

Removal of Cd (II) and Pb (II) Ions from Aqueous Solutions Using Raw and Modified Activated Carbon

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Abstract: The main objective of this study is to investigate the feasibility of using raw and modified activated carbon with ammonia for the maximum removal of Pb^{2+} and Cd^{2+} ions from aqueous solutions and polluted water samples at optimized process parameters such as initial metal concentration, adsorbent dose, contact time and solution pH. The treatment of a commercial granular activated carbon by ammonia was performed to increase the power of the heavy metal ions removal from aqueous samples. In this work, the adsorption of these ions on raw and modified activated carbon was studied using the batch equilibrium technique, and the equilibrium adsorption data was described by Langmuir isotherm models. In the current work, Pb^{2+} and Cd^{2+} ions were adsorbed out of aqueous solutions using raw and modified activated carbon as an adsorbent. Investigations have been done into the effects of solution pH, contact time, initial metal ion concentrations, and adsorbent dosage on removal efficiency. The pH studies demonstrated that Pb^{2+} and Cd^{2+} ion removal efficiency is pH-dependent, increasing with increasing pH value, peaking at pH 6.5, and then remaining nearly constant. Due to an increase in the number of adsorption sites, an increase in adsorbent mass causes an increase in Pb^{2+} and Cd^{2+} adsorption. According to the data, activated carbon has removal efficiency (96.0 - 98.0%) for removing Pb^{2+} and Cd^{2+} ions from aqueous solutions in the initial metal concentration range of 10 to 50 mg/l. The experimental data suited the Langmuir and Freundlich adsorption isotherms well, and their constants were assessed. The effectiveness of Pb^{2+} ions removal by adsorption (starting Pb^{2+} concentration ranging from 1 - 10 mg/l) is shown by the treatment results of various polluted water samples to be between (81.5 - 86.7%), between (91 - 98%), utilizing raw Activated carbon (R-AC) and modified activated carbon with ammonia (A-AC), respectively. The results for cadmium ions reveal that the effectiveness of Cd^{2+} ions removal by adsorption (starting Cd^{2+} concentration ranging from 1 to 10 mg/l) is ranged from (74.3 to 83.7%), and from (97.6 to 98.4%) when the raw activated carbon (R-AC) and modified activated carbon with ammonia (A-AC) are used, respectively.

Keywords: Activated carbon, cadmium removal, lead removal, carbon modification, functional material

INTRODUCTION

Egypt and many other countries around the world already have limited supplies of fresh water. It will become much more constricting in the ensuing decades as a result of population growth, urbanization, and climate change. Increased water demand is a contributing factor to this restriction, but so does contamination of freshwater ecosystems. The availability of potable water is reduced due to pollution, and the expense of purifying it is increased. Numerous organic and inorganic substances, including heavy metals, dyes, and industrial compounds, are major water pollutants. They may have an impact on human health or hinder the use of water in industry or agriculture. The water is deemed hazardous or too deteriorated for that usage if the level of a pollutant in the water supply exceeds an acceptable level for certain water uses. As a result, solutions to these pollution issues typically concentrate on reducing pollution at the source and/or treating contaminated water before consumption (Larous *et al.*, 2005; Ansari and Fahim, 2007; Ansari and Mosayebzadeh, 2010; Bulutand and Tez, 2007; Stankovic *et al.*, 2009). "Wastewater" is any water whose quality has been damaged by human activity. It may come from a variety of sources, including home, commercial, industrial, or agricultural activity.

Many industrial wastewaters, including those produced by mines, battery manufacturing processes, paint and pigment production facilities, and the glass industry, are contaminated with heavy metals. This

effluent frequently contains lead, cadmium, nickel, chrome, and copper. Due to their inability to biodegrade, these heavy metals cause bioaccumulation in living things, which in turn causes health issues in animals, plants, and people (Bailey *et al.*, 1999). It has been demonstrated that some biomass and microbes can take up hazardous and heavy metals from diluted aqueous solutions. The chemical makeup of the metal ions (such as size, valence, electron orbital structure, and the stability of the chemical forms in nature), the chemical makeup of the biomass (such as charge density, the structure of the polymer chain, and functional groups), and the conditions of the medium all affect the binding properties or their affinity for a metal dissolved in aqueous media (*e.g.* pH, temperature, ionic strength and the presence of competing for organic or inorganic metal chelators). Large amounts of water may typically be extracted from metal ions quickly and effectively using bio-sorptive processes (Habte *et al.*, 2020).

Chronic cadmium exposure has been associated with renal damage. Due of its bio-persistence, cadmium remains in the body for a very long time after absorption. High exposure has been linked to obstructive lung diseases and lung cancer. Cadmium exposure can lead to bone deformities in both humans and animals. On average, it is estimated that each day, humans take in 0.15 g of air and 1 g of water (Stankovic *et al.*, 2009).

Depending on the length and intensity of exposure, lead can cause a wide spectrum of biological abnormalities in people. High exposure can harm the neurological system, kidneys, gastrointestinal tract, joints, reproductive system, and cause issues with hemoglobin synthesis (Bulutand and Tez, 2007; Stankovic *et al.*, 2009). A collection of extremely carbonaceous chemicals that cannot be classified by a structural formula are referred to as "activated carbon." It is an amorphous solid made up of non-polar, very porous micro crystallites with a graphite lattice and is normally generated as small pellets or a powder. The drawback is that it only works at temperatures above 300°C, where reactions with oxygen occur. Carbonaceous material is used in both production steps, carbonization and activation.

Activated carbon modification by ammonia refers to the process of enhancing the surface properties of activated carbon by treating it with ammonia gas. This process involves exposing the activated carbon to an ammonia gas stream under controlled conditions of temperature and pressure. The ammonia gas reacts with the surface functional groups of the activated carbon, creating new surface functional groups such as amine and amide groups. The modification of activated carbon by ammonia increases its surface area, porosity, and adsorption capacity, making it more effective in removing heavy metals from water or wastewater.

