

Removal of Pb(II) from aqueous solutions by chitosan coated saw dust activated carbon

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ABSTRACT

The removal of Pb (II) from aqueous solutions by chitosan coated saw dust activated carbon (CCSDAC) was investigated. The higher percentage removal of Pb (II) from aqueous solutions in the presence of saw dust activated carbon (SDAC) and CCSDAC was observed. The later adsorbent (CCSDAC) has the higher percentage removal than that of the former (SDAC). The mechanism of adsorption was studied by conducting pH as well as kinetic studies. Batch adsorption experiments were conducted to study the effect of adsorbent dose, initial concentration and temperature on the removal of Pb (II) using SDAC and CCSDAC. When compared to SDAC, CCSDAC has higher adsorption at pH 4.0. The kinetic and equilibrium adsorption data were well modeled using pseudo-first- order kinetic and Langmuir isotherm models.

KEY WORDS: Adsorption, Pb (II) removal, SDAC, CCSDAC, Kinetics, Thermodynamics

I. INTRODUCTION

Metal painting, metal finishing and metal processing industries eliminate the toxic metal lead along with wastewater [1]. Lead is non-bio-degradable and its presence in streams and lakes lead to bio accumulation in living organisms, causing health problem in animals, plants and human beings. Human intake of lead causes distortion of the biosynthesis of haemoglobin, rise in blood pressure, kidney damage, miscarriages, abortions, brain damage and diminished learning activities in children. This heavy metal is also a known carcinogen. Therefore the removal of excess heavy metal ions from wastewater is essential to protect human health and environment [2].

The usages of many treatment methods are limited due to high cost and tedious procedure. Many treatment methods are available for the removal of toxic metals like lead which is a difficult task due to high cost [3]. There are various methods for the removal of toxic metal ions from solutions: reverse osmosis [4], membrane filtration [5], precipitation [6], adsorption [7] etc., among these methods, adsorption is by far the most versatile and widely used for the removal of different heavy metals and other pollutants. Bailey *et al.*, 1999 [8] reviewed the potential use of adsorbents for the removal of Pb (II) from aqueous solutions. The adsorbents used for the removal of Pb (II) from waste water include natural materials such as tree fern [9], siderite [10], hydroxyapatites [11], saw dust [12] and Mangifera indica seed shell [13]. Waste lignocellulosic materials are widely used as adsorbents for effluent treatment and are reported by many authors for the removal of heavy metals from aqueous solutions [14-17]. The effectiveness of the adsorbent material is of much importance in water and waste water treatment strategies. The chemical and physical properties of lignocellulosic materials play a vital role in the adsorption capacity of the materials [17, 18 and 19].

Chitosan is an abundant biopolymer in nature and is a major derivative of chitin. It is a novel scavenger for metal ions possessing amine and hydroxyl functional group in its structure [20-22]. The adsorption capacity of chitosan can be increased by modifying the physical conditions of the biopolymer as a coated polymer or impregnated polymer. Several studies of metal ions adsorption by chitosan have been carried out in the recent years, such as the removal of copper [23], chromium [24], cadmium [25], iron [26], nickel and lead ions from aqueous solutions [27].

In the present work, SDAC is prepared by acid activation and the adsorption capacity is compared with CCSDAC. The adsorption equilibrium and kinetics of Pb(II) ions in aqueous solutions with SDAC and CCSDAC were also investigated. Comparison of SDAC and CCSDAC adsorption of Pb(II) ions shows that CCSDAC has higher adsorption capacity than SDAC. The influences of experimental equilibrium parameters were obtained by fitting the experimental data to Langmuir & Freundlich models. Adsorption rates were determined quantitatively and compared by the pseudo first order, pseudo second order and intra-particle diffusion models.

II. MATERIALS AND METHODS

2.1. Preparation of sawdust activated carbon

Sawdust was collected from a local timber industry and was used as the precursor material for the preparation of sawdust activated carbon (SDAC). Saw dust was washed with distilled water to remove surface adhered dirt, mud and water soluble materials and dried in sunlight. Dried sawdust was treated with 5% H₂SO₄ and kept at room temperature for about 24 hours with occasional stirring and soaked with de-ionized water until the solution pH was stable.

2.2. Preparation of chitosan gel

About 5.0 g of chitosan was slowly added to 1000ml of 10% oxalic acid with constant stirring. The mixture was also heated to 40-50°C to facilitate mixing. At room temperature, a whitish viscous gel is formed. The residual acid content present in the saw dust is removed by soaking in 5% NaHCO₃. The product was dried overnight in an oven at 110°C and further cooled at room temperature and stored in desiccators until use.

2.3. Surface coating of SDAC with chitosan

About 500 ml of the chitosan gel was diluted with water and heated to 40-50°C followed by the addition of 500g of the SDAC to the diluted gel and mechanically agitated using the rotary shaker at 150 rpm for 24 hrs. The gel coated SDAC was then washed with de-ionized water. The process was repeated 5 times to form a thick coating of chitosan on the surface of SDAC. The amount of chitosan coated was determined to be about 29% by weight. The CCSDAC was removed and neutralized by putting them in 0.5% NaOH solution for 3 hrs. The CCSDAC was then extensively rinsed with de-ionized water and dried at room temperature.

