

Physicochemical studies on removal performance of Pb^{+2} from simulated wastewater by Chitosan/Activated carbon composite

¹Ahmed S. Ahmed, ²Ali M. Hassan, ³Mohammed Hamdi Nour

¹Environmental Engineering Program, School of Science and Engineering, The American University in Cairo, P.O.Box 74, New Cairo 11835, Egypt. (Corresponding author e-mail asaad@aucegypt.edu).

²Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City 11884, Cairo, Egypt

³Civil Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

Abstract: In the recent decades, there has been a concern on heavy metals in wastewater and high cost of conventional methods which used in their removal, for this reason search on adsorbents with biological origin, low cost and efficient is necessary. In this work a composite of chitosan shrimp shells (CH) coalesced with activated carbon (AC) was prepared and used for removal of Pb^{+2} from simulated wastewater. The particles of the CH/AC composite were characterized by Surface area and particle size analyzer, *pH point of zero charge* (pH_{pzc}) analysis, Fourier Transform Infrared (FTIR) spectrometer, Scanning Electron Microscope (SEM), and Energy Dispersive X-ray (EDX). The effect of operational parameters including initial pH, contact time, composite dose, and initial metal ions concentration are explored and optimized through completely mixed batch reactors. The results revealed that, the optimum condition for lead (II) removal by CH/AC composite were pH equal 5.0-5.5, and adsorbent dose equal to 2.0-3.0 g/l. The composite has positive surface charge at optimum pH that means chemisorption is the dominant mechanism for lead (II) sorption by the composite. The equilibrium data for lead adsorption well fitted to Langmuir equation with maximum adsorption capacity (Q_{max}) of 41.15 mg/g. The adsorption kinetics is best described with the pseudo-second-order model, with a correlation coefficient (R^2) close to unity, which indicate that, the chemical sorption is the rate – limiting step.

Keywords: Adsorption; Chitosan; Composite; Equilibrium ;Heavy metals; Isotherm; Kinetics; Lead (II).

1. INTRODUCTION

One of the challenges facing the water industry worldwide is the increasing presence of toxic substances in both surface and underground water. Heavy metals are considered the main constitute of toxic substances in wastewater. Unlike organic pollutants; the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. Due to their high toxicity, non-biodegradability, and accumulation in food chain and in living organisms, they can cause serious illnesses, such as cancer, nervous system damage, and kidney failures, and can be deadly at high concentration [1,2]. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5gm/cm³ [3]. Toxic heavy metals of particular concern in industrial wastewater include, lead, copper, cadmium, mercury, chromium, zinc, and nickel. The main sources of heavy metals in wastewater are discharged waste stream from several industries; such as metal plating, mining activities, fertilizer and pesticides industries, ceramic industry, textile and leather industries, tanneries, electric battery manufacturing, lead smelting, glass industry, gasoline additive, electroplating, stabilizer in plastics, cable sheeting, tetraethyl lead manufacturing, mine drainage, paint and ink

formulation, and ceramic and porcelain enameling industries, etc..... [4,5,6,7,8]. The major sources of lead in wastewater discharge include battery manufacturing, welding, printing and pigment, metal plating and finishing, ceramic and glass industries, textile industries, and iron and steel manufacturing [9]. Lead can cause central nervous system damage, it can also damage the kidney, liver, and reproductive system [10]. The permissible limit of Lead in industrial effluents of wastewater was reported by the United State Environmental Protection Agency (USEPA) to be 0.05 mg/l, while it was stated by World Health Organization (WHO) that Lead content in drinking water should not exceed 0.05 mg/l (11, 12). According to the Environmental Protection Agency (EPA) in 2014 [13], the long-term exposure of lead can be severe and tends to decrease the growth, hyperactivity, impaired hearing, and brain damage. High concentrations of lead may cause problems in the synthesis of hemoglobin, effects on the kidney, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. Several techniques have been employed to mitigate or removal of heavy metals from wastewater, including phytoremediation, chemical precipitation, electrocoagulation, cementation, ion exchange, carbon adsorption, membrane filtration, oxidation or reduction, resin sorption, and reverse osmosis. Most of these technologies have disadvantages like, they are economically expensive, not eco- friendly, incomplete metal removal, high energy requirement, and complicated or hard to control. Moreover, production of secondary waste (generation of contaminated solid sludge instead of contaminated liquid) Among these techniques, sorption is one of the most effective and simplest approaches to remediation process for a wide variety of applications, and in many cases, it will generate high-quality treated effluent [14, 15]. As the biosorbents are relatively inexpensive and available in large quantities, in recent years, a considerable attention has been focused on the employment of sorbent materials from natural resources- especially the by-product or waste product materials-as an efficient, low cost, and environment friendly for the removal of heavy metals. One of such kind is Chitosan; **Poly-(1, 4- β -D-glucopyranosamine)**, which can be produced from fishery waste by alkyl de-acetylation of chitin. Chitin, poly-N-acetylglucosamine, found in crustacean shells (such as crab shells, shrimp shells, and crawfish shells), and fungal cell walls. Chitosan has a large variety of applications in many areas such as biochemistry, pharmacy, medicine, cosmetics, agriculture, nutrition additives, and wastewater treatment [16]. Over the last several years, Chitosan has a particular attention as one of the promising renewable polymeric material and effective biosorbent due to its unique and distinctive features like, biodegradability, nontoxicity, high reactivity, excellent chelation behavior, high content of amine and hydroxyl functional groups which show high adsorption potential for various aquatic pollutions, and low cost in comparison with other adsorbents as it prepared from crustacean shells waste. The amine and hydroxyl groups of chitosan have the capacity to sorb metals through several mechanisms including chemical interactions (such as chelation) and electrostatic interactions (such as ion exchange). The type of interaction depends on the metal type, the metal chemistry, and the solution pH. However, it is difficult to apply chitosan in its raw form in the practical use for removal of metal ions in wastewater, because of its poor chemical resistance such as swelling, solubility in acidic conditions, and its low mechanical strength. In recent years, immobilization of chitosan on common substances has become a method for improve its performance and giving it desirable properties for practical applications [17,18,19]. To implement those ideas, different kinds of substances have been used to form a composite with chitosan such as sand, silica gel, clay, PVC beads, activated carbon, etc..... [20, 21]. As the activated carbon has unique porous structure, high specific surface area, and high mechanical and chemical resistance, it can be used as a support for chitosan in the form of composite. Also, these properties of activated carbon will compensate the deficient that might be happen in the chitosan efficiency by immobilization. Moreover, activated carbon can be prepared from cheap sources such as agriculture waste such as cotton stalks, rice straw, coconut shells and husk, sugar can bagasse, etc.....[22]. Polymeric composite containing chitosan as a waste product of sea food industry and activated carbon as an agriculture waste product represents one of the eco-friendliest solutions by transforming the materials with negative value to valuable materials. This work aims to optimize the influence of various experimental parameters (solution pH, contact time, sorbent dose, and initial metal concentration) on the removal of lead from aqueous solution by chitosan/activated carbon composite, and to investigate the possible mechanisms of the sorption process. To achieve these aims, characterizations of the biosorbent were determined, batch equilibrium isotherm **adsorption experiments were** conducted under various (pH, contact time, sorbent dose, and initial metal concentration) conditions, and Langmuir and Freundlich isotherm models, pseudo first order, and pseudo second order kinetic models were applied. To get results with high level of confidence, all the experiments and the analyses were conducted twice, and mean values were used.

