Removal of Lead (II) from Aqueous Solution Using Chitosan Impregnated Granular Activated Carbon

Ali Mousa Ridha
Engineering Technical College– Baghdad, Middle Technical University
Email: alimreng1966@yahoo.com

ABSTRACT

The use of biopolymer material Chitosan impregnated granular activated carbon CHGAC as adsorbent in the removal of lead ions pb^{2+} from aqueous solution was studied using batch adsorption mode. The prepared CHGAC was characterized by Scanning Electronic Microscopy (SEM) and atomic-absorption spectrophotometer. The adsorption of lead ions onto Chitosan-impregnated granular activated carbon was examined as a function of adsorbent weight, pH and contact time in Batch system. Langmuir and Freundlich models were employed to analyze the resulting experimental data demonstrated that better fitted by Langmuir isotherm model than Freundlich model, with good correlation coefficient. The maximum adsorption capacity calculated from the pseudo second order model in conformity to the experimental values. This means that the adsorption performance of lead ions onto CHGAC follows a pseudo second order model, which illustrates that the adsorption of Pb^{2+} onto CHGAC was controlled by chemisorption. The granular activated carbon GAC impregnated by Chitosan was effectively applied as adsorbent for the elimination of lead ions from aqueous solution.

Keywords: adsorption, heavy metal ions, chitosan, granular activated carbon.

ازالة ايون الرصاص من المحلول المائي باستخدام الجيتاسون المحمل على الكاربون المنشط الحبيبي

علي موسى رضا
مدرس
الكلية التقنية الهندسية-بغداد، الجامعة التقنية الوسطى

الخلاصة

في هذا البحث تم استخدام مادة البوليمر الحيوي الشيتوزان المحمل على الكاربون المنشط الحبيبي CHGAC كمادة مازة في إزالة أيونات الرصاص Pb^{2+} من محلول مائي باستخدام الامتزاز نمط الدفعات (Batch adsorption mode). يعتبر البوليمر الحيوي من المواد المازة المهمة الواسعة الاستخدام لامكانياته العظيمة في الكثير من التطبيقات. تم دراسة تاثير كل من الاوزان المختلفة من الجيتاسون المحمل على الكاربون، pH الوسط الحامضي، وزمن التماس على عملية الامتزاز ايون الرصاص على الشيتوزان المحمل على الكاربون المنشط الحبيبي CHGAC. تم اجراء تحليل للمادة المازة المحضرة (CHGAC) بواسطة المسح الإلكتروني المجهري (SEM) ومقياس الطيف الضوئي للامتصاص الذري. ان ثوابت موديل لانكماير وفرندلخ المبنية على النتائج التجريبية لعملية الامتزاز لازالة ايون الرصاص وجد منها معامل الارتباط التي اوضحت بان الموديل لانكمايرهو الافضل مقارنة مع موديل فرندلخ واكثر ملائمة لوصف امتزاز ايون الرصاص على الجيتاسون المحمل على الكاربون المنشط. تم حساب اعلى قدرة امتزاز من نموذج التفاعل من الدرجة الثانية وفقا للقيم التجريبية. وهذا يعني أن أداء عملية امتزاز أيونات الرصاص على المادة المازة CHGAC يتبع نموذج التفاعل من الدرجة الثانية، كذلك اوضحت أن امتزاز pb^{2+} على جيتاسون المحمل على الكاربون CHGAC هو كيميائيا.

الكلمات الرئيسية: الامتزاز، المعادن الثقيلة، جيتاسون، الكاربون المنشط الحبيبي.

1. INTRODUCTION

Water pollution caused by lead is a universal matter and has received worldwide attention. Lead is very toxic to human beings, animals, plants, and the general environment. Heavy metals such as lead, copper, mercury, and zinc in water that's used for drinking purpose can cause severe health hazards to human being and serious damage to the environment if not treated properly **Kundra, et al., 2012**.

Lead is present in low concentration in wastewater and is difficult to remove from water. Pollutants in industrial wastewater are almost invariably so toxic that the wastewater has to be treated before its reuse or disposal in water bodies **Singh,** and **Kaushal, 2013**. It was found that one-third of the total water pollution comes in the form of effluent discharge, solid wastes and other hazardous wastes **Lokhande, et al. 2011**. Wastewater is contaminated with lead from many industries such as battery manufacturing processes, metal-plating facilities, mining operations, paints, pigments, and other industries **Bernard, et al. 2013**.