2.4. Adsorption experiments

The stock Pb (II) solution was prepared by dissolving 1.599 grams of lead nitrate (Merck, Germany) in 1 litre of distilled water. The stock solution was further diluted to obtain solutions of various concentrations of Pb (II) 10 ppm, 20 ppm, 30 ppm respectively. pH of the solution was adjusted to constant values. A known amount of the adsorbent was agitated with a known volume of metal solution in a mechanical shaker at 200 rpm. Finally the supernatant liquids were filtered and the series of solutions were transferred into a 25mL volumetric flask. 10 ml of NH₃-NH₄Cl buffer solution was added to provide pH of 10 followed by the addition of 0.01% solution of PAR [4-(2-pyridylazo resorcinol)] reagent. The solution was diluted up to the mark with distilled water. The absorbance was measured at 520 nm against a reagent blank. The amount of adsorbed Pb (II) ions were calculated from the mass balance expression given by

$$q_e = \frac{(C_0 - C_t)}{W} V \quad (1)$$

Where C₀ and C_t (mg L⁻¹) are the liquid-phase concentrations of dye at initial and any time t, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

3. RESULTS AND DISCUSSION

3.1. Characteristic analysis

The surface area and pore volume for SDAC and CCSDAC are shown in table 1. Compared to SDAC, CCSDAC has higher surface area and pore volume. SEM analysis was exploited to illustrate the variation of morphology and surface texture of each adsorbent. SEM images of SDAC and CCSDAC are shown in Fig.1. SDAC displays a relatively rough structure Fig.1 (a), while CCSDAC shows a relative rough structure with higher surface area Fig.1 (b).

3.2. Batch adsorption experiment

3.2.1. Effect of initial pH

It is an important parameter for the adsorption of Pb(II) metal ion from aqueous solutions that affects the form and quantity of heavy metal ions, adsorbent surface sites in water, and the interaction between heavy metals and the functional groups on the adsorbent surface. Effect of pH on the adsorption of Pb (II) ions to SDAC and CCSDAC was evaluated by using initial Pb(II) concentration of 10, 20 and 30 mg /L at the pH range of 3–6, and the results are illustrated in Fig.2(a) and (b). The amount of Pb(II) uptake was very small at pH 2.0 (highly acidic), while the adsorption was enhanced over pH 3.0. At lower pH values the surface charge of the SDAC and CCSDAC is positive and, thus, Pb (II) adsorption on SDAC and CCSDAC is not favourable. In addition, hydronium ions compete with Pb (II) ions for the active sites on the surface of the adsorbent, so adsorption capacity is small. When pH was increased, electrostatic repulsion between Pb(II) ions and adsorbent surface sites and competing effect of hydronium ions were decreased, so Pb(II) uptake was increased [28]. Experiments were not conducted beyond pH 8.0 to avoid precipitation of Pb(II) ions as Pb(OH)₂. The optimum pH was established as 4.0. The percentage removal of CCSDAC at pH 4.0 is 94.8, that is, greater than that of SDAC with a percentage removal of 90.2 for a concentration of 10 mg/L Pb (II) solution. This may be due to the presence of active adsorption sites in CCSDAC. These sites will hold the metal ions by forming strong bonds.

3.2.2. Effect of agitation time

Effect of agitation time on adsorption of Pb(II) onto the SDAC and CCSDAC was studied in the time range of 10–300 min by using 10,20,30 mg/L of Pb(II) solutions at pH 4.0 with 120 mg /L of SDAC and CCSDAC. The mixtures were agitated at 200 rpm. Samples were taken at various periods of time, filtered immediately and then analyzed for their Pb (II) concentrations. Adsorption of Pb (II) ions increased within 90 minutes, after which it continued to increase at a lower rate until equilibrium was attained shown in Fig. 3.(a) and (b). Based on these results, a contact time of 180 minutes was assumed to be suitable for subsequent adsorption experiments. The percentage removal of Pb(II) ions at an equilibrium time of 180 minutes onto CCSDAC was 94.8 and for SDAC it was 90.2.

3.2.3. Effect of carbon dosage

The dependence of metal adsorption on carbon dose was studied by varying the amount of carbon from 0.02 to 0.2g / 50ml of the solution, keeping other parameters (pH, agitation speed and contact time) constant for the initial metal concentrations of 10, 20 and 30 mg L⁻¹ and which show the metal removal efficiency for different carbon doses. From figures 4(a) and (b), it can be observed that removal efficiency is generally improved with increasing the carbon concentration up to a certain value and then, there is no further increase of adsorption. The removal efficiency of Pb (II) ions with the increase in carbon concentration is due to the greater surface area with more functional groups consequent to the increase in the number of carbon particles with more number of exchangeable sites for adsorption and saturation which occurred as a result of non-availability of exchangeable sites on the adsorbent. The increased removal at high dosages is expected due to the increased adsorbent surface area and availability of more adsorption sites.

The equilibrium carbon dose (SDAC) required for the Pb(II) removal of 90.2%, 63.4% and 33.8% from 50 ml of 10, 20 and 30 mg/L initial metal concentrations was 0.12 g. The equilibrium carbon dose (CCSDAC) required for the Pb(II) removal of 94.8%, 69.2% and 40.66% from 50 ml of 10, 20 and 30 mg/L initial metal concentrations was 0.12 g. Maximum removal of Pb(II) ions from the solution is noted at a metal initial concentration of 10 mg/L. The % removal decreases at higher metal concentrations. Comparing the adsorbents, CCSDAC has the highest % removal of Pb(II) ions from the solution than that of SDAC with the same adsorbent dose of 0.12 g.

3.3 Adsorption kinetics

The kinetics of SDAC and CCSDAC-Pb (II) interactions were tested with different kinetic models including pseudo-first-order and pseudo second-order models. The pseudo-first-order equation is among the most widely used to predict metal adsorption experiments.