2. MATERIALS AND METHODS

2.1. Materials

Practical grade chitosan flakes (CH), with degree of de-acetylation $\geq 75\%$, and a molecular weight of 190-375 kilo Dalton (KDa) was purchased from Sigma-Aldrich Company (Germany). Commercial activated carbon (AC) granules were used in CH/AC composite preparation. Lead work solutions and calibration standards were prepared from lead stock solution of concentration 1000 mg/l, manufactured by MERCK Company. Deionized distilled water (DDW) is used in the preparation of all the solutions and standards in the experiments and the analyses. NaNO_3 salt (assay 99%) manufactured by Grainland Chemical Co. (GCC) UK was used as ionic background in the synthetic metals solution in order to simulate the ionic conditions of real wastewater. Concentrated nitric acid with American Chemicals Society (ACS) grade, and Sodium hydroxide pellet with ACS grade were purchased from MERCK Company-Germany. Acetic acid with concentration 96%, with ACS grade was purchased from Free Trade Egypt Company.

2.2. Preparation and characterization of adsorbent

2.2.1. Preparation of (CH/AC) composite

The CH/AC composite with ratio 3:1 (CH:AC) was prepared by the following method: 30 gm of CH was dissolved in 1 liter 2% (v/v) acetic acid solution under continuous stirring at 45-50 °C till formation of CH gel. About 10 gm of AC was added slowly to the CH gel and stirred for 24 h at 45-50 °C. Then, the CH/AC composite beads were prepared by injecting the CH/AC gel in droplets through a syringe nozzle into a 500 ml of 0.1 M NaOH precipitation bath. The composite beads were allowed to stay in the NaOH precipitation bath with slow stirring for 6 hours. The beads were filtered from NaOH solution and washed several times with deionized water to a slightly neutral pH (7.5 ± 0.5). The beads were dried for 24 h in an air oven at 60 °C, and grinded. After drying and grinding the materials were sieved, passed through Mesh No. 25 (0.7 mm) and collected on Mesh No. 35 (0.5 mm). The homogenous particles with particle sizes of 0.5 mm, were kept in desiccator.

2.2.2 Characterization of (CH/AC composite) composite, and CH

Characterization of adsorbents is important for their applications in sorption process. Chitosan/activated carbon composite was characterized by selected physical and chemical properties:

- **Bulk density:** Bulk density is defined as “the mass of many particles of the material divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume, and internal pore volume, i.e. it considers both the solids and the pore space. To measure bulk density, a pre-weighted 10 ml cylinder was filled to a specified volume with dried adsorbent; the dry adsorbent was freely settled. Then the cylinder was weighted with the dry material, and the weight of the dry material was calculated as:

$$\text{Weight of dry material (g)} = \text{weight of the cylinder with the material} - \text{weight of the empty cylinder} \quad (1)$$

The bulk density of the adsorbents was then calculated as [23]:

$$\text{Bulk density} = \frac{\text{weight of the dry material (g)}}{\text{volume of the dry material (cm}^3\text{)}} \quad (2)$$

- **The pH point of zero charge (pH_{pzc}):** is often used as an important parameter to study the impact of the electrostatic surface charge of the adsorbent on the adsorption process. The (pH_{pzc}) of the (CH/AC) composite was measured by salt addition method [24]. Ten sample of dry adsorbent, 0.1 g each, was added to 50 ml of purged 0.01 M sodium nitrate solution (as ionic background), in 125 ml high density polyethylene bottles. The initial pH (pH_i) of the solutions was adjusted to the specified pH values from (2 to 11) using 0.1 M NaOH or 0.1 M HNO_3 and sealed well. After 48 hours of continuous stirring on a rotary shaker, with speed of 150 round per minute (rpm), the solutions were filtered, through 0.45 μm cellulose nitrate membranes in plastic filtering device. The pH of each filtrate was measured and recorded as final pH (pH_f). The difference between initial pH and final pH was calculated and reported as ΔpH .

$$\Delta \text{pH} = \text{final pH (pH}_f\text{)} - \text{initial pH (pH}_i\text{)} \quad (3)$$

By plotting ΔpH against initial pH (pH_i), the (pH_{zpc}) was determine, it is the point at which the curve of ΔpH crosses the line of initial pH (pH_i)

- The specific surface area (S_{BET}), pore volume, and average pore diameter of the (CH/AC) composite was determined from adsorption-desorption isotherm of nitrogen gas at 77K, by using a Micrometrics –ASAP 2020 surface area and porosity analyzer. The samples were degassed at 60 °C for 4 hours under a vacuum 10um Hg prior to the analysis. The specific surface area was calculated using Brunauer – Emmett- Teller (BET) method, while pore volumes and average pore diameter were calculated by the Barrett-Joyner-Halenda (BJH) method.
- In order to determine the main functional groups responsible for the sorption of lead, the surface chemistry of the composite and chitosan was determined before and after lead (II) sorption using *Fourier transform infrared spectroscopy (FTIR)* analysis. The FTIR analysis of the substances was carried out using a (JASCO 4100 FTIR spectrometer, Japan), with resolution of 4cm⁻¹, in the range of 400-4000 cm⁻¹, and scanning speed of 2mm/sec, with sample/KBr pellets technique method with ratio of 1/100. Grinded samples which had been dried overnight at 60°C were thoroughly blended with analytical grade dried KBr and compacted to produce 0.5 mm thick disks (micro pellets). The pellets were conditioned for 24 hrs at 110 °C then kept in a desiccator prior to the analysis.
- A field emission scanning electron microscope (SEM) (LEO SUPRA 55, manufactured by ZEISS Germany), was utilized to determine the surface morphology of the composite and chitosan before and after lead (II) sorption. The chemical composition of the composite and chitosan before and after lead (II) sorption was analyzed by an energy dispersive X-ray system (EDX), a complementary technology to the SEM. Coating the samples with a thin layer of conducting material is the primary request for all non-conducting samples to be examined by SEM and EDX. So, prior to analysis, the samples were coated with a thin layer of gold under argon atmosphere to improve electron conductivity and image quality.

2.3. Batch Equilibrium Isotherm Studies

The sorption isotherm is the ratio between the quantity adsorbed and the remaining in solution under fixed temperature at equilibrium [25]. The optimum environmental factors such as initial pH of the solution, contact time, initial composite dose, and initial metal concentration are studied in this set of experiments. These factors are known with their significant effect on the sorption equilibrium. The batch experiments are carried out in well-sealed 125 ml high density polyethylene (HDPE) bottles, when these bottles agitated, they can be assumed to function as completely mixed batch reactor. Synthetic solution (50 ml) of metal samples were poured into each bottle. The pH of the samples was adjusted using 0.1M NaOH or 0.1 M HNO₃ to the specified pH value as needed. The desired dose of raw composite was weighted and added to the solution, except for the control samples. The samples were mixed on the orbital shaker at 150rpm up to the desired contact time. The test was done at room temperature of 22.0 ± °C. Each sample was subsequently filtered using prewashed cellulose acetate filter paper of 0.45 μm pore size as per standard methods for the examination of water and wastewater (Eaton et al., 1998). Finally, the samples were acidified using concentrated nitric acid to a pH <2 **and analyzed** by flame atomic absorption spectrometer (model Sense AA). The tests were done in duplicate for confirmation of the results, and average values were used.