Treatment processes for metal contaminated waste streams include chemical precipitation, ion exchange, membrane separations (ultra filtration, reverse osmosis, electrodialysis) and adsorption. Natural materials or low cost material from industrial or agricultural operations may have a potential as inexpensive sorbents for heavy metal removal where, the cost is an important parameter for the comparison of sorbent materials. Adsorption is considered the simplest and most cost-effective technique **Vereš,** and **Orolínová, 2009** . These low-cost adsorbents include cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste, tea waste, rice husk, coconut husk, name leaves, and biomass **Thomas,** and **Crittenden, 1998; Kumar, et al., 2013; Abdelhamid et al. 2012; Parmar,** and **Thakur, 2013**.

The maximum lead limit for industrial wastewater discharged is 0.1 ppm maximum concentration according to Iraqi regulation 2001 for the preservation of water sources, 2001.

Biopolymers are high potential adsorbents due to their biodegradability, non-toxicity, efficiency. These are cheap and thus are competitive with ion-exchange resins and activated carbon. They contain chemically active functional groups that serve as efficient sites to bind metal ions. Notably, Chitosan has the highest adsorption capacity among the biopolymers. It is a deacetylated derivative of chitin, the second most abundant organic compound in nature next to cellulose, and is extracted from the shells of crustaceans. It has several desirable characteristics such as biocompatibility, biodegradability, renewability, bioactivity, and non-toxicity **Juang, et al., 1997; Varma** and **Kennedy 2004; Zhoua,** and **Yangb, 2007**. For over a decade, Chitosan has received considerable attention as an adsorbent for transition metal ions and organic species **Annadurai, et al., 2008**. It chelates larger amounts of metal than chitin due to its excellent binding capacity, mostly attributed to the free amino groups exposed after chitin deacetylation. Moreover, Chitosan is soft and has a tendency to agglomerate or form gel. It is partially soluble in dilute mineral acids such as nitric acid (HNO_3), hydrochloric acid (HCl), and phosphoric acid (H_2PO_4) **Gyliene,** and **Visniakova, 2008; Nomanbhay, and Palanisamy, 2005** , and also soluble in dilute organic acids such as acetic acid (HAc), formic acid, etc. **(Chen, et al., 2008)**. In recent year, numerous studies of metal ion adsorption by Chitosan have been performed such as the removal of copper **Sağ,** and **Aktay, 2002**, chromium **Boddu, et al., 2003**, cadmium **Evans, et al., 2002**, iron **Wan, et al., 2005**, nickel, and lead ions from aqueous solution **Paulino, et al., 2007**.

The objective of this work is to use chitosan impregnated onto granular activated carbon as low cost adsorbent materials for the removal of lead from aqueous solution. Equilibrium is studying and carrying out for batch adsorption lead onto the chitosan impregnated granular activated carbon. The effect of batch adsorption parameters such as the mass of adsorbent, pH, and contact time had been investigated and the adsorption isotherms experiments have been interpreted by Langmuir and Freundlich isotherms.

2. MATERIALS AND METHOD

2.1 Materials

2.1.1 Adsorbent

Chitosan (moderate molecular weight, by Sigma–Aldrich Company) is used as received without any treatment. The granular activated carbon GAC (Filtrasorb 400, Calgon, Pittsburg, PA) was dried in the oven at 100 ^oC and 24 h to elimenate any moisture existing and then kept in an air tied bottle until use. The physical properties of GAC were examined at laboratory of Cincinnati University, USA and presented in Table 1.

2.1.2 Adsorbate

Anhydrous lead nitrate salt $pb(NO_3)_2$ was used as pb^{2+} metal ions. Analytical-grade of lead nitrate salt (99% purity, and molecule weight 331.2 g/mol). 1000 mg/l standard stock solution of lead ions pb^{2+} was obtained by dissolving lead nitrate salt $pb(NO_3)_2$ in deionized water. The chemicals used in this research are annular grade produced by Sigma–Aldrich company.

2.2 Preparation of Chitosan impregnated over granular activated carbon

Impregnation of chitosan over granular activated carbon CHGAC was done using the methods of **(Wan, et al., 2004)** with only slight modifications. “Standard stock solution of the chitosan was prepared as 10 g/L in 1% (v/v) of acetic acid solution. The granular activated carbon GAC was soaked in the chitosan solution for 24 h at room temperature. After filtration and washing with distilled water to remove excess chemicals and reach neutral pH, the adsorbent was immersed in sodium hydroxide 0.1M solution in order to obtain the adsorbed Chitosan. Finally, the prepared adsorbent was dried in oven at 80 ^oC for 6 h and kept in a desiccator until experimental use”.