3.3.1. Pseudo-first-order kinetic model

The pseudo-first-order equation can be expressed as reported by Onal et al., 2007 [29] as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where q_e and q_t are the amounts of metal adsorbed at equilibrium and at time (min) and k_1 is the rate constant of the pseudo-first-order adsorption. The straight line in the graph of $\log(q_e - q_t)$ versus t suggests the applicability of this kinetic model, and q_e and k_1 can be determined from the intercept and slope of the plot, respectively. It is shown in the Fig.5 (a) and (b).

The pseudo-first-order data falls on straight lines indicating that this model is appropriate. The pseudo-first-order rate constant k_1 and the value of q_e for SDAC were calculated from the model and are presented in Table 1. The pseudo-first-order rate constant k_1 and the value of q_e for CCSDAC were calculated from the model and are presented in Table 1. The correlation coefficient is 0.979 for SDAC and 0.989 for CCSDAC, which is indicative of a good correlation and also $q_{e, cal}$ determined from the model is in a good agreement with the experimental values of $q_{e, exp}$. Therefore, the pseudo-first-order model is suitable for modelling the adsorption of Pb (II) on the SDAC and CCSDAC. Comparing the efficiency of the SDAC and CCSDAC, the later has high efficiency than the former.

3.3.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is based on the assumption that the sorption follows second order chemisorption. Pseudo-second-order kinetic model is given as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

After integrating we get

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where k_2 [$g\ mg^{-1}\ min^{-1}$] is the rate constant of the pseudo-second-order adsorption and q_t is the adsorption capacity at time 't' ($mg\ g^{-1}$).

The initial sorption rate h [$mg\ g^{-1}\ min^{-1}$] is defined as:

$$h = k_2 q_e^2 \quad (5)$$

The plot of t/q_t versus t should give a straight line if second order kinetics is applicable, and q_e and k_2 can be determined from slope and intercept of the plot, respectively. The linear plot of t/q_t versus t for the pseudo-second-order kinetic model is shown in Fig.6(a) and (b). The pseudo-second-order rate constant k_1 and the value of q_e for SDAC were calculated from the model and are presented in Table 1. The pseudo-second-order rate constant k_1 and the value of q_e for CCSDAC were calculated from the model and are presented in Table 1. The correlation coefficient is 0.889 for SDAC and 0.912 for CCSDAC, which is indicative of a poor correlation and also $q_{e, cal}$ determined from the model is not in a good agreement with the experimental values of $q_{e, exp}$. Therefore, the pseudo-second-order model is not suitable for modelling the adsorption of Pb (II) on the both SDAC and CCSDAC.

3.3.3 Intra-particle diffusion model

The intraparticle diffusion equation is expressed as [31];

$$q_t = K_{int}t^{0.5} + C \quad (6)$$

Where q_t (mg g^{-1}) is the amount of adsorption at time t (min) and k_{id} ($\text{mg g}^{-1} \text{min}^{-1}$) is the rate constant of intra-particle diffusion. A straight line in the graph of qt versus $t^{0.5}$ suggests the applicability of the intra-particle diffusion model. k_{id} and c can be determined from the slope and intercept of the plot respectively. The intra-particle rate constant k_{id} and C parameters were obtained from the plot of q_t versus $t^{1/2}$ and the results are given in Table 1. The correlation coefficient obtained from the model is not satisfactory, and also the value of c is not zero, indicating that the intra-particle diffusion model may not be the controlling factor in determining the kinetics of the process. As a result, compared to pseudo-second-order and intraparticle diffusion kinetic models, a good correlation coefficient was obtained for pseudo-first-order kinetic model which indicates that the Pb(II) adsorption on both SDAC and CCSDAC follows pseudo-first-order rate expression.

As a result, compared to pseudo-second-order kinetic model, a good correlation coefficient was obtained for pseudo-first-order kinetic model, which indicates that the Pb (II) adsorption on SDAC and CCSDAC follows pseudo-first-order rate expression. Also comparatively, CCSDAC has the highest correlation coefficient than that of SDAC.

3.4. Isotherm study

The equilibrium adsorption isotherms provide very useful data to understand the mechanism of adsorption. Several isotherm models are used to describe the behaviour of adsorbent–adsorbate couples. Langmuir and Freundlich isotherm models were preferred in order to evaluate the data in this study. These isotherm models are widely used to establish the relationship between the amount of Pb (II) ions adsorbed on an adsorbent and its equilibrium concentration in aqueous solution.

3.4.1. Langmuir isotherm

Langmuir isotherm has been extensively used for the adsorption of heavy metals, dyes, organic pollutants, etc. [32, 33]. It is applicable for monomolecular layer adsorption. This isotherm is described as a homogeneous one assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [34]. The Langmuir isotherm is used to obtain a maximum adsorption capacity produced from the complete monolayer coverage of adsorbent surface. The isotherm equation is represented in terms of the fractional coverage (θ) as given by Eq. (7):

$$\theta = \frac{q_e}{Q_m} = \frac{bC_e}{1 + bC_e} \quad (7)$$

Where, b is adsorption equilibrium constant (L/mg) that is related to the apparent energy of adsorption and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg g^{-1}) and q_e is the amount adsorbed on unit mass of the adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg/L). Eq. (7) can be rearranged to get the linear form, as given by Eq. (8):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{1}{Q_m + C_e} \quad (8)$$

It shows that a plot of (C_e/q_e) versus C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the values of constants Q_m and b respectively.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [35], and it is also known as the separation factor, given by Eq. (9):

$$R_L = \frac{1}{(1 + b C_0)} \quad (9)$$

The value of R_L lies between 0 and 1 is for a favourable adsorption, while $R_L > 1$ represents an unfavourable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L=0$.