Batch-type experiments were conducted with raw and modified activated carbon, cadmium, and lead aqueous solutions at concentration ranges of (10-50) mg/l and at different pH values between (2-9), to determine their influence on the adsorption process and set these values as parameters in the performance of subsequent experiments. This was done in order to set the pH values which have a higher metal removal rate and also determine the influence of material parameters on activated carbon. These pH levels were changed by appropriately introducing modest volumes of 0.1 M HCl or NaOH solutions. Activated carbon modified with ammonia is a promising material for removing heavy metals from wastewater due to its high adsorption capacity and selectivity. The modification process involves impregnating activated carbon with ammonia gas, which creates surface amine functional groups that can bind heavy metal ions. The adsorption process involves the interaction of heavy metal ions with the amine functional groups on the surface of the modified activated carbon. This interaction occurs through a complex process that involves electrostatic forces, ion exchange, and complexation reactions.

In this study, the surface of activated carbon was modified by adding ammonia to investigate the impact of modification on the removal of heavy metals. Activated carbon is a commonly used adsorbent for removing heavy metals from aqueous solutions due to its high surface area and pore volume. However, the modification of activated carbon can enhance its adsorption capacity and selectivity towards heavy metals. The addition of ammonia to the surface of activated carbon is expected to introduce functional groups that can enhance the affinity between the

activated carbon and heavy metal ions. Therefore, the modified activated carbon may exhibit improved adsorption performance towards heavy metals compared to unmodified activated carbon. This study aims to evaluate the effectiveness of the modified activated carbon in removing heavy metals from aqueous solutions and to provide insights into the potential mechanisms underlying the improved adsorption performance.

The results have shown that modified activated carbon can effectively remove heavy metals such as lead and cadmium from aqueous solutions more than unmodified activated carbon which has less efficiency. The efficiency of the removal process depends on various factors, such as the pH of the solution, contact time, concentration of the heavy metal ions, and the surface area of the modified activated carbon. One of the advantages of using modified activated carbon for heavy metal removal is its cost-effectiveness compared to other treatment methods. Additionally, the modified activated carbon can be regenerated and reused, reducing waste and making the process more sustainable. However, it's essential to note that modified activated carbon can't remove all heavy metals, and the efficiency of the removal process may vary depending on the specific heavy metal and the wastewater characteristics. Therefore, it's crucial to conduct a thorough analysis of the wastewater before selecting the treatment method.

The novelty of this work lies in the investigation of the removal efficiency of Cd (II) and Pb (II) ions from aqueous solutions using both raw and modified activated carbon. Activated carbon has been widely used as an adsorbent for removing heavy metals from wastewater. However, the modification of activated carbon with various agents is a relatively new approach that has shown promising results in enhancing its adsorption capacity. So that it is urgent need to develop effective and affordable technologies for removing heavy metals from water sources. Heavy metals such as Cd (II) and Pb (II) are known to cause severe health problems, including neurological and developmental disorders, even at low concentrations. Activated carbon is a promising adsorbent for heavy metal removal, but its effectiveness can be enhanced by modification with various agents.

Therefore, this study investigates the potential of both raw and modified activated carbon for removing Cd (II) and Pb (II) ions from aqueous solutions. The findings of this study could provide insights into the efficiency of different types of activated carbon for heavy metal removal and the potential of modification to enhance their adsorption capacity. This information is essential for developing efficient and cost-effective technologies for heavy metal removal, which could have significant environmental and health benefits.

The process of altering activated carbon's surface structure using ammonia

The method of modified activated carbon with ammonia involves treating the activated carbon with activated ammonia gas, washing and drying it,

characterizing the surface structure using various techniques, and evaluating the adsorption capacity through batch adsorption studies. The modification process is expected to change the surface structure of activated carbon, thereby enhancing its adsorption capacity for heavy metals.

A- Preparation of Activated Carbon: The activated carbon used in this study was prepared by carbonizing coconut shells at 600°C for 2 hours followed by activation with 1 M HCl at 80°C for 6 hours. The activated carbon was then washed with distilled water and dried at 110°C for 24 hours.

B- Ammonia Modification: The modified activated carbon was prepared by treating the activated carbon with ammonia gas. The process involved the following steps:

a. Activation of Ammonia: Ammonia gas was activated by passing it through a glass column filled with quartz sand at a flow rate of 30 mL/min. The column was heated to 350°C for 2 hours before use to activate the ammonia gas.

b. Ammonia Treatment: The activated carbon was placed in a glass reactor and exposed to the activated ammonia gas for 2 hours at 100°C. The ammonia gas was allowed to pass through the activated carbon at a flow rate of 50 mL/min.

c. Drying: After treatment, the modified activated carbon was washed with distilled water and dried at 110°C for 24 hours.

C- Characterization: The modified activated carbon was characterized using various techniques to evaluate the changes in the surface structure. The following parameters were measured:

a. Functional Groups: Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the functional groups on the surface of the modified activated carbon.

b. Surface Morphology: The surface morphology of the modified activated carbon was evaluated using Scanning Electron Microscopy (SEM).

c. Adsorption Studies: The adsorption capacity of the modified activated carbon was evaluated by batch adsorption studies. A stock solution of Cd (II) and Pb (II) ions was prepared by dissolving the salts in distilled water. The solution was then diluted to various concentrations for the adsorption studies. The modified activated carbon was added to the solution and shaken for 24 hours at room temperature. The adsorption capacity was determined by measuring the concentration of the metal ions before and after adsorption using Atomic Absorption Spectroscopy (AAS).