2.3 Batch Adsorption Experiments

The removal of pb^{2+} from aqueous solution onto CHGAC was achieved in a batch adsorption system. The effect of operating variables on the adsorption process has been studied by:

2.3.1 Effect of Adsorbent weight

The removal of pb^{2+} from aqueous solution onto CHGAC was performed in a batch adsorption system. To evaluate the best dosage of the CHGAC for removal of pb^{2+} ions, the different dosages (5, 15, 25, 50, 75,100, 200, 300, 400 mg) of CHGAC were placed to 50 mL of lead ions solution pb^{2+}. The initial concentration of pb^{2+} solution was maintained at 100 mg/L. All experiments were carried out at 25^oC, pH 7, and 100 mg/L initial concentration of pb^{2+} ion solution. The desired pH was kept using 1 M HCl and 1 M NaOH. The CHGAC solution was added in bottles and then shaken for 10 days in a rotary shaker. The agitation speed was fixed at 140 rpm. The samples were then separated after shaking by filtration employing filter paper. The pb^{3+} ion concentrations of supernatant were measured by using the atomic-absorption spectrophotometer.

2.3.2 Effect of pH

The effect of pH on the removal process of lead ions pb^{2+} from aqueous solution onto biopolymer adsorbent was studied in batch adsorption system. The experiments were conducted to evaluate the best pH of metal ions solution, the best amount of adsorbent was placed in 50 ml of metal ions pb^{2+} solution at initial concentration of 100 ppm and desired pH value. The pH of the initial metal ions Pb^{2+} concentration was varied at 2, 4, 6, 8, and 10. The contents in the bottles were shaken in the rotary shaker at 150 rpm and 25°C. Then the samples were filtered and the lead ions pb^{2+} solution concentration of the filtrate was analyzed by the atomic-absorption spectrophotometer.

2.3.3 Effect of time

The effect of contact time for the removal of Pb^{2+} onto biopolymer composite was investigated for varied time range 2h to 10 days. The best amount of adsorbent was added to the bottles containing 50ml of lead ions solution at initial concentration of 100 ppm. The contents in the bottles were mixed in the rotary shaker at 150 rpm and 25°C. The bottles were then pulled out of the shaker at predetermined time intervals. Then the samples filtered and the lead ions solution concentration of the filtrate was analyzed by the atomic-absorption spectrophotometer.

2.4 Adsorption isotherm models

An adsorption isotherm is a curve relating the equilibrium concentration of an adsorbent onto the surface of solid substance, qe, to the concentration of the adsorbent in the liquid phase, C_e, with which it is in contact. The analysis of the equilibrium adsorption isotherms data is very important to study the adsorption capacity and equilibrium coefficient for **Sulaymon, et al., 2012**. The applicability of relationship between the experimental adsorption capacities and the metal ions concentrations (adsorption isotherm) have been widely used by the Langmuir and Freundlich models **Kaushal, and Upadhyay, 2014.** The amount of adsorption at equilibrium, qe(mg/g), is given by Eq. (1): **Grassi, et al., 2012**.

$$qe = \frac{(Co-Ce)V}{m} \tag{1}$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentration of the solute, respectively, V is the volume of the liquid (L), and m is the mass of solid substance (g). Sorption efficiency can be described by an adsorption isotherm according to the general Eq. (2) **Oliveria, et al., 2005**.

$$Sorption\ efficiency = \frac{C_o-C_e}{Co} \times 100\% \tag{2}$$

There are several models for predicting the equilibrium distribution.

2.4.1 Langmuir isotherm model

The Langmuir sorption isotherm (Langmuir, 1916) model maybe the well known and most widely used in sorption isotherm. This model is used to illustrate quantitatively the formation of a monolayer adsorbate (metal ions) on the outer surface of the adsorbent solid substance), and after that no further adsorption takes place. Thereby, the Langmuir is valid for representing the equilibrium distribution of adsorbate (metal ions) between the solid surface and bulk solution

Dada, et al., 2012. It has provided significant agreement with a wide range of experimental data. The Langmuir isotherm equation is shown in Eq. (3)**Abdul Latif, et al., 2013 .**

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{3}$$

Then Eq. (3) can be rearrangement in linear form: **Saibaba,** and **King, 2013**.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_L}\frac{1}{C_e} \tag{4}$$

Where C_e is the equilibrium concentration of metal ions (adsorbate) in the bulk solution (mg/l), q_e is the equilibrium adsorption capacity (mg/g), k_L (L/g) is Langmuir parameters and q_m (mg/g) the maximum adsorption capacity.