The isotherm data has been linearized using the Langmuir equation and is plotted between C_e/q_e versus C_e which is shown in Fig. 7(a) and (b). The Langmuir constant q_m , which is a measure of the monolayer adsorption capacity of sawdust, is obtained as 22.10 mg g^{-1} for SDAC and 23.4 mg g^{-1} for CCSDAC in the equilibrium. The Langmuir constant, b , which denotes adsorption energy, is found to be 0.041 L mg^{-1} and 0.038 L mg^{-1} for SDAC and CCSDAC respectively. The high value of coefficient of determination ($R^2 = 0.974$ for SDAC and 0.984 for CCSDAC) obtained indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Pb (II) onto both the adsorbent surfaces. The dimensionless parameter, R_L , which is a measure of adsorption favourability is found in the range of 0.5495 for SDAC and 0.5682 for CCSDAC ($0 < R_L < 1$) which confirms the favourable adsorption process for Pb (II) removal using SDAC and CCSDAC. Comparing the adsorbents in our present work the CCSDAC has the highest regression co-efficient value than SDAC and proves to be having a better monolayer adsorption.

3.4.2. Freundlich isotherm

Freundlich isotherm describes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. For many systems, the heat of adsorption decreases in magnitude with increasing the extent of adsorption [36]. This has been well taken care of by the Freundlich isotherm, previously considered to be an empirical isotherm. For adsorption from solution, the Freundlich isotherm is expressed by Eq. (10):

$$q_e = K_f C_e n \quad (10)$$

where, K_f (mg g^{-1}) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n_f is the heterogeneity factor representing the deviation from linearity of adsorption

and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of $\log q_e$ versus $\log C_e$ on the basis of the linear form of equation as given by Eq. (11):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (11)$$

The Freundlich constants, K_f and n are obtained by plotting the graph between $\log q_e$ versus $\log C_e$ as shown in Fig. 8(a) and (b). The values of K_f and n_F for SDAC were 1.05 and 0.19 respectively. The values of K_f and n for CCSDAC are 1.10 and 0.21 respectively. It is found that the coefficient of determination obtained from the Freundlich isotherm model for SDAC and CCSDAC is 0.604 and 0.802, which is very lower than that for Langmuir isotherm model as given in Table 3. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity. The obtained result indicates that the equilibrium data is not fitted well with the Freundlich isotherm model.

3.5 Thermodynamic study

In order to investigate the effect of temperature on the uptake of Pb (II), the process was carried out at different temperatures ranging from 303K, 313K and 323K. The temperature affected the equilibrium uptake as shown in Fig.9 (a) and (b). The equilibrium Pb(II) ion adsorption capacity of both the adsorbents were better at higher temperatures as the adsorbed amount of Pb(II) ions increased with the rise in temperature. Higher uptake at high temperature is due to the increase in molecular diffusion or may be attributed to the availability of more active sites on the surface of the adsorbents by expansion of the pores. Temperature dependence of the adsorption process is related with several thermodynamic parameters including free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), which are used to decide whether the adsorption is a spontaneous process or not. Thermodynamic parameters can be calculated from the following equation;

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

Where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the temperature (K), and K_d is the distribution coefficient. If the value of ΔG° is negative, the chemical reaction can occur spontaneously at a given temperature. The K_d value was calculated using the following equation [11];

$$K_d = \frac{C_e}{q_e} \quad (11)$$

Where q_e and C_e are the equilibrium concentrations of metal ions (mg L^{-1}) on the adsorbent and in the solution, respectively. The enthalpy change (ΔH°) and entropy change (ΔS°) of Biosorption can be calculated from the following equation;

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

This equation can be written as;

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

The thermodynamic parameters of ΔH° and ΔS° were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$ respectively [Fig. 10 (a) and (b)]. The Gibbs free energy changes (ΔG°) were calculated from Eq. (12), and the values of ΔG° , ΔH° , and ΔS° for the adsorption of Pb(II) on SDAC and CCSDAC were given in Table 3. The negative values of ΔG° indicated the spontaneous nature of the adsorption process. The magnitude of ΔG° also increased with increasing temperature indicating that the adsorption was more favorable at higher temperatures. The value of ΔH° was positive, indicating the endothermic nature of the adsorption of Pb (II) on the SDAC and CCSDAC in the temperature range of 303K, 313K and 323K. The magnitude of ΔH° gives an idea about the type of sorption. There are two main types of adsorption: physical and chemical. The enthalpy for physical adsorption is usually not more than 1 kcal mol^{-1} (3.0 kJ mol^{-1}) and the enthalpy for chemical adsorption is more than 5 kcal mol^{-1} (15 kJ mol^{-1}) [37]. Therefore, the adsorption of Pb(II) ions on the SDAC and CCSDAC was a physical process because the obtained ΔH° value is 6.25 kJ mol^{-1} for the former and 8.09 kJ mol^{-1} for later. Hence the adsorption equilibria were rapidly attained and there were weak interactions between the Pb(II) ions and the functional groups on the surface of the adsorbents. In addition, the positive value of ΔS° suggested an increase in randomness at the solid/liquid interface during the adsorption of Pb(II) ions on the adsorbents.

