\(_2\)O\(_3\)/AC(1) and Fe\(_2\)O\(_3\)/AC(2), respectively.

Acknowledgements

M. El-Sheeta is very grateful for the Academy of Scientific Research and Technology (ASRT), Egypt for the SNG scholarship to achieve this work towards her M.Sc. degree.

References