The percentage removal of Pb (II) was calculated using equation (3):

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (4)$$

The sorption capacity is obtained by using the mass balance equation:

$$q_e = \frac{C_i - C_f}{m} \times V \quad (5)$$

$$q_t = \frac{C_i - C_t}{m} \times V \quad (6)$$

Where, q_e and q_t are the amounts of metal ions adsorbed at equilibrium and time t respectively in (mg/g), C_i and C_f are the initial and final lead ions concentration in (mg/l), C_t is the residual metal ion concentration at time t in (mg/l), V is the volume of solution in (L), and m represents mass of adsorbent in (g).

Effect of initial pH

Based on the preliminary experiments for precipitation of lead (II) ions, the batch equilibrium experiment to study the effect of initial pH was performed at the following conditions: samples of CH/AC composite 0.1 g each, were added into

HDPE bottles containing 50 ml of Pb^{+2} solutions with concentration of 30 mg/l, and 0.01 M sodium nitrate as ionic background each, and shaken for about 5 hours, at 22.0 ± 0.5 °C. The pH of the samples was initially adjusted to the values (2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, and 6.0).

Effect of contact time

Depending up on the results of the previous experiment which investigate the optimum pH, the batch equilibrium experiments are performed as the following, CH/AC composite samples with 0.1 g each, were added to 50 ml of Pb^{+2} solutions with concentration of 30 mg/l, and 0.01 M sodium nitrate as ionic background. The pH of the solutions was adjusted to the pH value of (5.5), at 22.0 ± 0.5 °C). The time intervals studied were in the range of 0-600 min.

Effect of composite dose

Batch equilibrium experiments are performed using different composite doses (0.5,1,1.5,2,2.5,3,3.5,4,4.5) g/l in 50 ml solution with an initial lead (II) concentration of 30 mg/l containing 0.01 M sodium nitrate at the pH of 5.5, , and shacked for of 4 hours, at 22.0 ± 5 °C.

Effect of initial metal concentration

In order to identify the impact of the initial metal concentration on the adsorption of Pb^{+2} by CH/AC composite, the batch equilibrium experiments are performed using different lead (II) concentrations: 10, 30, 50, 70, 100, 150, and 200 mg/l, with a CH/AC composite dose of 0.1 g in 50 ml of Pb^{+2} solutions each, and 0.01 M sodium nitrate, at pH value of 5.5, and shacked for 4 hours at 22.0 ± 0.5 °C. .

2.4. Sorption Isotherm Models

Isotherm models predict the maximum adsorption capacity of sorption system, which helps in the assessment of feasibility of the treatment process for a specific application, the required dose of biosorbent, and the selection of the most suitable sorbent for the given case [26]. They are simulating the relation between the equilibrium concentration of adsorbent (C_e) and the adsorption capacity of adsorbent (q) (27). For isotherms adsorption interpretation there are several empirical models. The Langmuir and Freundlich isotherm models are the most popular models in the literature.

Langmuir Isotherm model: The Langmuir isotherm (1918) is an empirical model assumes homogenous sorption sites and sorption energies on the surface of adsorbents. Also, it assumes that, there is not any interaction between the adsorbed molecules i.e. the ability of molecule to adsorb at a given site is independent on the occupation of the neighboring sites (28, 29, 30). According to the model, adsorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further adsorption can be carried out (31). The linear form of the model is presented by the equation:

$$\frac{1}{q_e} = \frac{1}{C_e q_m b} + \frac{1}{q_m} \quad (7)$$

Where q_e (mg /g) is the amount of adsorbate (metal ions) per unit mass of adsorbent (composite) at equilibrium (adsorption capacity), C_e (mg / l) is the equilibrium (residual) concentration of the metal ions (adsorbate) in the solution, q_m (mg /gm) is the maximum (ultimate) adsorption capacity (monolayer capacity) , and b (liter / mg) is the Langmuir constant related to the binding energy of adsorption, it also known as binding constant or association constant K_a [32], the higher the value of b the higher the affinity of the sorbent to the sorbate. Plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ would give the Langmuir constants q_m and b . The experiment was carried out at a constant temperature 22.0 ± 0.5 °C

Freundlich Isotherm model: The Freundlich isotherm model is based on the heterogeneity. It assumes that the sorption sites have heterogeneous energy, varied strength, and work in multi-layer [33]. The linear form of the model is presented by the equation:

$$\text{Log } q_e = \text{log } K_F + \frac{1}{n} \text{log } C_e \quad (8)$$

Where, q_e (mg/g) is the mass of adsorbate (metal) per gram of adsorbent at equilibrium (adsorption capacity), C_e (mg/liter) is the equilibrium concentration of metal ion in the solution, K_F and $1/n$ are Freundlich isotherm constants (empirical constants). They are indicator of adsorption capacity, and adsorption intensity (strength of adsorption)

respectively. The smaller the value of $\frac{1}{n}$ the stronger the adsorption bonds. These constants can be obtained by plotting $\text{Log } q_e$ versus $\text{log } C_e$ (34, 35, and 36]. The experiment was carried out at a constant temperature 22.0 ± 0.5 °C.

2.5. Kinetic Models

In order to investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo-second order kinetics were applied in the data of adsorption.

Pseudo First - Order Kinetic

The pseudo first-order kinetics can be expressed as:

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{K_1}{2.303} t \quad (9)$$

Where K_1 is the rate constant of pseudo first – order adsorption (min^{-1}); q_e and q_t are the amount of metal ion adsorbed per gram adsorbate at equilibrium and at any time t respectively, (mg/g). A straight line for the plot of $\text{Log } (q_e - q_t)$ versus t would give the first – order rate constant K_1 and equilibrium adsorption capacity q_e from the slope and intercept of the line .

Pseudo Second - Order Kinetic

The pseudo second – order kinetics can expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where K_2 (g / mg min) is rate constant of pseudo second-order adsorption. The plot of t/q_t versus t would give the pseudo second – order rate constant K_2 and q_e . This model is based on the assumption that the rate-limiting factor may be chemisorption involving valence forces through sharing of electrons between the amino groups of chitosan and metal ions (37).

3. RESULTS AND DISCUSSION

3.1. Characteristics Analysis.

The bulk density, surface area, pore volume, and pore size for chitosan -activated carbon (CH./AC) composite, and chitosan are shown in Table 1. The CH/AC composite illustrates significant increase in surface area and pore volume in comparison with chitosan. Obviously the metal uptake capacity of the composite will be higher due to its free adsorption sites. The lower surface area and pore volume of CH/AC composite in comparison with AC was due to the CH molecules blocking the pores of AC.