3.6. Desorption studies

Desorption of adsorbed Pb(II) ions from SDAC and CCSDAC were studied in a batch system. Desorption experiments were carried out by using 0.1M H_2SO_4 solution. Pb (II) ions were adsorbed according to the process described above (Section 2.4). The adsorbents loaded with Pb (II) ions was collected by filtration and washed with deionized water for five times, then dried in air for one day. The adsorbents loaded with Pb(II) ions was treated with 10mL of H_2SO_4 solutions in the concentration range of 0.1 – 0.5 M, and shaking the content of tubes at 300rpm for 3 h. The solution was separated by vacuum filtration through $0.45 \mu\text{m}$ nitrocellulose membrane and the filtrate was analyzed to determine the concentration of Pb (II) ions desorbed.

Desorption is of utmost importance when the adsorbent preparation/generation is costly, as it is possible to decrease the process of adsorption cost and also dependency of the process on a continuous supply of adsorbent. After desorption, the adsorbent should be close to its original form, and should not lose its adsorption ability. A successful desorption process requires the proper selection of the eluents, which strongly depends on the type of adsorbent and the mechanism of adsorption [37]. The selected eluent must be effective, harmless for the biosorbent, non-polluting, and cheap. For that purpose, dilute solutions of mineral acids such as hydrochloric acid, sulfuric acid, acetic acid, and nitric acid can be used.

In this study, H₂SO₄ solution was selected as an eluent to desorb Pb(II) ions from the metal-loaded adsorbents. In acidic conditions, heavy metal cations are displaced by protons from the binding sites. The effect of H₂SO₄ concentration on the desorption of Pb (II) is investigated. The regeneration efficiency reached from 62.6 to 91.7% when the concentration of H₂SO₄ increased from 0.01 to 0.5 M, indicating that higher concentration of H₂SO₄ was more efficient in releasing Pb(II) ions. However a complete desorption of Pb(II) ions could not be obtained even with 0.5M HCl, which might be due to Pb(II) ions becoming trapped in the intrapores and, therefore, difficult to release [38].

IV. CONCLUSIONS

Activated carbon prepared from saw dust for the removal of Pb (II) from the industrial effluent is investigated. Sawdust activated carbon is coated with chitosan which is a natural polymer and compared with the adsorption capacity of SDAC which is found to be a better adsorbent for the removal of Pb (II) as compared to SDAC and many other low-cost and commercially available adsorbents. The maximum percentage removal of Pb (II) is obtained at pH 3. The equilibrium time for Pb (II) adsorption on SDAC is obtained as 180 minutes with a percentage removal of 90.2 lower than CCSDAC of 94.8 at the same equilibrium time. With the increase of adsorbent amount, the percentage removal of Pb (II) increases and the adsorption capacity of adsorbents to adsorb Pb (II) decreases because of the availability of more unsaturated adsorption sites. The percentage removal decreases and the adsorption capacity increases with an increase in the initial Pb (II) concentration. The equilibrium adsorption data are tested with various isotherm models such as Langmuir and Freundlich isotherm models. The equilibrium data are best fitted with Langmuir isotherm model which confirms the monolayer adsorption of Pb (II) onto the CCSDAC. The maximum adsorption capacity is obtained with the application of Langmuir isotherm model by Langmuir constant q_m , which is a measure of the monolayer adsorption capacity of SDAC is obtained as 22.10mg/g and 23.4 mg/g for CCSDAC in the equilibrium, which is comparatively good adsorption capacity. The kinetics of Pb (II) adsorption using SDAC and CCSDAC as an adsorbent for different values of initial Pb(II) concentration is explained by Pseudo-first-order and Pseudo-second-order kinetic model. The kinetics of Pb (II) ion adsorption followed pseudo-first-order equation with a correlation coefficient of 0.979 for SDAC and 0.989 for CCSDAC. The saturated adsorption is regenerated by acid and base treatment. The adsorption efficiency of the regenerated sawdust is found to be more than 90% of fresh sawdust for the removal of Pb (II).

The adsorbed amount of Pb (II) ions increased with increasing temperature. The negative ΔG° values indicated that the adsorption of Pb (II) ions on both SDAC and CCSDAC was feasible and spontaneous. The positive value of ΔH° confirmed the endothermic nature of adsorption.

In order to desorb the Pb (II) ions from metal-loaded adsorbents, 0.1M H₂SO₄ solution was used as an eluent. The higher concentration of some interfering ions including Na⁺, K⁺, Mg²⁺, and Ca²⁺ are efficient in suppressing Pb(II) uptake by SDAC and CCSDAC. The results indicated that CCSDAC is a better adsorbent compared to SDAC in the removal of Pb(II) ions from aqueous solutions.

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TABLES:

TABLE 1: Kinetic Parameters for the adsorption of Pb (II) onto SDAC and CCSDAC.

Kinetic model	Adsorbent	
	SDAC	CCSDAC
Pseudo- first order		
q_e (mg g ⁻¹)	12.67	13.85
q_{calc} (mg g ⁻¹)	7.45	8.23
k_1 (min ⁻¹)	1.36×10^{-2}	1.55×10^{-2}
R^2	0.979	0.988
Pseudo-second order		
q_{calc} (mg g ⁻¹)	9.02	9.48
k_2 (g mg ⁻¹ min ⁻¹)	2.65×10^{-3}	4.22×10^{-3}
R^2	0.889	0.912
Intra-particle diffusion		
k_{int} (mg g ⁻¹ min ^{-0.5})	0.406	0.4
C	5.44	6.34
R^2	0.789	0.819

TABLE 2: Langmuir, Freundlich and Temkin Isotherm Parameters for the adsorption of Pb (II) onto SDAC and CCSDAC.