Batch adsorption studies

In order to perform batch adsorption studies, a certain quantity of unprocessed and modified activated carbon was combined with 50 ml of synthetic Pb²⁺, Cd²⁺ solutions, or polluted water samples. The pH of the solution was changed by adding 0.1 M HCl or 0.1 M NaOH solution depending on the desired pH value. The contents of all adsorption experiments were shaken for the required contact period at room temperature (25°C)

and then filtered through Whatman 42 filter papers. In this study, the initial concentration varied between 10 and 50 mg/l, the contact time was between 15 and 90 min, the pH of the solution ranged between 2 and 9, and the amount of adsorbent varied between 5 and 30 mg/l. A Perkin-Elmer model 2380 atomic absorption spectrometer (AAS) was used for the lead and cadmium analysis. The results are reported in terms of the raw and modified activated carbon as adsorbent for lead and cadmium ions, the removal efficiency (%) and adsorption capacity (mg/g) for the adsorbent was calculating using the following relationships:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\text{Adsorption capacity (mg/l)} = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where V is the volume of the Pb²⁺, Cd²⁺ solution in the bottle, M is the mass of adsorbent (g), C₀ is the initial Pb²⁺, Cd²⁺ concentration, and C_e is the Pb²⁺, Cd²⁺ concentration at equilibrium

EXPERIMENTAL PART

Characterization of the adsorbent surface

Characterization Using FT-IR

A valuable method for characterizing carbon chemistry (Sciban and Klasnja, 2003), assessing chemical and structural changes brought on by various treatments on activated carbon components (Marin and Ayele, 2003; Taty-Costodes *et al.*, 2005; Igwe *et al.*, 20005; Ansari and Raofi, 2006), and investigating the purity of the activated carbon is infrared spectroscopy (IR). In this study, we used infrared spectra to enhance the occurrence of activated carbon alteration using ammonia. The spectrum of activated carbon exhibits the same fundamental pattern as all samples of original carbon: Significant broad superposition with sharp and distinct absorptions in the range from 1000 to 1772 cm⁻¹, as well as strong broad stretching with a center at 3405 cm⁻¹, are both seen (Diab *et al.*, 2015). Comparing the spectra of the O-H stretching vibration, C double bond O groups (in carboxylic and lactone structures), C double bond C groups, aromatic ring, and C-O stretch of ethers are all responsible for the peaks at 3571, 1729, 1613, 1422, and 1140 cm⁻¹ in the spectra of virgin carbon, respectively. Additionally, the spectrum shows two additional peaks at 856 and 781 cm⁻¹, which are associated with the existence of C-H groups (located at the edges of aromatic rings) (Yu *et al.*, 2001; Argun and Dursan, 2006) reveals that C≡N is responsible for the absorptions at 1510 and 1651 cm⁻¹, while holocellulose is responsible for the absorption at 1742 cm⁻¹, which denotes the C=O stretch in non-conjugated ketones, carbonyls, and ester groups (Habib-Ur-Rehman *et al.*, 2006; Adouby *et al.*, 2007). Table (1) provides band assignments based on the available literature. Comparing the spectra of original and modified activated carbon (Yu *et al.*, 2001; Sciban and Klasnja, 2003) reveals that, the absorptions situated at 1510 and 1651 cm⁻¹ (aromatic skeletal vibrations) are caused by

the addition of ammonia, and the absorption located at 1742 cm^{-1} is caused by carbon and nitrogen bond (Yu *et al.*, 2001); and this indicates also the C=O stretch in non-conjugated ketones, carbonyls and in ester groups (Diab *et al.*, 2015; Argun *et al.*, 2007). Band assignments according to the literature are listed in Table (1).

Table (1): Band assignments according to the literature

Band position (cm^{-1})	Assignment
3330-3450	O-H
2800 -2900	C-H
1740	C=O (carboxyl)
1570-1500	C=C

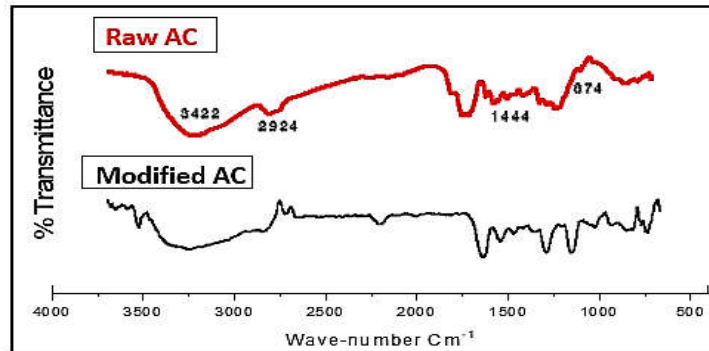


Fig. (1): FTIR for activated carbons which prepared in high temperature around 600°C for 75 min. (reference sample) and activated carbon post-treated with Ammonia

The FTIR spectra of activated carbon and modified activated carbon with ammonia will differ due to the changes in the surface functional groups caused by ammonia treatment. In general, activated carbon exhibits peaks corresponding to various functional groups such as hydroxyl (-OH) groups, carboxyl (-COOH) groups, and ether (-C-O-C-) linkages. The presence of these functional groups contributes to the adsorption capacity of activated carbon for various contaminants.

After modification with ammonia, the FTIR spectrum of the activated carbon will show changes in the peak intensities and shifts in the peak positions. The ammonia treatment introduces new functional groups, such as amino (-NH₂) groups, onto the surface of activated carbon. The amino groups will generate new peaks in the FTIR spectra. Specifically, the peaks at around 1650 cm^{-1} and 3400 cm^{-1} in the modified activated carbon spectrum can be assigned to the amino group's stretching and bending vibrations, respectively (Shafeeyan *et al.*, 2011).

SEM characterization

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. The fracture surfaces of the flexural test specimens were characterized with scanning electron microscopy. The scanning data are analyzed at magnifications of 500 X. All SEM images were taken and analyzed for pure activated carbon and modified with ammonia. Fig. (2A and B) show SEM images at a magnification of 500 x of fracture surface of the pure activated carbon and the one which modified with Ammonia, respectively. SEM images show that the surface of pure sample is smoother than that of the modified one with ammonia because of in homogeneity in distributing of ammonia on the surface of activated carbon. SEM images also show that, there are clear gaps between carbon layers and the modifying agents indicating the limited interface bonding. In general, modifying agents are randomly distributed on the surface of activated carbon and randomly reacted with the surface.