Table 1: Physical characteristics of CH/AC composite, CH, and AC

Parameter	CH/AC composite	CH	AC
Bulk density (g/cm^3)	0.32	0.198	0.5007
Surface Area			
BET surface area (m^2/g)	287.3529	0.5437	773.73
Langmuir Surface Area (m^2/g)	420.2633	0.9338	1132.2405
BJH adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter (m^2/g)	22.067	0.375	
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter (m^2/g)	10.7005	0.4703	
Pore Volume			
Total pore volume (cm^3/g)	0.160	0.001	0.4171

BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter (cm ³ /g)	0.025898	0.001853	
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter (cm ³ /g)	0.017862	0.001990	
Pore Size			
Average pore diameter (4V/A by BET) nm	2.23217	10.97715	2.156
BJH Adsorption average pore diameter (4V/A) nm	4.6944	19.789	
BJH Desorption average pore diameter (4V/A) nm	6.6769	16.924	

SEM-EDX analysis

SEM-EDX analysis was exploited to illustrate the variation of morphology and chemical composition of each absorbent. The SEM images for the surface morphology of CH/AC composite and CH are shown in Fig. 1. Fig. 1. (a) indicates that the presence of many pores and cracks on the surface of CH/AC composite confirming the higher surface area of the composite, while Fig 1 (b) displayed a relative smooth structure of the surface of chitosan with less surface area. The EDX analysis showed that, the elemental composition of CH/AC composite and CH significantly changed after lead (II) adsorption as in Table 2 (a and b). The Atomic percentage (At. %) of major elements (N- and O-) were decreased from 10.38 and 80.54 to 7.35 and 77.62 respectively in case of composite, while they were decreased from 8.09 and 91.46 to 6.37 and 89.71 in case of chitosan which confirm the role of N- and O- in lead (II) adsorption. This means that, the lead (II) adsorption could covalently bound with N-, and O- of the amino and hydroxyl functional groups. Moreover, At. % of Al , Ca, and Fe in the composite decreased from 6.42 , 2.29 and 0.22 to 2.57 , 1.18 and zero respectively after lead (II) adsorption, which revealed that Pb(II) possibly exchanged with Al, Ca, and Fe in the composite.

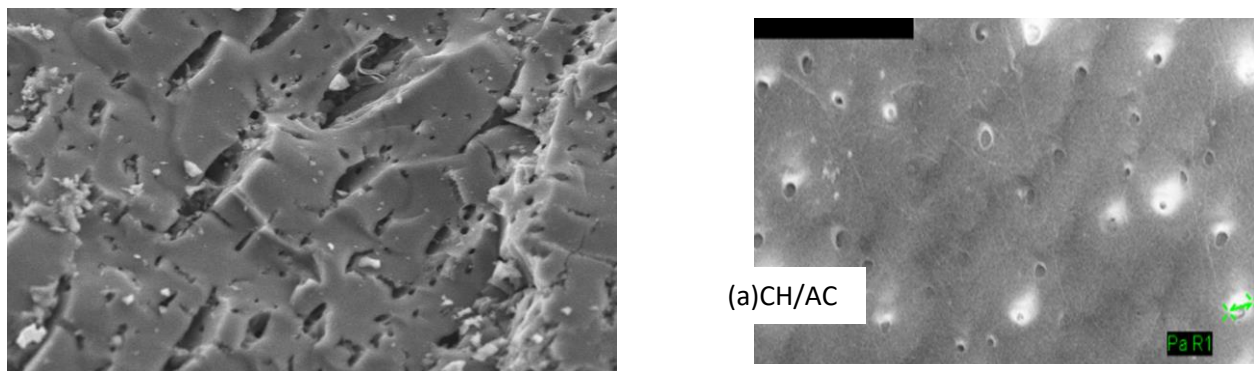


Fig. 1. SEM images of (a) CH/AC composite, (b) Chitosan

Table 2: EDX analysis of a) CH/AC composite and b) CH before and after Pb (II) ions sorption

Element	Before		After	
	Wt. %	At. %	Wt. %	At. %
N K	8.34	10.38	2.72	7.35
O K	73.94	80.54	32.76	77.62
Al K	9.93	6.42	1.83	2.57
Ca K	5.26	2.29	1.25	1.18
Fe K	0.72	0.22	-	-
Pb M	-	-	58.34	10.67
Au M	1.81	0.16	3.10	0.60
Totals	100.00		100.00	

Table: 2 (a)

Element	Before		After	
	Wt. %	At. %	Wt. %	At. %
N K	6.80	8.09	3.82	6.37
O K	87.85	91.46	61.55	89.71
Pb M	-	-	30.47	3.43
Au M	5.35	0.45	4.16	0.49
Totals	100.00		100.00	

Table: 2 (b)

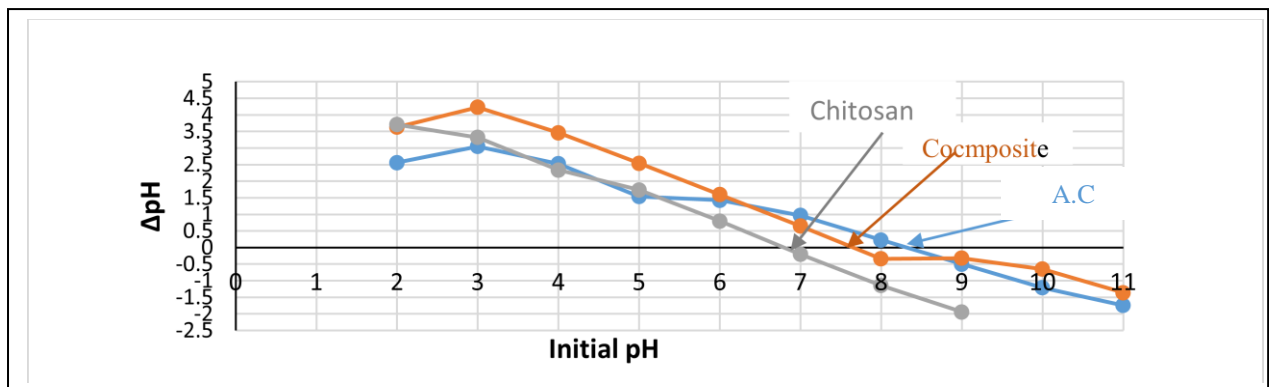
pH point of zero charge (pHpzc) of adsorbents

Fig. 2. pH point of zero charge (pHpzc) of chitosan, CH/AC composite, and activated carbon

Determination of pH point of zero charge (pHpzc) plays a key role in the surface science of environmental interface, where it indicates how easily adsorptive materials are able to adsorb the ions of target pollutants. The (pHpzc) is the pH when the charge on the adsorbent surface is zero, below this value the surface is positively charged, beyond this value it is negatively charged. So, normally it is allows easier to adsorb a cation on a negatively charged surface, and an anion on the positively charged surface by the electrostatic forces. However, other interactions may be stronger than purely electrostatic forces. The (pHpzc) of chitosan, CH/AC composite, and activated carbon are shown in Figure 2, where they are 6.8, 7.6, and 8.36 respectively. The (pHpzc) of chitosan was determined to be approximately 6.8 which is a reasonable (pHpzc), given that the pka of chitosan ranges from 6.3 to 6.6 (9). The results showed that, the (pHpzc) of CH/AC composite is about 7.6, consequently below this value (optimum pH of the sorption process was 5.5) the charge of composite surface will be positive, and that the electrostatic force of interaction between the metal ions M^+ and the surface of the composite could be hard, so that, the dominant mechanism could be the surface reaction between the active sites on the composite surface ($-OH$, $-NH_2$, RNH_3^+ , $COOH$) and M^+ to form a ligand.