2.4.2 Freundlich isotherm model

The Freundlich equation isotherm (Freundlich, 1906) is an adsorption isotherm, which is a relation of the solute concentration on the surface of an adsorbent (solid substance), to the solute concentration in the liquid with which it is in contact.

Freundlich adsorption isotherm is applicable for heterogeneous systems and involves formation of multilayers. Freundlich adsorption isotherm can be provided from the following formulas **Ho, 2003**:

$$q_e = k_f C_e^{1/n}. \tag{5}$$

The logarithmic form of the equation gives:

$$log\, q_e = log\, k_f + \frac{1}{n} log\, c_e, \tag{6}$$

where n and K_f are Freundlich constants. They provided from the intercept and slope of a linear plot of log $q_e$verses log C_e **Saibaba,** and **King, 2013**.

2.5 Kinetic of Adsorption

The kinetic of adsorption of metal ions Pb^{2+} on polymer composite has been evaluated. The experimental data were examined by pseudo-first-order kinetics, pseudo-second-order kinetics of adsorption process.

2.5.1 Pseudo first-order kinetics

The pseudo-first-order kinetics model also known as the Lagergren kinetic equation is widely used to understand the kinetic behavior of the system **Ho, 2003**. It is given by the Eq. (7)

$$log\,(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}\, t, \tag{7}$$

Where q_e and q_t are the adsorption capacity of metal ions pb^{2+} at equilibrium and at time($mg.g^{-1}$), k_1 is reaction rate constant of the pseudo first order (min^{-1}).

2.5.2 Pseudo second-order kinetics

The pseudo-second-order kinetics model is represented by the Eq. (8)

$$\frac{t}{q_e} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e}, \tag{8}$$

Where k_2 is the reaction rate constant of the pseudo-second-order model.

3. RESULTS AND DISCUSSION

3.1 Scanning Electronic Microscopy

The scanning electronic microscopy (SEM) images of the surface morphology of activated carbon, chitosan, and chitosan-impregnated activated carbon are presented in Figure 1. It is clear that the surface of GAC before the impregnation of chitosan is irregular with coarse particles with different particle sizes and rough surface (**Fig. 1a**). The chitosan surface has regular shape with smooth structure and larger particle sizes than CHGAC as shown in (**Fig. 1b**).The morphology of CH-GAC obtained by SEM in **(Fig. 1c**) has irregular surface with many pores on the surface. These results might explain the enhancing of adsorption capacity of CHGAC for lead ions. This phenomenon could have been due to the reduction of the pores. Consequently, the reduction of the particles size increases the adsorption capacity of lead ions onto adsorbent GAC. The above results are confirmed by **Maghsoodloo, et al., 2011**.

3.2 Adsorption Equilibrium

3.2.1 Effect of adsorbent weight

The effect of different chitosan impregnated GAC adsorbent dosage 5, 10, 20, 30, 40, 50, 60, 80,100 mg on the percentage of adsorption efficiency is presented in **Fig. 2**. This figure illustrates that the increase of adsorbent amount will increase the percentage of adsorption efficiency. It has been observed that the adsorption rate increased quickly in the beginning adsorption period at adsorbent dosages from 5 to 50 mg. This behavior could be explained by large surface area of composite adsorbent as well as large number of sites for the adsorption of lead ions. In addition, it can be found that the observed constancy in the percentage of lead adsorption efficiency at upward of 50 mg. This behavior may be due to very weak interaction between the adsorbent and adsorbate. In solution, the concentration appears to obtain a steady state with adsorbed species and so regardless the amount of adsorbent present, there will be a residual concentration of ions in solution. Adsorption of metal ions on these types' materials is generally attributed to weak interaction between the adsorbents and absorbents. In conclusion, according to the reasons mentioned, the 50 mg is selected as an optimum amount of chitosan impregnated GAC.