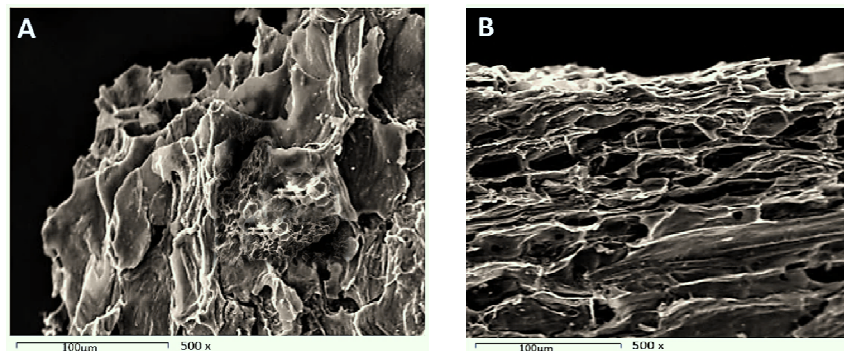


Fig. (2): (A) and (B) show SEM images at a magnification of 500 x of fracture surface of the pure activated carbon, and activated carbon that modified with ammonia, respectively.

RESULTS AND DISCUSSION

Adsorption studies using raw (R-AC) and modified activated carbon with ammonia (A-AC)

Effect of pH

In an adsorption process, the initial pH of a solution is crucial. This is due to the fact that a change in pH has an impact on the species of adsorbate present as well as the nature and properties of the adsorbent present (Nwosu *et al.*, 2007; Lim *et al.*, 2008). As demonstrated in Fig. (3A and B) the effect of pH on the adsorption of Pb^{2+} and Cd^{2+} ion from synthetic solutions on raw and modified activated carbon has been investigated. According to Fig. (3A), the removal effectiveness of the Pb^{2+} ion is pH-dependent and increases as the pH value rise, reaching its maximum removal at pH 6, after which it nearly stays constant. As a result, pH 6 was chosen as the ideal pH for further research. The surface change on the adsorbent material can be used to explain the influence of pH. The surface of the adsorbent acquires a positive charge at acidic pH levels due to the presence of H^+ ions in the solution, which electrostatically repels the cations (Asadi *et al.*, 2008). The removal efficiencies were also found to be low at pH levels below 4 as a result of the competitive adsorption of H^+ ions and Pb^{2+} ions for the same available adsorption sites. Because there is less competition between the heavy metal cations and H^+

ions for the active sites on (R-AC), adsorption increases with increasing pH in the acidic region (Meena *et al.*, 2008). The amount of H^+ ions on the surface of the adsorbent decreases as pH rises, which reduces the repulsion between the heavy metal cations' positive surface charges and those (Stankovic *et al.*, 2009). As pH rises, the adsorption surface becomes less positive, and as a result, electrostatic attraction between the lead ions and activated carbon surface is likely to increase. On the other hand, by altering pH in the range of 2–9, as shown in Fig. (3B), the impact of pH on the adsorption of Cd^{2+} ion from synthetic solutions on (R-AC) has been investigated.

The removal efficiency of the Cd^{2+} ion depends on pH, as seen in this Figure (3B), and it rises as pH increases. As a result, it was determined that pH 6 was a good pH for further research because cadmium hydroxide may precipitate at $pH > 7$. The surface change on the adsorbent material can be used to explain the influence of pH. The competing adsorption of H^+ ions and Cd^{2+} ions for the same accessible adsorption sites led to low removal efficiency at pH values lower than 4. Electrostatic attraction between the cadmium ions and adsorbent surface is anticipated to increase when the pH rises because the adsorption surface becomes less positive.

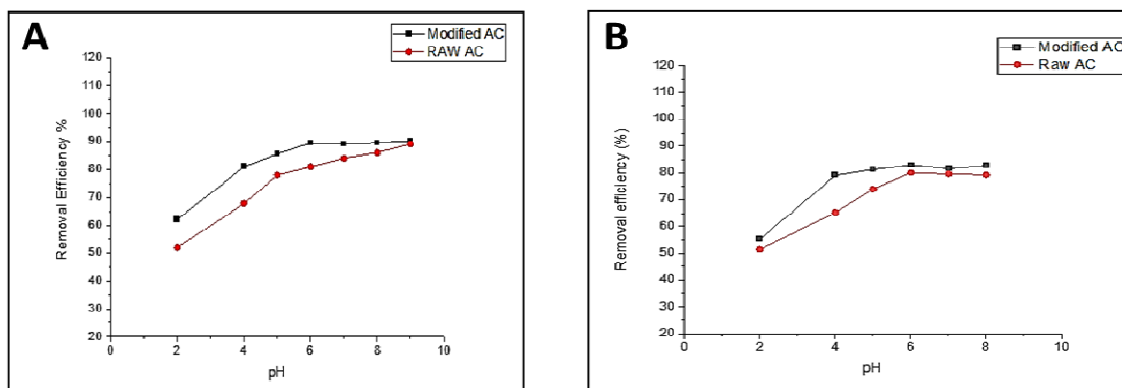


Fig. (3): (A) Effect of pH on adsorption of Pb^{2+} ions, (B) Effect of pH on adsorption of Cd^{2+} , by raw and modified Activated carbon (AC dose = 20 g/l, contact time = 90 min.)

Effect of initial concentration

In batch adsorption processes, the initial metal ion concentration in the solution plays a key role and a driving force to overcome the mass transfer resistance between the solution and solid phases. Therefore, the amount of metal ions adsorbed was expected to be high with a higher initial concentration of metal ions (Rafatullaha *et al.*, 2009). The effect of initial concentrations of Pb^{2+} ions while, keeping the other parameters constant, on the adsorption process is shown in Fig. (4A and B). From the results, it is apparent that the adsorption capacity, q_e (mg/g), increased with the increase of initial metal ion concentration. While, by increasing the initial concentration of Pb^{2+} solution from 10 to 50 mg/l, the lead removal reduced from 95.0% to 86.7% when the modified activated carbon used while it

reduced from 84.0% to 68.0% when the raw carbon used. In case of Cd^{2+} ions (Fig. 4B) and from the obtained results, it is apparent that the adsorption capacity, q_e (mg/g), increased with the increase of initial metal ion concentration. While, by increasing the initial concentration of Cd^{2+} solution from 10 to 50 mg/l, the cadmium removal reduced from 89.0% to 65.6% when the modified activated carbon used and decreased from 80.0% to 40.0% when the pure carbon was used. An explanation for this result is that at low metal ion/adsorbent ratio, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in a decrease in the removal efficiency. Also, the modified carbon shows high removal percentage to remove the lead and cadmium ions.