FTIR analysis of adsorbents

FTIR spectra are a useful tool to identify the presence of certain functional groups in a molecule, as each specific chemical bond often has a unique energy adsorption band. To identify the possible sites of lead (II) binding to CH/AC composite, FTIR spectra were obtained for the composite before and after lead (II) adsorption as shown in Figure 3 (A,B) and table 3. The bands at 3550.3 cm^{-1} and 3464.5 cm^{-1} at the spectrum of CH/AC composite before lead (II) adsorption can be attributed to the stretching vibration of $-NH$ and $-OH$ groups of chitosan respectively (38,39). In the spectrum of the composite after Pb (II) adsorption they are shifted and overlapped at lower wavenumber in a peak at 3426.9 cm^{-1} . A band at 1633.4 cm^{-1} at the spectrum of composite before lead (II) adsorption can be attributed to $-NH$ bending vibration of $-NH_2$ group of chitosan (38), is shifted to lower frequency at 1583.3 cm^{-1} after lead (II) adsorption. Another major change in the transition can be also observed in the band at wavenumber of 2922.6 cm^{-1} after lead (II) adsorption to the wavenumber of 2903.3 cm^{-1} . This band region may be assigned to both methyl C-H and $-OH$ stretching. As lead unlikely to be attached to a carbon atom, the results may be therefore suggest that oxygen atoms in the hydroxyl could also be involved in lead adsorption, but their effect appears to be much less significant than nitrogen atom (9). The band at 1025.0 cm^{-1} in the spectrum of the compost before lead (II) adsorption is suggested to represent the C-O of chitosan, it is moved to 1068.4 cm^{-1} after lead (II) adsorption. These displacements of bands after lead(II) adsorption are indication that surface complexation between Pb^{+2} ions and $-OH$ and $-NH_2$ functional groups of chitosan is one of the mechanisms responsible for the sorption of Pb^{+2} ions by CH/AC composite.

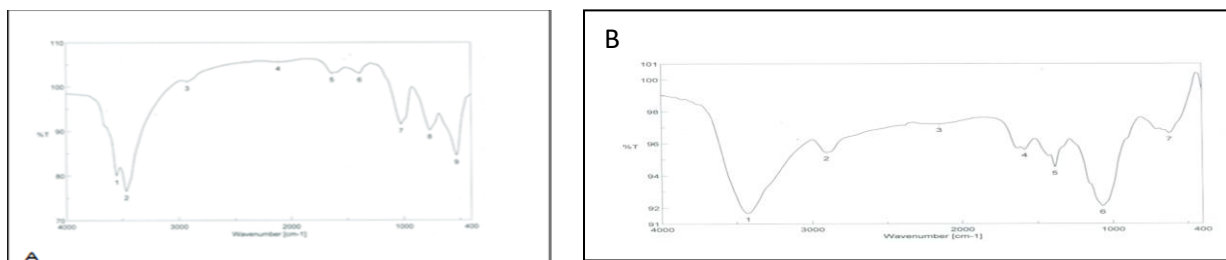


Fig. 3. FTIR spectra of (A) CH/AC composite before Pb^{+2} sorption, (B) CH/AC composite after Pb^{+2} sorption

Table 3. FTIR analysis of CH/AC composite before and after Pb (II) adsorption

Peak No.	CH/AC composite before Pb (II) Wavenumber (cm^{-1})	Peak No.	CH/AC composite after Pb (II) Wavenumber (cm^{-1})
1	3550.3	1	3426.9
2	3464.5	2	2903.3
3	2922.6	3	2149.3
4	2109.7	4	1583.3
5	1633.4	5	1383.7
6	1388.5	6	1068.4
7	1025.0	7	619.0
8	768.5		
9	531.3		

3.2. Batch Equilibrium Studies

3.2.1. Effect of initial pH :

- Metal Hydroxide Precipitation: Precipitation experiments show that the metal hydroxide precipitation limits the suitable operation pH for adsorption. This is because, at higher pH values, metals start precipitation that making interference with the true result of adsorption. So that, prior to the experiment preliminary experiment was carried out at pH range (2 – 11) with 30 mg/l of lead (II) solution to investigate the lead hydroxide precipitation as function of pH . As shown in Figure 4, a drastic change in lead (II) precipitation started at pH 6.5 to reach to 67.6 % at pH7. So, to evaluate the influence of pH on the sorption of Pb^{+2} , the experiments were carried out in the pH range of 2.0 – 6.0. The precipitation of Pb^{+2} ions at $pH > 6.0$ should be taken into consideration in the evaluation of optimum pH.

- Effect of initial pH: Adsorption of metal ions from aqueous solutions is related to the pH of the solution, as the later affects the surface charge of the metal binding sites in the sorbent and the degree of ionization and the type of metal species in the solution (40, 41).

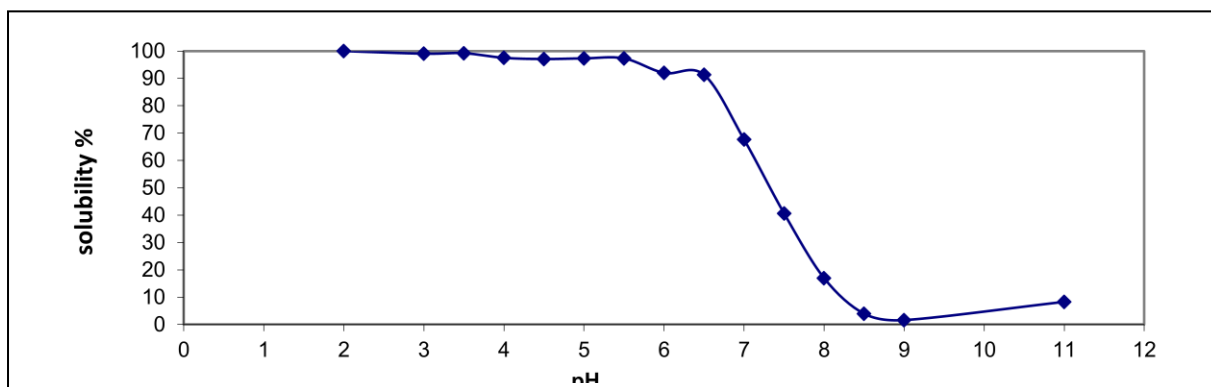


Fig. 4. Solubility of lead hydroxide as function of pH

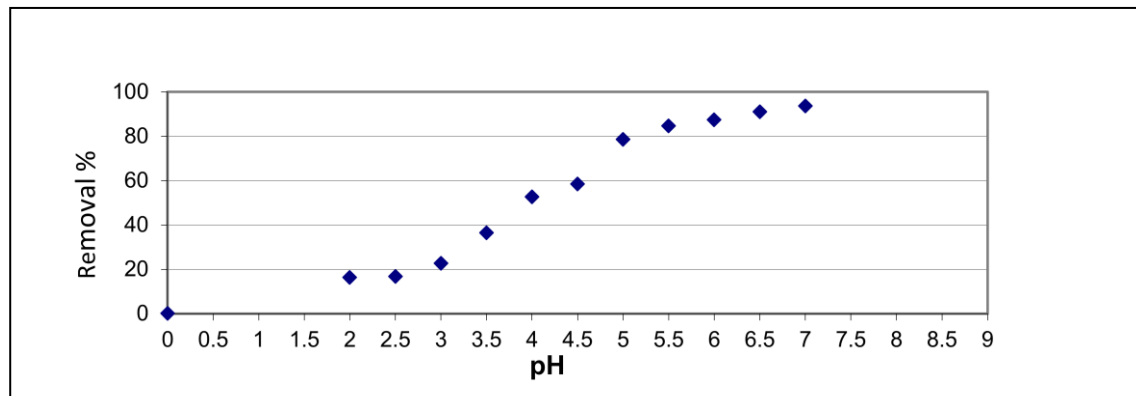


Fig. 5 a. Effect of pH on adsorption of 30 mg/l lead (II) using 2 g/l CH/AC composite, for 5 hours, at 22.0 ± 0.5 °C