3.2.2 Effect of pH

The pH is one of the most important operational parameters of adsorption of heavy metals. The effect of different pH 2, 4, 6, 8, and 10 on the lead adsorption at chitosan impregnated GAC (adsorbent) are shown in **Fig. 3**. The experiments of batch adsorption were conducted with the metal solution of 50mL in volume and 50 mg/L initial concentration, 10 days agitation time at 150rpm, and optimum dosage of 50 mg for composite adsorbent. **Fig. 3** shows that the rate of lead adsorption is mainly controlled by the pH of lead ion solution, the percentage of lead adsorption efficiency started to increase with the increase in pH from 2-5.5. Therefore, the percentage of lead adsorption efficiency increased from 18.8 % to 99.4%, for composite adsorbent. Whereas, the percentage of adsorption efficiency gradually decreased with increase pH from 5.5-10. At pH higher than 5.5 the lead ions is precipitated due to the formation of hydroxide and removal process due to lead ions adsorption was very low. In contrast, at pH less than 5.5, the concentration of protons was high and lead ions binding sites became positively charged repelling the lead. Consequently, the optimum pH value for synthetic solution of lead ion can be obtained at (5.5).

3.2.3 Effect of time

The effect of contact time on the lead adsorption onto composite adsorbent is presented in **Fig. 4**. The optimum weight of CHGAC adsorbent was added to the bottles containing metal ion solutions pb^{2+} of optimum pH. The bottles were mixed in a rotary shaker at different time-periods varying between 3 and 30 hours at 140 rpm and 25^oC. The lead solution was then filtered by filter paper. The remaining of pb^{2+} ion concentrations in the filtrate was determined by using the atomic-absorption spectrophotometer. It can be seen that the adsorption efficiency of lead onto composite adsorbent increased with an increase in contact time. Thus, the adsorption rate was very high at the beginning of adsorption period. Lead adsorption efficiency of 99 % was obtained within first 2 hours using composite adsorbent. This behavior could be explained by the availability of large number of vacant sites for lead adsorption, which is well agreed with **Wan, et al., 2011**. Therefore, the optimum contact time for lead ions removal was selected at 6 hr.

3.3 Adsorption Isotherms models

The adsorption isotherms curves from experimental data are evaluated by plotting the mass of the metal ions adsorbed per unit mass of adsorbent (q_e) and the equilibrium concentration of the adsorbate (C_e). The experimental data for the lead adsorption onto the CHGAC adsorbent was examined over an initial concentration range from 20 mg/l to 200 mg/l. **Fig. 5** describes the adsorption isotherm curves for Pb ions onto Chitosan-impregnated activated carbon. The efficiency of the lead ions adsorbed was obtained using Eq. (2).

The isotherm adsorption models were applied to the experimental data for Pb adsorption onto chitosan-impregnated activated carbon to understand the potential adsorption mechanism. These models comprised Langmiur isotherm theoretical model and Freundlich isotherm theoretical model. **Fig. 5** demonstrates the experimental data and the isothermal models data obtained from Langmiur and Freundlich isotherm. The correlation coefficients and constants for Langmiur and Freundlich isotherm models are presented in Table 2. The resulting data in **Fig. 5** showing that the adsorption capacity of Pb metal ions onto chitosan impregnated activated carbon increases with increasing the solution concentration. This could be explained according to the amino functional group in chitosan composition where the suitable chemical attracting such as electrostatic binding can take place between adsorbent and adsorbate.

All the adsorption sites on the adsorbent surface were relatively free of lead metal ions (vacant). After that lead metal molecules were reached to the adsorbent surfaces may attach instantly to the protonated functional groups of the chitosan ($-NH_3$). The values of the correlation coefficient R^2 from Table 2 demonstrate that Langmuir isotherm better fit to the experimental adsorption data than Freundlich adsorption isotherm.

3.4 Kinetics of Lead Adsorption

The experimental data were analyzed by pseudo first order kinetics Eq. (7) and the pseudo second order kinetics Eq. (8) to describe the mechanism of adsorption reaction.

3.4.1 Pseudo first order model

The value of rate constant k_1 and qe are obtained from the slope and intercept of plots of log (qe-qt) against time respectively as shown in **Fig. 6**. The calculated values of qe as listed in Table 3 are much lower than the experimental values. The values of correlation coefficients R^2 of pseudo first order model are lower than pseudo second order model indicating that the Pb adsorption does not obey pseudo first order kinetic.