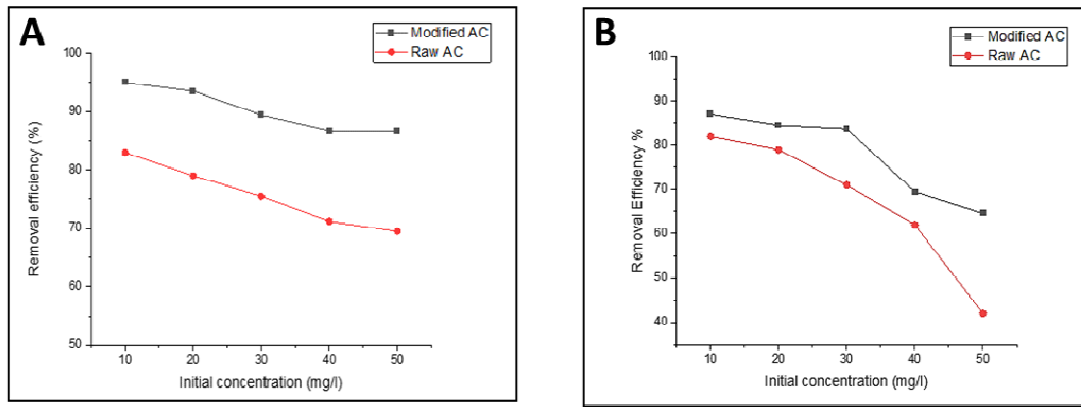


Fig. (4): (A) Effect of initial concentration (C_0) on the adsorption of Pb^{2+} ions, (B) Effect of initial concentration (C_0) on the adsorption of Cd^{2+} by raw and modified activated carbon at ($pH = 6 \pm 5$, adsorbent dose = 20 g/l and contact time = 90 min.)

Effect of contact time

The results of the experimental test measuring the effect of contact time on the batch adsorption of Pb^{2+} and Cd^{2+} at metal ion concentration of 30 mg/l, initial pH value of 6 and adsorbent dose of 20 g/l are represented in Figs. (5A, B). The adsorption rate was relatively fast in the initial stage. The fast metal uptake by this carbon material may be attributed to its highly fine structure, which provides ready access and large surface area for the sorption of metals on the binding sites, showing 91.0% equilibrium attained within 30 min for Pb^{2+} and around 88% within 45 min for Cd^{2+} ions. This probably resulted from saturation of

adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation (Lucaci and Duta, 2009; Ansari and Pornahad, 2010). These results indicate that adsorption of Pb^{2+} and Cd^{2+} ions is mainly occurring at the surface of the adsorbent. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transportation from the exterior to the interior site of the adsorbent particles (Ansari *et al.*, 2006), Modified carbon shows a higher removing efficiency for both lead and cadmium.

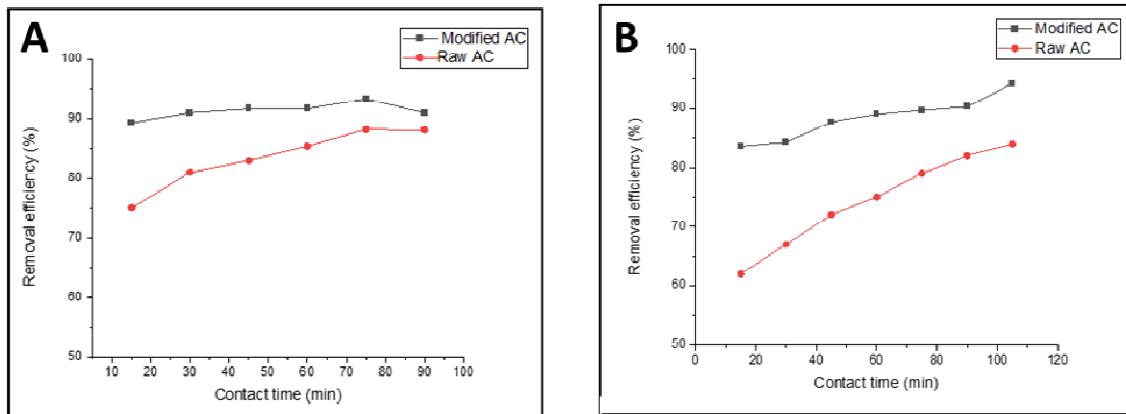


Fig. (5): (A) Shows the effect of contact time on the removal of Pb^{2+} ions, (B) the effect of contact time on the removal of Cd^{2+} by raw and modified activated carbon ions at ($pH = 6 \pm 5$, adsorbent dose = 20 g/l)

Effect of adsorbent dose

The adsorption studies of Pb^{2+} and Cd^{2+} ions on (R-AC) were done at room temperature ($25 \pm 2^\circ C$) by varying the quantity of adsorbent from 5 to 30 g/l, while keeping the other parameters. The influence of adsorbent dosage in percent adsorption of Pb^{2+} and Cd^{2+} ions are represented in Figs (6A and B). The adsorptive removal by adsorbent increased for Pb^{2+} from 62.3% to

98.5% and from 80.3% to 98.2% for Cd^{2+} by increasing the adsorbent dosage from 5 to 30 g/l under equilibrium conditions. It is apparent that the percent removal of Pb^{2+} and Cd^{2+} ions increases rapidly with increase in the dose of the adsorbent due to the greater availability of the exchangeable sites or surface area. The increase in active sites on the adsorbent making the penetration of the metal ions to the sorption sites is so easy.