Figure 5a shows that, CH/AC has significantly lower sorption capacity for Pb^{+2} ions uptake at pH values below 3. At pH >3.0 a considerable jump in the adsorption capacity of the CH/AC composite is observed to reach to 58.5 % at pH 4.5. The lead (II) adsorption reached its optimum capacity (78.5 – 84.6%) at pH 5.0 – 5.5. Even though, further increase in the percent removal was observed at pH ≥ 6.0 to reach 93.6 at pH 7, the pH value of the lead (II) solution shall not exceed pH 6, because of this increment is basically due to precipitation as demonstrated at Figure 4. Since the optimum pH of sorption process was 5.0 - 5.5 the upper pH limit was revised to pH 6.0 in the following experiments. The decrease of lead (II) uptake at lower pH values might be related to the increase in the positively charged active sites (NH_3^+) of chitosan, this leads to more positive charge over all surface of the composite and increase in the concentration of (H^+) ions in the solution. This cause an electrostatic repulsion between the Pb^{+2} ions and the positive charge on the composite, moreover, the H^+ ions in the solution at lower pH will compete with Pb^{+2} ions for binding with the active sites (NH_2) groups of chitosan and therefore reducing the adsorption capacity (42). With the increase of pH, there would be a decrease in the protonation of the active sites, and the H^+ ions in the solution, leading to a decrease in repulsion between the lead $+2$ ions and the active sites as well as the competition of H^+ with metal ions for sorption sites and therefore the adsorption capacity increase. Above pH 6, lead (II) tends to form insoluble $Pb(OH)_2$ micro-precipitates complex (43).

3.2.2. Effect of Contact Time

Figure 5b shows that, the rate of lead (II) adsorption is rapid at first 5 minutes to reach to removal of 30.2 %, after then, the uptake capacity of the composite increases slowly until it reaches its breakthrough after 240 minutes, at which the uptake efficiency reaches to 79%, then the amount of adsorbed lead (II) did not significantly change with time. The adsorption capacity of the composite at equilibrium (q_e) is 11.85 mg/g, as represented in Figure 6. Generally, The fast initially process at first 5 minutes, involved physical adsorption on surface of composite or/and ion exchange with the elements of the composite, and the slow adsorption at the later stage involved chemical complexation with the active sites.

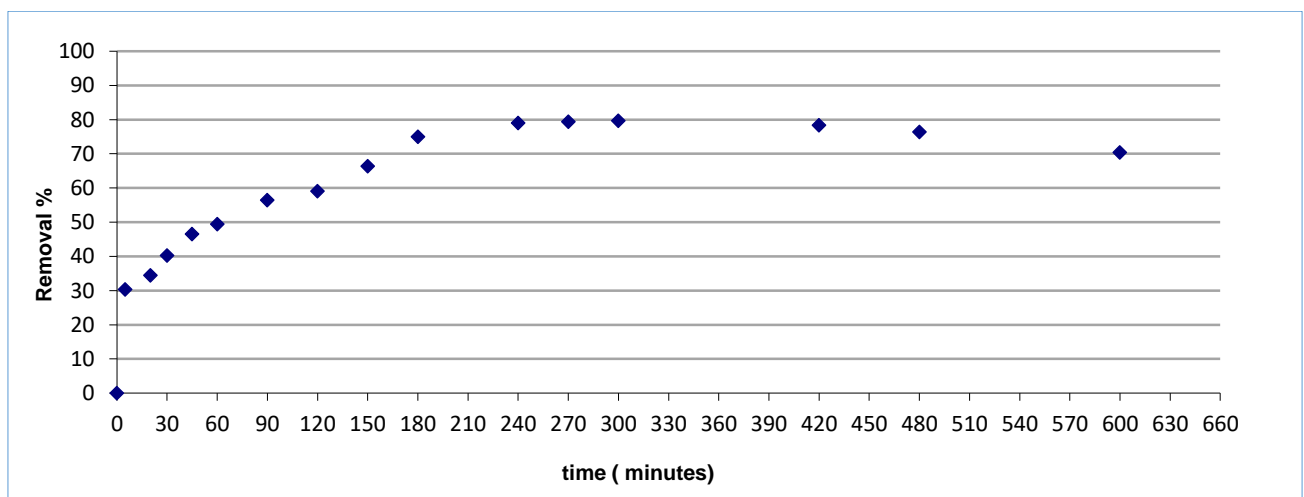


Fig. 5 b. Effect of contact time on adsorption of 30 mg/l lead (II) using 2 g/l CH/AC composite at pH 5.5, and 22.0 ± 0.5 °C,

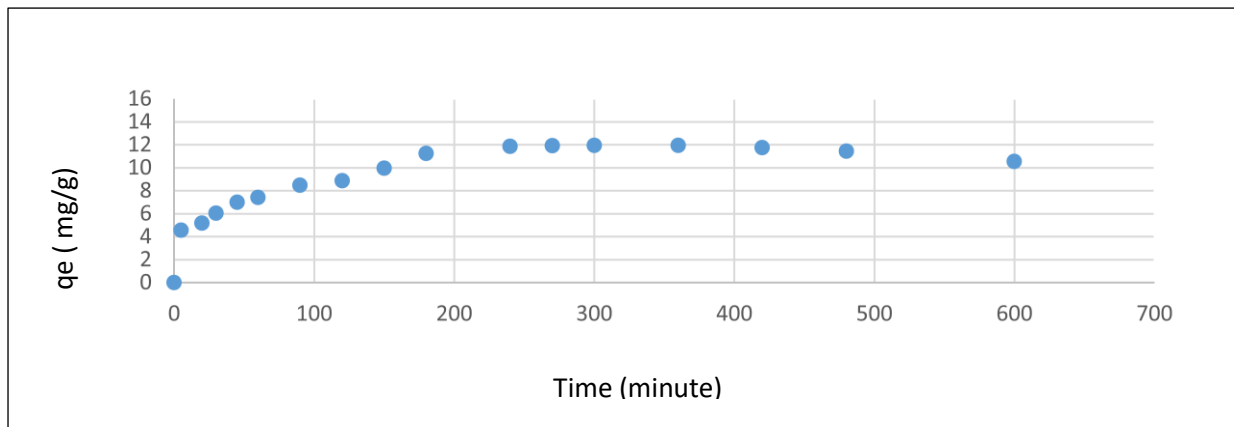


Fig. 6. Adsorption capacity Q_t (mg/g) at each time (t) of 30 mg/l lead (II) using 2 g/l CH/AC composite at pH 5.5, and 22.0 ± 0.5 °C