3.4.2 Pseudo second order model

The value of rate constant k_2 and qe can be evaluated from the slope and the interception of plot of (t/qt) against time respectively as shown in **Fig. 7.** The values of the rate constants, maximum adsorption capacity, and the correlation coefficients are presented in the Table 3. The pseudo second order models depend on the assumption that the rate-controlling step may be chemisorption, which involves valence forces by sharing or electron exchange between the adsorbent and the adsorbate. The maximum adsorption capacity calculated from the pseudo second order model is in accordance with the exponential values. This implies that the adsorption obeys a pseudo second order model. The plot of (t/qt) versus t directly increases with linear slope showing that chemisorption is the main rate-controlling step of the adsorption process.

The granular activated carbon impregnated by chitosan was effectively used as an adsorbent for the elimination of lead ions from aqueous solution. The experimental data have been analyzed by Langmuir isotherm model is more acceptable than using Freundlich model. Where, the parameters of these models with correlation coefficients were calculated. The results of adsorption data exhibited a better fit to Langmuir isotherm model. The adsorption performance of lead ions onto CHGAC followed a pseudo second order kinetic model, which described that the adsorption of Pb^{2+} onto CHGAC was controlled by chemisorption. The maximum adsorption capacities calculated from the pseudo second order model are in accordance with the exponential values.

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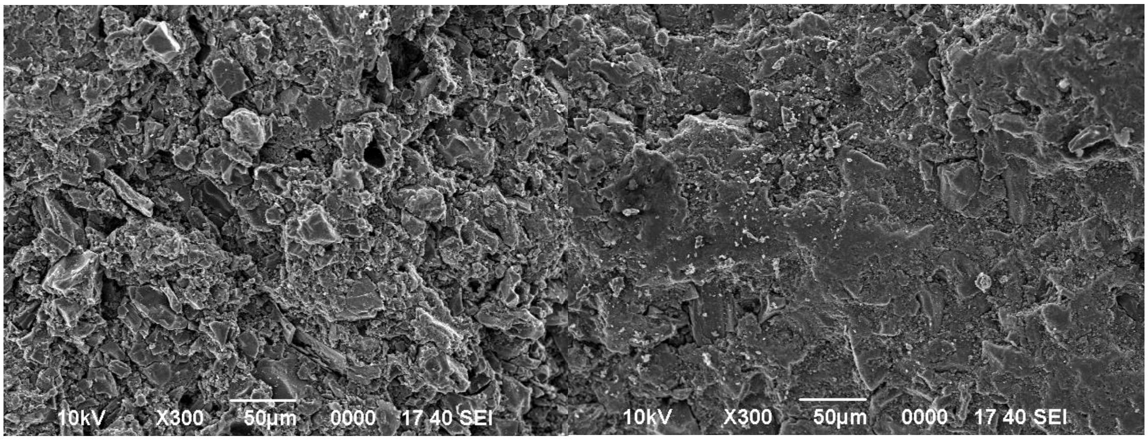
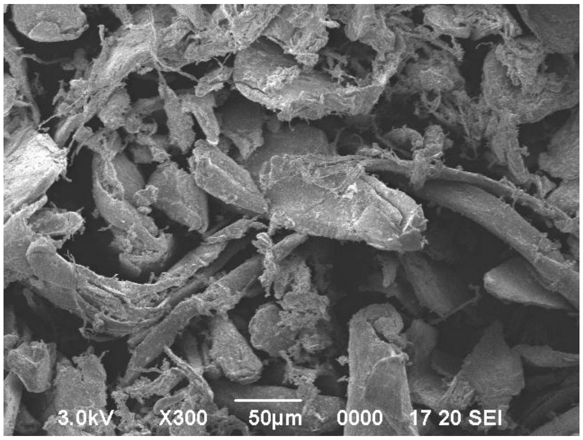
Table 1. The Physical Properties of Granular Activated Carbon (Sigma–Aldrich Company).

Product name	Granular Activated Carbon, GAC
Composition	Carbon C
BET Surface area m^2/g	819.2815
Average pore diameter (4V/A):	49.890 Å
BJH adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.307097 cm³/g
T-Plot Micropore volume	0.315204 cm³/g



(a) (b)



(c)

Figure 1. SEM images of (a) Chitosan (b) Granular Activated Carbon GAC and(c) Chitosan impregnated granular activated carbon CHGAC.