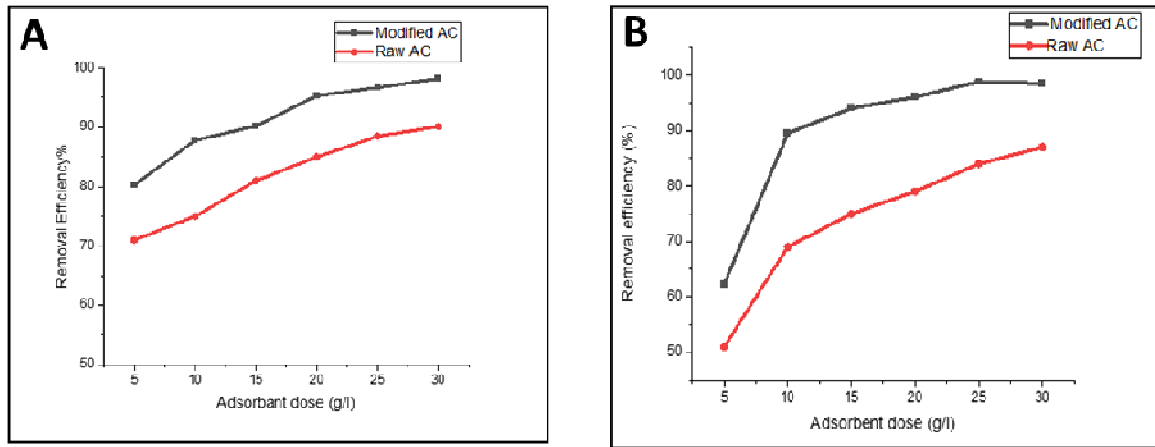


Fig. (6): (A) Effect of adsorbent dose on the adsorptive removal of Pb²⁺, (B) Effect of adsorbent dose on the adsorptive removal of Cd²⁺ ions by raw and modified activated carbon (initial concentration = 30 mg/l, contact time 90 min, and pH 6)

Adsorption isotherms

Adsorption is usually described through an isotherm. The adsorption isotherms reveal the relationship between adsorbate concentration and its adsorption degree on the adsorbent surface at a constant temperature. Several models describe the process of adsorption. Although many theories of adsorption have been put forward to explain the phenomenon of adsorption, the isotherms of Langmuir had been widely used by several researchers. Therefore, Langmuir and isotherms are used to understand the extent and degree of favorability of lead and cadmium sorption onto raw and modified activated carbon with ammonia.

Langmuir isotherm

This model assumes that the adsorption occurs at specific homogeneous sites on the adsorbent surface and is used successfully in many monolayer adsorption processes (Ghorbani *et al.*, 2010; Yang *et al.*, 2010). The linear form of Langmuir isotherm is given by Eq 3.

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (3)$$

Where:

q_e = The amount of metal ions adsorbed per mass of adsorbent (mg/g).

C_e = The metal concentration in aqueous phase at equilibrium (mg/l).

K_L = Langmuir isotherm constant related intensity of adsorption.

q_{max} = Langmuir monolayer sorption capacity.

The parameters were obtained by fitting the experimental data of the plot $1/q_e$ versus $1/C_e$ for lead and cadmium ions removal at different concentrations. The values of q_{max} and K_L (Langmuir constants) were obtained from the intercept and slope of Eq. (3). The plot of Eq.(3) is shown in Figs (7,8) for Pb²⁺ and Cd²⁺.

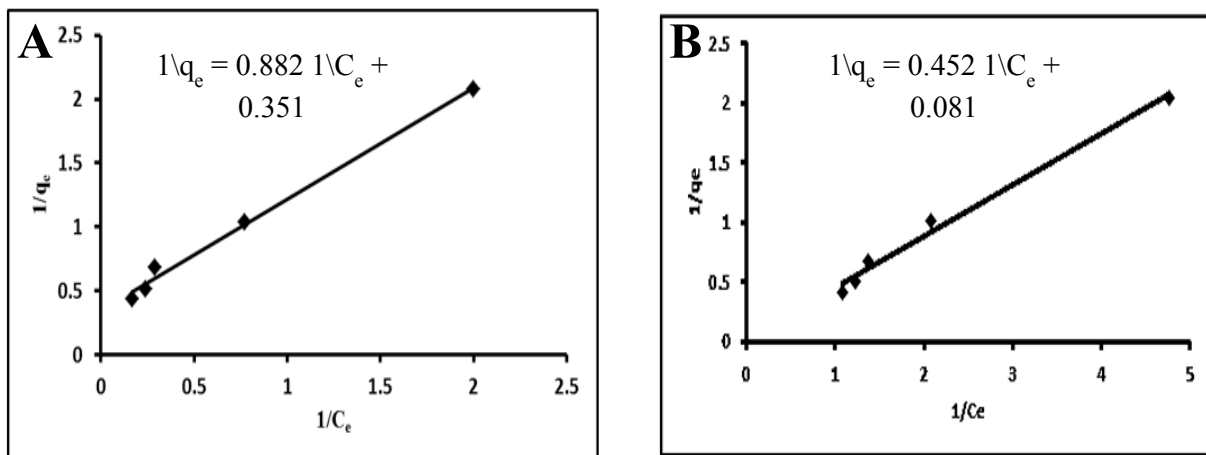


Fig. (7): (A) Linear Langmuir isotherm of Pb²⁺ ion adsorption onto raw Activated carbon, (B) modified activated carbon

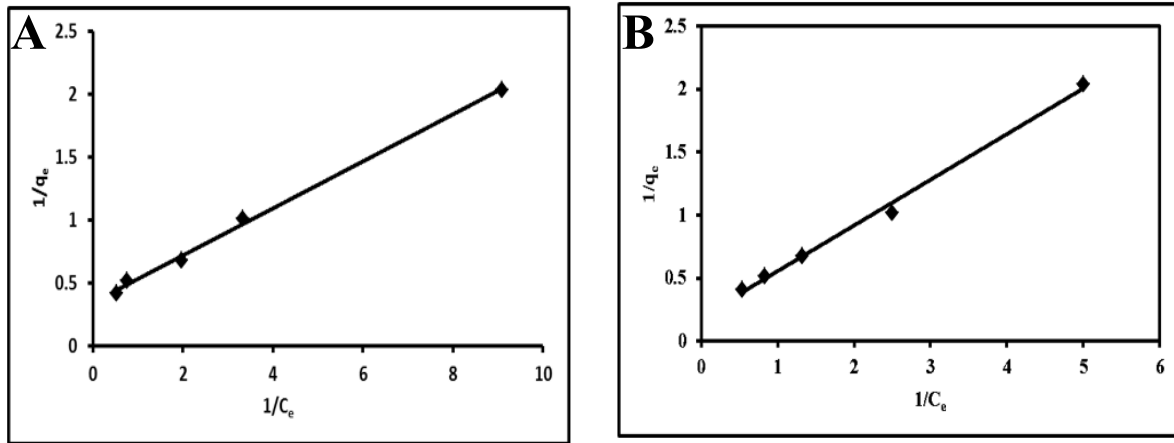


Fig. (8): (A) Linear Langmuir isotherm of Cd^{2+} ion adsorption onto raw Activated carbon, (B) modified activated carbon