Isotherm model	Adsorbent	
	SDAC	CCSDAC
Langmuir isotherm		
Q_m (mg g ⁻¹)	22.10	23.40
K_L (L mg ⁻¹)	0.041	0.038
R^2	0.974	0.984
Freundlich Isotherm		
k_f (mg g ⁻¹)	1.05	1.10
N	0.19	0.21
R^2	0.604	0.822

Table: 3: Thermodynamic parameters of adsorption of Pb (II) onto SDAC and CCSDAC.

SDAC		Thermodynamic parameters		
T (K)	K_d	ΔG° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)
303	9.0	- 5.5		
313	15.7	-7.2	22.8	6.25
323	32.3	-9.3		
CCSDAC				
303	19	-7.4		
313	49.2	-10.1	29.2	8.09
323	99.3	-12.3		

FIGURE CAPTIONS

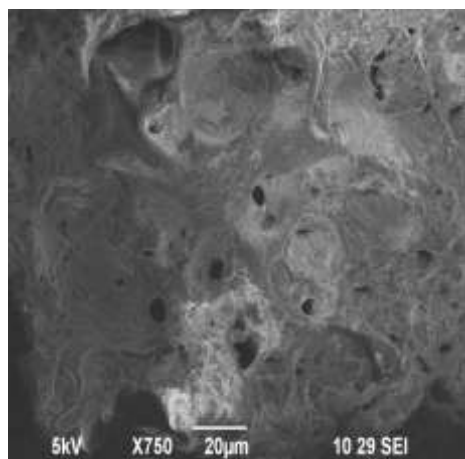


Fig.1 (a) SEM images of SDAC

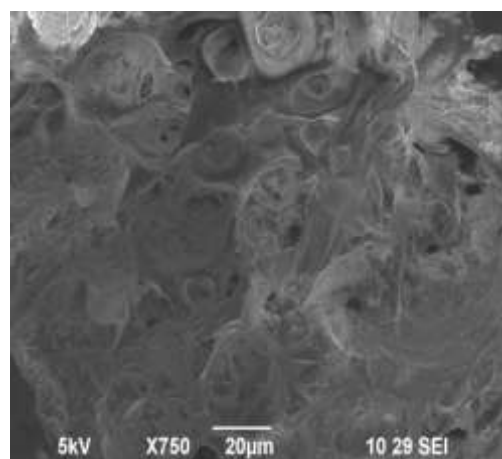


Fig.1 (b) SEM images of CCSDAC

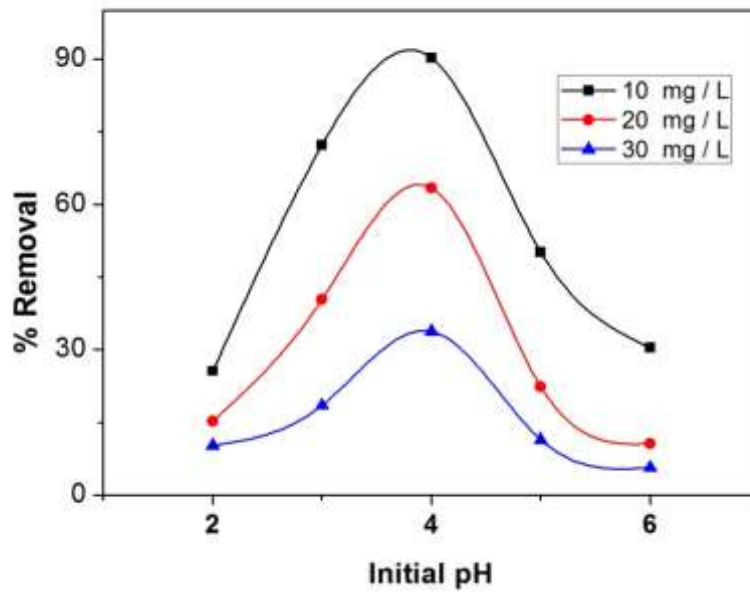
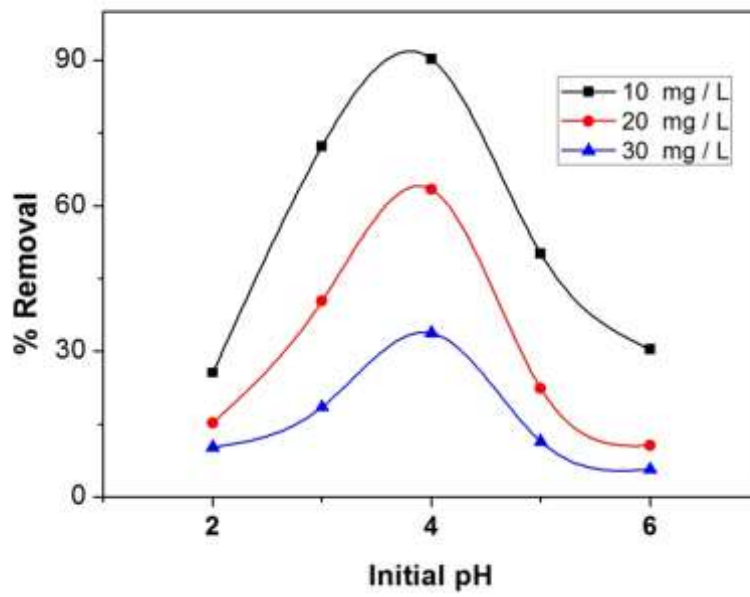


Fig. 2(a). Effect of solution pH on Pb (II) uptake by SDAC
(b). Effect of solution pH on Pb (II) uptake by CCSDAC