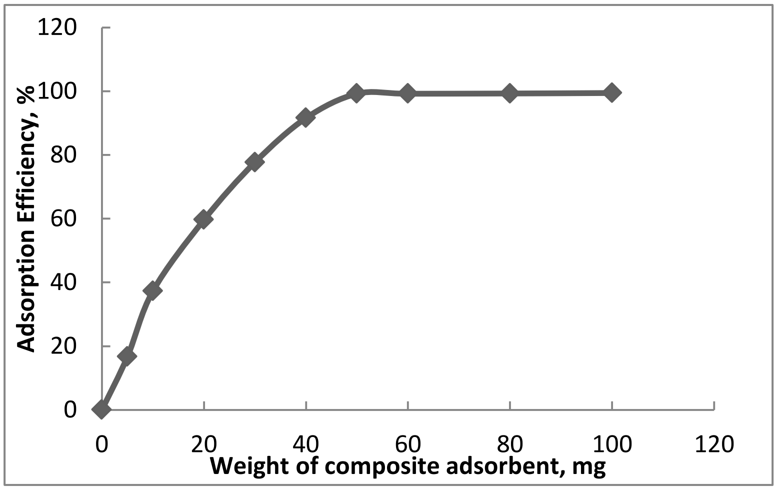


Figure 2. Effect of amount of chitosan impregnated GAC on the adsorption of lead ions (pb^{+2}).

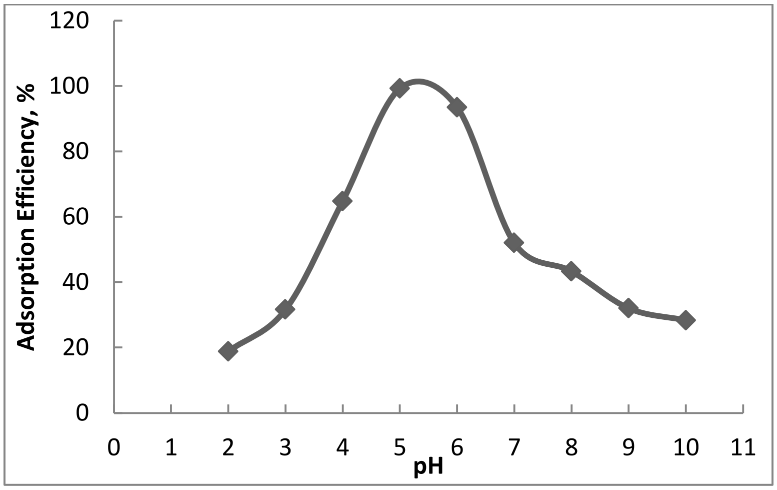


Figure 3. Effect of pH on the removal efficiency of Pb^{+2} onto CHGAC.

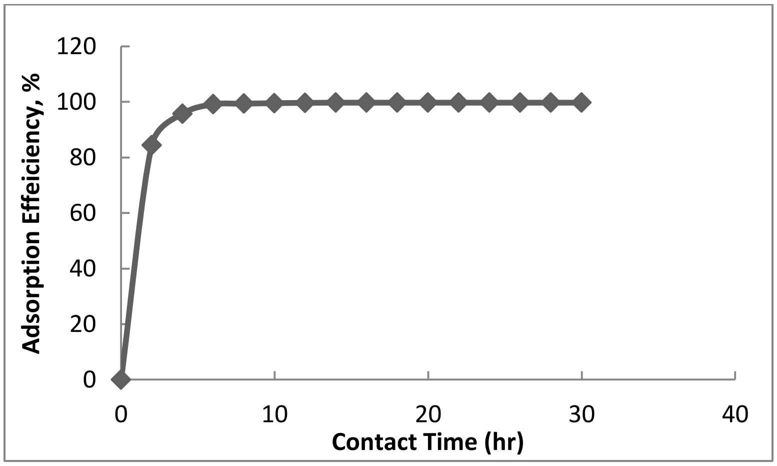


Figure 4. Effect of time on the removal efficiency of Pb^{2+} onto CHGAC.