Freundlich isotherm

The Freundlich isotherm model is used to assess the extent of heterogeneity (Prado *et al.*, 2010), on the surface of an adsorbent. It connects the concentration of solute at equilibrium (C_0) in solution and the amount of solute adsorbed (Q_e) through the equation.

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where K_F and n are the Freundlich constants that indicate the adsorption capacity and intensity of adsorption, respectively. The linear form of this equation is given by

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

A plot of $\log q_e$ versus $\log C_e$ for Pb^{2+} and Cd^{2+} should form a straight line with a slope of $1/n$ and an intercept of $\log K_F$.

The Freundlich isotherm model deals with the multilayer adsorption of the substance on the adsorbent and is indicative of surface heterogeneity. In contrast, the Langmuir isotherm model suggests surface homogeneity of the adsorbent. The study calculates the

Freundlich isotherm constants and correlation coefficients (R^2) for both raw and modified adsorbent, as presented in Table (2). A value of n between 1 and 10 ($1/n < 1$) represents favorable adsorption. In this case, the values of n range from 1.40 to 1.82, indicating good adsorption of Cd^{2+} and Pb^{2+} ions onto raw and modified Activated carbon. The adsorption capacity K_F is highest for modified activated carbon, followed by the unmodified one for both heavy metals.

The linearity of the plots, as expressed by R^2 , indicates the fit between experimental data and the isotherm model. More linearity suggests better description of the adsorption equilibrium in a given system. The experimental equilibrium data of adsorption of Cd^{2+} and Pb^{2+} ions on raw and modified activated carbon fit well with both Langmuir and Freundlich adsorption isotherms. This implies that the surface of activated carbon comprises small heterogeneous adsorption patches that are similar to each other with respect to the adsorption phenomenon.

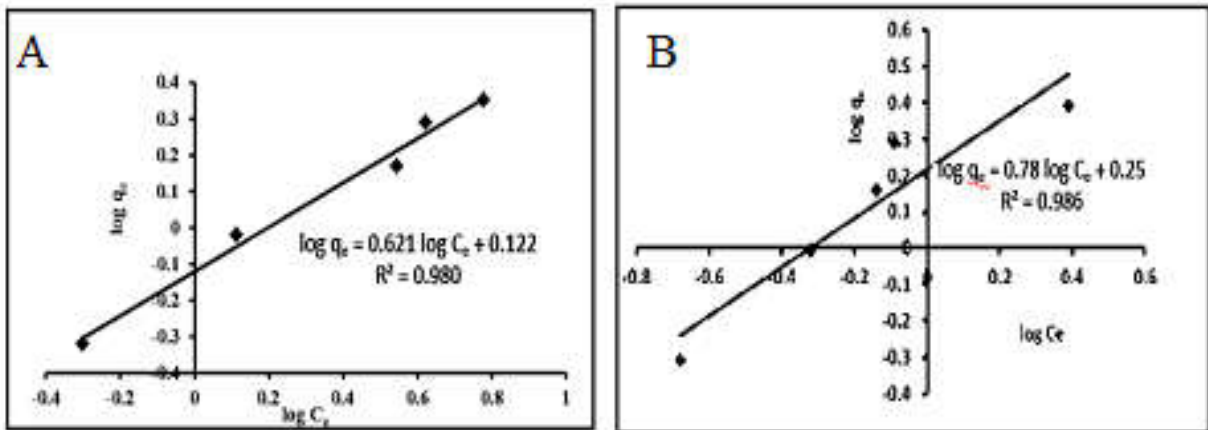


Fig. (8): (A) Linear Freundlich isotherm of Pb^{2+} ion adsorption onto raw activated carbon. (B) Linear Freundlich isotherm of Pb^{2+} ion adsorption onto modified activated carbon

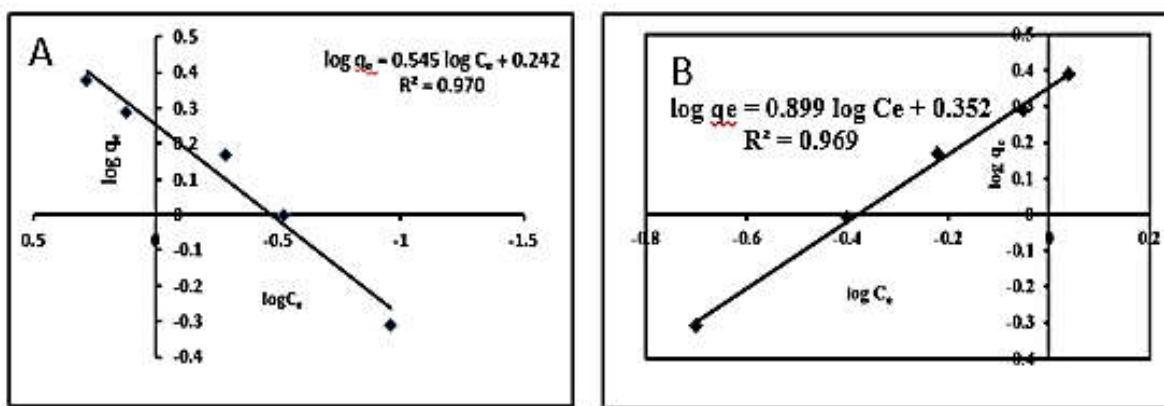


Fig. (9): (A) Linear Freundlich isotherm of Cd²⁺ ion adsorption onto raw activated carbon.
(B) Linear Freundlich isotherm of Cd²⁺ ion adsorption onto modified activated carbon