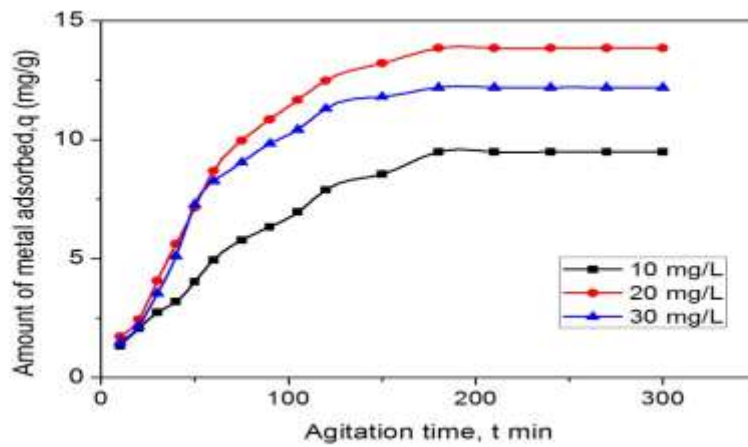
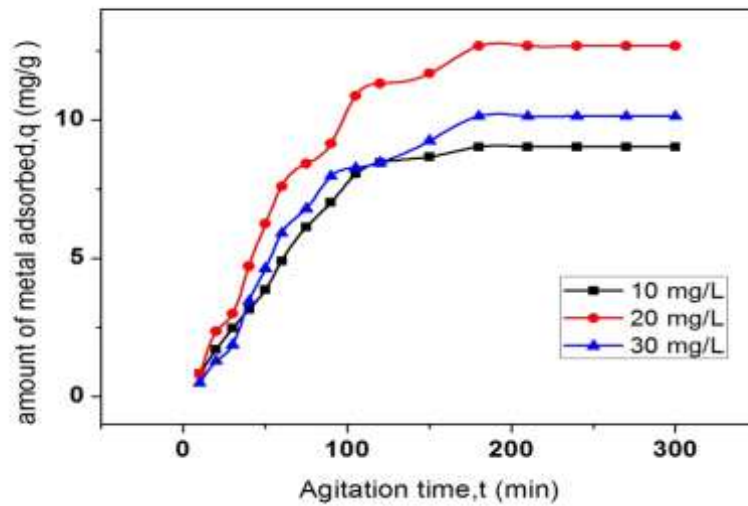


Fig. 3. (a) Effect of agitation time on Pb (II) uptake by SDAC
 (b) Effect of agitation time on Pb (II) uptake by CCSDAC

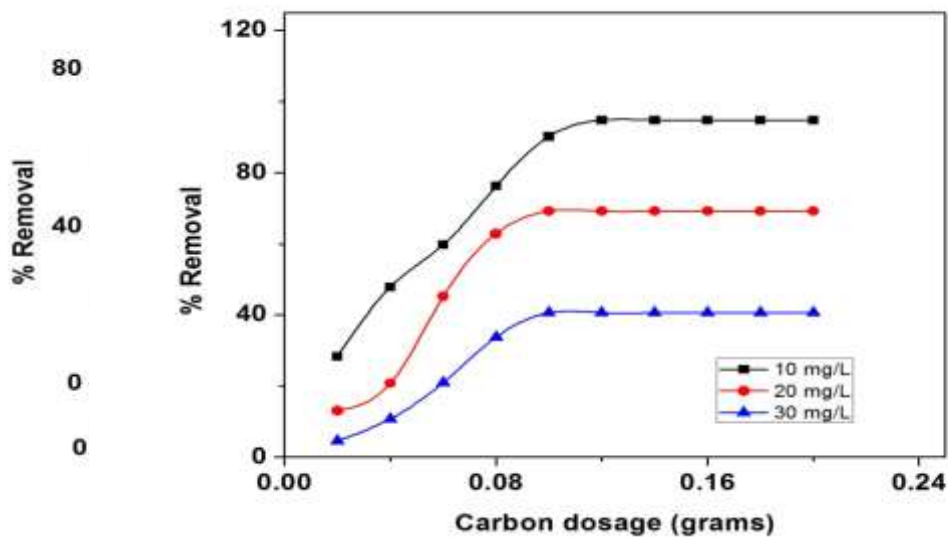


Fig.4. (a) Effect of Carbon dosage on Pb (II) uptake by SDAC
 (b) Effect of Carbon dosage on Pb (II) uptake by CCSDAC