3.2.3. Effect of Sorbent Dose.

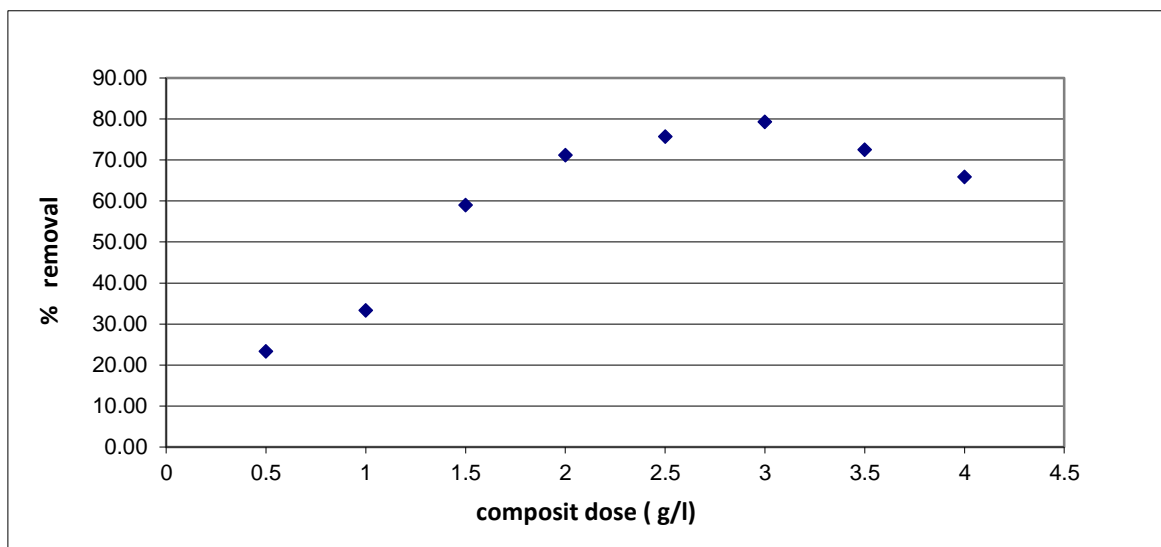


Fig. 7. Effect of CH/AC composite dose on adsorption of 30 mg/l Pb^{+2} at pH 5.5, 22.0 ± 0.5 °C, and 4 hours contact time

Figure 7 depicts the influence of composite dose on lead (II) ions uptake capacity. It is obvious that, the increase in composite dose from 1 g/l to 3.0 g/l results in dramatically increasing in the uptake of Pb^{+2} ions from 33.3% to 85.9%. However, the trend of uptake value tends to decrease at composite dose >3.0 g/l. This phenomenon might be attributed to, at lower concentration of composite, the ration between the number the lead (II) ions available around the composite particles and the number of composite particles become higher, and hence more easily bound to the active sites of the composite will occur till a certain case as long they are not saturated (44). By increasing the composite concentration, the collision between the composite particles in the solution will increase, so that, the rate of desorption of the adsorbed lead (II) will increase and the metal uptake capacity will decrease (45).

3.2.4. Effect of Initial Metal Concentration

The influence of the initial metal concentration has the same important like the influence of the composite dose as the metal uptake efficiency (% removal) is affected by the sorbent (composite) to the sorbate (Pb^{+2}) ratio.

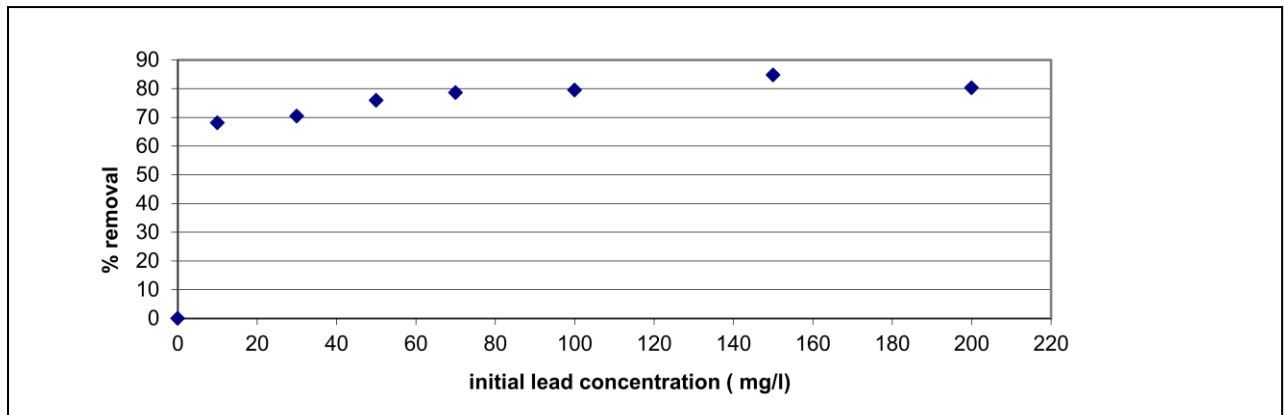


Fig. 8. Effect of initial Pb^{+2} concentration, adsorbed by 2g/l composite, at pH 5.5, 22.0 ± 0.5 °C, and 4 hours contact time

Figure 8 shows that, percentage of metal uptake increases by increasing the initial metal concentration to certain ratio between the sorbent and sorbate, after then more increasing in the metal concentration leads to decrease in the percentage uptake. Decreasing in the percentage of metal uptake by increasing the metal concentration might be attributed to the competition between the metal ions to bind with the limited number of the active sites and the previous one (3.2.3):

If $(X) \gg (C_0)$, the removal efficiency will increase.

If $(C_0) \gg (X)$ the removal efficiency will decrease.

Where X, is the sorbent concentration, and C_0 is the initial metal concentration (46).

3.3. Sorption isotherm Models

Langmuir & Freundlich isotherm models:

Considering the value of R^2 in both models, we can observe that, the adsorption process of Pb (II) by CH/AC composite is more fitted to Langmuir model, which indicated that the possible mechanism is chemisorption. The smaller value of b in Langmuir model and the higher value of $1/n$ in Freundlich model give indication that, the bond strength between lead (II) ions and active sites of composite is weak which facilitate the desorption process. Q_{max} . Equal to 41.15 mg/g.