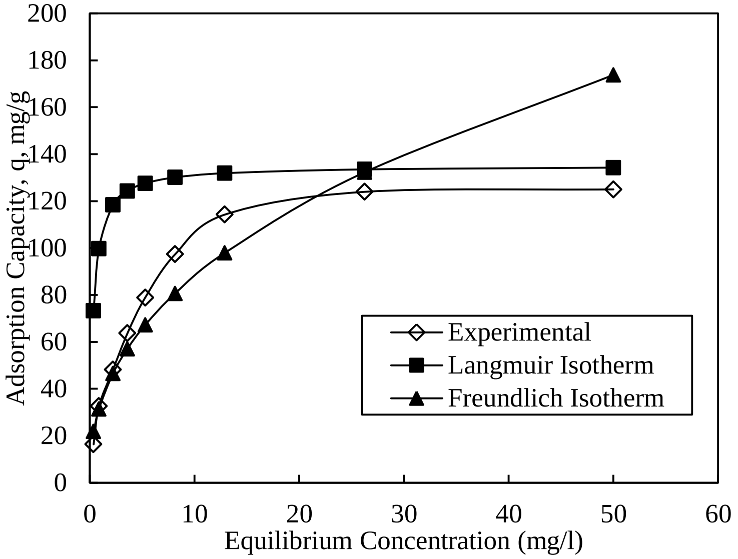


Figure 5. Adsorption isotherm of experimental, Langmuir, and Freundlich of CHGAC 20^{o}C.

Table 2. Langmuir isotherm and Freundlich isotherm constants of CHGAC.

Langmuir Constants			Freundlich Constants		
q_m	k_L	R^2	1/n	k_f	R^2
135.1351	3.155405	0.9981	0.4232	33.18945	0.9232

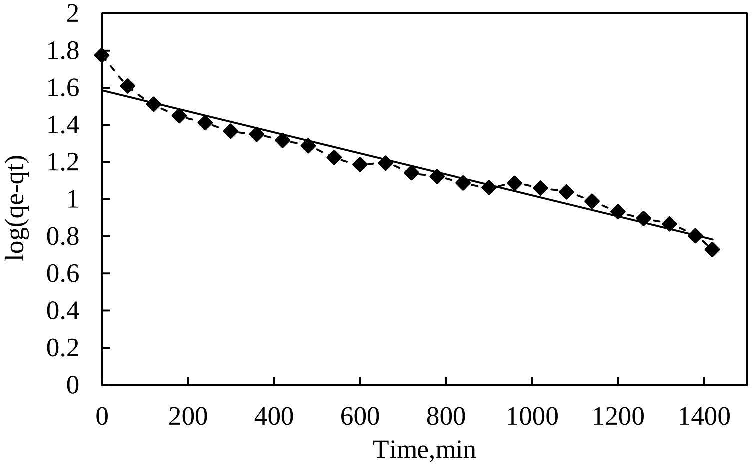


Figure 6. Pseudo first order kinetic for Pb adsorption onto chitason impregnated GAC at room temperature.

Table 3. Kinetics models parameters for Pb adsorption onto Chitason impregnated GAC.

Pseudo first order			Pseudo second order			qe, exp
k_1	qe, cal	R^2	k_2	qe, cal	R^2	
-0.00139	38.4858	0.9545	0.00011	56.8182	0.9891	59.3533

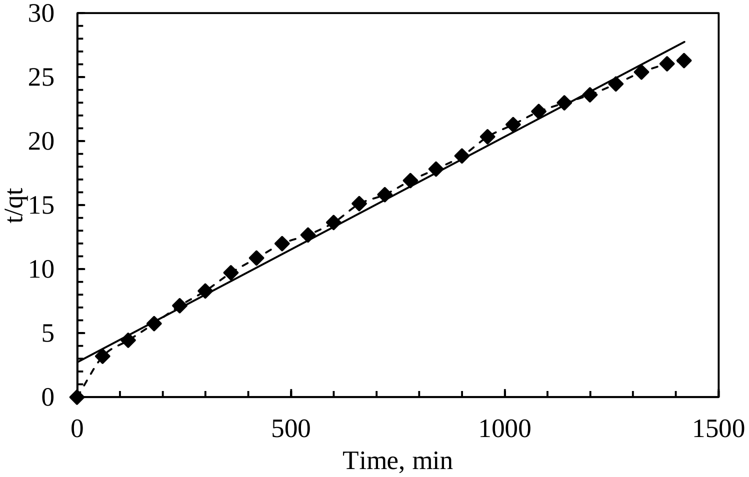


Figure 7. Pseudo second order kinetic for Pb adsorption onto chitason impregnated GAC at room temperature.