Table (2): Adsorption isotherm model constants and correlation coefficient for the adsorption of Pb²⁺ and Cd²⁺ ions on raw and modified (*activated carbon*)

Metal ion	Adsorbent	Langmuir			Freundlich		
		K _l (l/mg)	q _{max} (mg/g)	R ²	K _F (mg/g)	n	R ²
Pb ²⁺	Raw-AC	0.351	2.924	0.991	0.748	1.68	0.980
	Modified-AC	0.081	34.456	0.986	1.522	1.48	0.986
Cd ²⁺	Raw-AC	0.321	2.881	0.993	1.076	1.82	0.970
	Modified-AC	0.023	5.120	0.998	1.656	1.40	0.969

In this study the efficacy of activated carbon as an adsorbent for the removal of lead and cadmium, from aqueous solutions was investigated. The impact of contact time, initial metal ion concentration, and temperature on the removal of metal ions was studied. The findings revealed that the equilibrium time required for the adsorption of metal ions was approximately 60 minutes. Three kinetic models including pseudo first-order, second-order, and intra particle diffusion were fitted to the adsorption data, and the adsorption rate constants were calculated (Ansari and Raofi, 2006). The Freundlich and Langmuir isotherm models were used to describe the adsorption data at temperatures of (25-45). The thermodynamic parameters such as energy, entropy, and enthalpy changes for the adsorption of heavy metal ions were computed and discussed. Ion exchange was identified as one of the major adsorption mechanisms for binding divalent metal ions to the modified activated carbon. The selectivity order of the adsorbent was determined to be Pb²⁺ ≈ Cd²⁺. These results suggest that the adsorbent of interest could be an effective and low-cost adsorbent for the removal of heavy metal ions from aqueous solutions.

CONCLUSION

Batch adsorption experiments were performed for the removal of Pb²⁺ and Cd²⁺ ions from aqueous solutions by using raw activated carbon and activated carbon modified with ammonia. The adsorption characteristics have been examined at different pH values, initial metal concentrations, contact time, and adsorbent doses. The pH experiments showed that the removal efficiency of Pb²⁺ and Cd²⁺ ions depends on pH; it increases with the increase in pH value reaching the maximum removal at pH 6 and then remained

almost constant. Increase in mass of adsorbent leads to increase in Pb²⁺ and Cd²⁺ adsorption due to increase in number of adsorption sites. The adsorptive removal of the heavy metals ions by raw activated carbon and modified carbon increased from 62.3 to 88.5 % and from 80.3% to 98.2%, respectively by increasing the adsorbent dosage from 5 to 30 g/l under equilibrium conditions. The Langmuir adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The results obtained in this study show that modifying activated carbon with ammonia significantly increases the metals ion adsorption capacity. Taken into consideration of the above results, it can be concluded that the raw activated carbon (R-AD) and ammonia modified activated carbon (A-AD) could be used as an adsorbent for heavy metals ions removal from aqueous solutions and industrial wastewaters in terms of low cost, natural and abundant availability. Moreover, the removal of these kind of metal ions from industrial wastewaters is important to Egypt both environmentally or/and for water re-use.

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إزالة أيونات الكاديوم (II) والرصاص (II) من المحاليل المائية باستخدام الكربون المنشط الخام والمعدل

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الهدف الرئيسي لهذه الدراسة هو دراسة إمكانية استخدام الكربون النشط الخام والمعدل بالأمونيا لإزالة أقصى كمية ممكنة من أيونات الكاديوم والرصاص من المحاليل المائية وعينات المياه الملوثة في ظروف معينة مثل تركيز المعادن، الكربون النشط، وقت التلامس وحموضة المحلول. تم تنفيذ معالجة الكربون النشط بالأمونيا لزيادة قدرة الكربون لإزالة أيونات المعادن الثقيلة من العينات المائية. في هذا العمل، تم دراسة قدره الكربون النشط على امتزاز هذه الأيونات على سطح الكربون النشط الخام والمعدل بالأمونيا باستخدام تقنية الامتصاص الذري. أظهرت النتائج أن كفاءة إزالة أيونات Pb^{+2} و Cd^{+2} تعتمد على درجة الحموضة، وتزداد مع زيادة قيمة الحموضة، وتصل إلى ذروتها عند pH (6.5)، ثم تبقى ثابتة تقريباً. أيضاً يؤدي زيادة كتلة الكربون النشط إلى زيادة امتزاز الكاديوم والرصاص وذلك لزيادة فرص الامتزاز. ولكن عند زيادة تركيز المعادن الثقيلة يقل كمية الامتزاز على سطح الكربون النشط. وبعد عمل مقارنة عملية بين الكربون الغير معدل والكربون المعدل وجد أن الكربون المعدل أكثر كفاءة في إزالة معادن الكاديوم والرصاص حيث أن يتمتع الكربون النشط المعدل بكفاءة إزالة (٩٦.٠ - ٩٨.٠%) بسبب الزيادة في عدد مواقع الامتزاز. أيضاً تتناسب البيانات العملية مع *Langmuir and Freundlich adsorption* جيداً، وتم حساب ثوابتهم التي أكدت فاعلية إزالة أيونات الكاديوم والرصاص. من خلال نتائج معالجة عينات المياه الملوثة المختلفة تبين أنه أن نسب إزالة الرصاص هي (٨١.٥% - ٨٦.٧%)، و (٩١ - ٩٨%)، باستخدام الكربون النشط الخام (R-AC) والكربون النشط المعدل مع الأمونيا (A-AC)، على التوالي. وأيضاً أظهرت نتائج أيونات الكاديوم أن فعالية إزالة أيونات الكاديوم عن طريق الامتزاز تتراوح من (٧٤.٣% إلى ٨٣.٧%) ومن (٩٧.٦% إلى ٩٨.٤%) عندما يتم استخدام الكربون الغير معدل (R-AC) والكربون المعدل مع الأمونيا (A-AC)، على التوالي.