Table 4: Parameters of Langmuir and Freundlich isotherm models for adsorption of Pb (II) by CH/AC composite

Langmuir			Freundlich		
R^2	b	Q_{max}	R^2	$1/n$	K_f
0.995	0.024 (l/mg)	41.15 (mg/g)	0.975	0.742	0.687

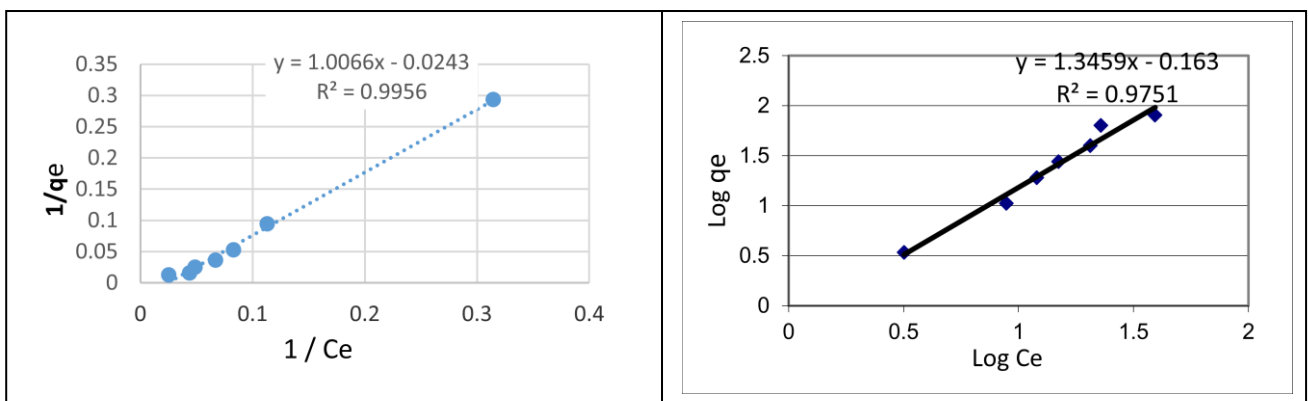


Fig.9. Langmuir isotherm for Pb (II) adsorption by CH/AC composite Figure 10 Freundlich isotherm for Pb (II) adsorption by CH/AC composite

3.4. Kinetic Models

Kinetic study is helpful in prediction of adsorption rate constants, adsorption capacity, and adsorption mechanism. The capability of pseudo-first order and pseudo-second order kinetic model were examined in this study at constant room temperature (22.0 ± 0.5 °C). The pseudo-first order and pseudo-second order kinetic parameters are presented in Table #

Table 5: Adsorption Kinetic study of 30 mg/l Pb (II) by 2g / l CH/AC composite at pH 5.5, and 22.0 ± 0.5 °C

q_e (mg/g) (Experimental)	Pseudo first order			Pseudo second order		
	q_e (mg/g) (Calculated)	K_1 (min) ⁻¹	R^2	q_e (mg/g) (Calculated)	K_2 (g/mg min)	R^2
11.85	4.826	0.0034	0.587	11.35	0.0039	0.994

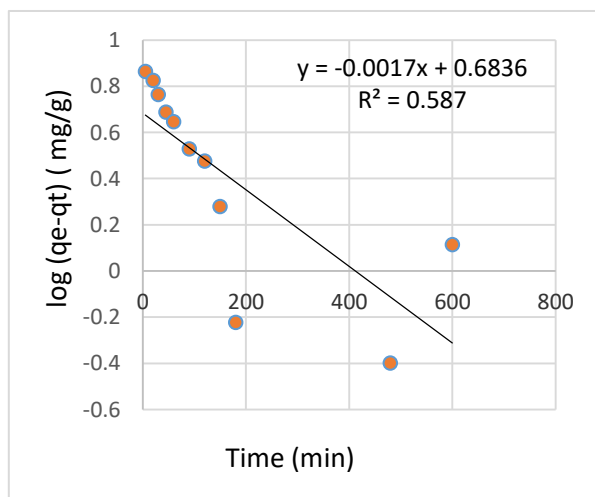


Figure. 11. Pseudo first order kinetic

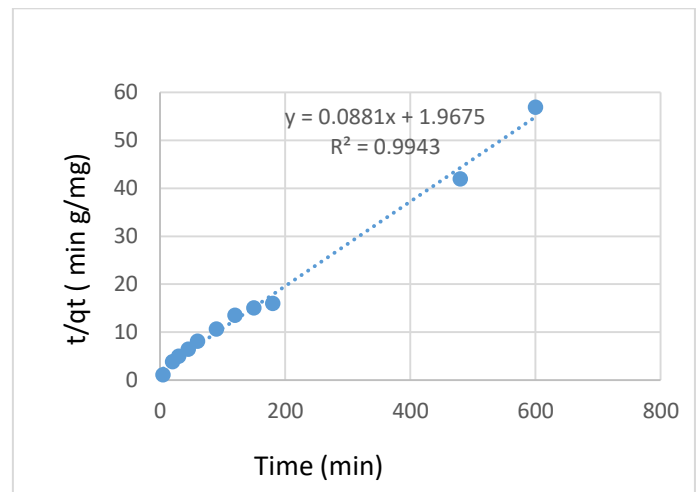


Figure 12 Pseudo second order kinetic

From the results at table 5 it can be seen that, the value of q_e (experimental) does not agree with the (calculated) q_e value that was deduced from pseudo-first order model. That indicates the applicability of pseudo-first order model to the adsorption process of lead (II) onto CH/AC composite is infeasible. While the value of q_e (experimental) is quite closer to q_e (calculated) for the pseudo-second order kinetic model, also the pseudo-second order equation fitted the experimental data well with a correlation coefficient (R^2) close to unity. Hence, it can be concluded that, the adsorption of lead (II) on CH/AC composite is described by pseudo-second order kinetic model. The pseudo-second order kinetic model assumes that the rate-limiting factor might be chemisorption involving valence forces through sharing of electrons between the amino groups of chitosan and the metal ions (47).

3.5 Mechanisms investigation

Removal of Pb^{+2} ions using CH/AC composite is attributed to several mechanisms:

- Surface complexation of Pb^{+2} with the functional groups in the chitosan of composite, mainly amine and hydroxide groups as demonstrated from the FTIR analysis, *pH point of zero charge* (pH_{pzc}). This mechanism is the main one of the possible mechanisms
- Langmuir isotherm model and pseudo second order kinetic model confirm the chemisorption mechanism.
- Ion exchange of Pb^{+2} with the minerals in the composite is illustrated by EDX results. This mechanism has small contribution in the lead (II) removal.

- Precipitation had also a small contribution to the removal of Pb^{+2} . Insoluble species of Pb^{+2} are formed mainly at a pH > 6 ; however , a very slight amount of precipitation can occur at lower pH values as demonstrated in 3.2.1 and Figure 4.

3.6. Conclusion

- This study developed CH/AC bio-sorbents composite for removal from aqueous solution
- CH/AC composite demonstrates potential to adsorb Pb^{+2} from aqueous solution.
- The effect of operational parameters, e.g., pH, contact time, metal concentration, and composite dose on the adsorption of lead(II) by the composite was explored in detail
- The adsorption pH edge indicates that there is a notable removal before pH 5.0; the removal reached its peak value at pH 5.0 ~ 5.5. Metal removal at pH > 6.0 is attributed to the metal precipitation.
- The maximum uptake (Q_{max}) of lead (II) ions by the CH/AC composite is 41.15 mg/g.
- Adsorption process of lead (II) ions by the CH/AC composite reached its equilibrium (q_e) after 240 minutes with amount equal to 11.85 mg/g
- The sorption process well fitted with Langmuir isotherm model, and pseudo second order kinetic model.
- Chemisorption is dominant mechanism of lead adsorption process by CH/AC composite.
- CH/AC composite can be successfully used as effective, low cost sorbent for lead and can be used as alternative to more costly materials.

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