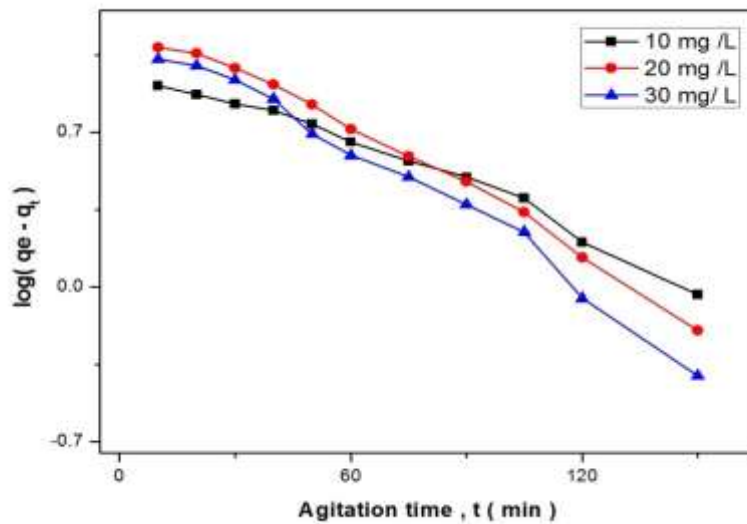
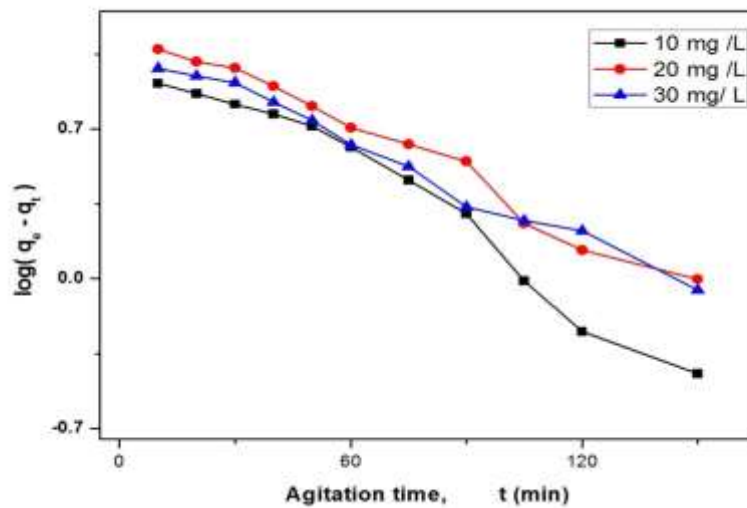
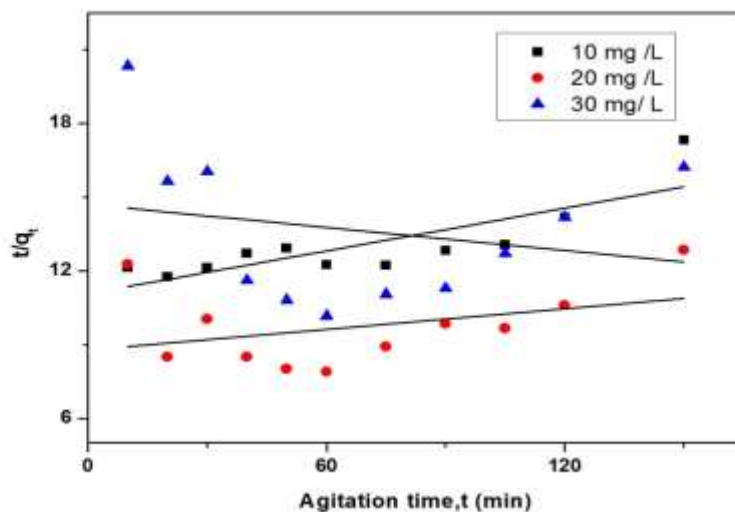


Fig.5. (a) Pseudo first order kinetics of Pb(II) uptake by SDAC
 (b) Pseudo first order kinetics of Pb(II) uptake by CCSDAC



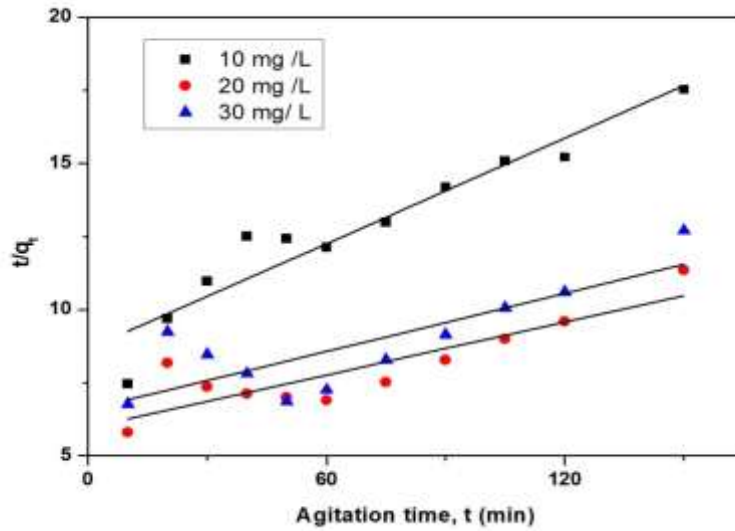


Fig.6. (a) Pseudo second order kinetics of Pb (II) uptake by SDAC
(b) Pseudo second order kinetics of Pb (II) uptake by CCSDAC

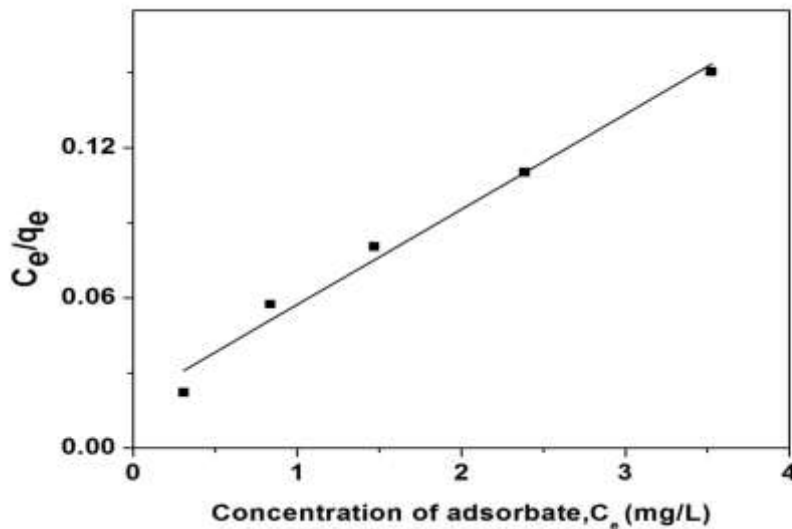
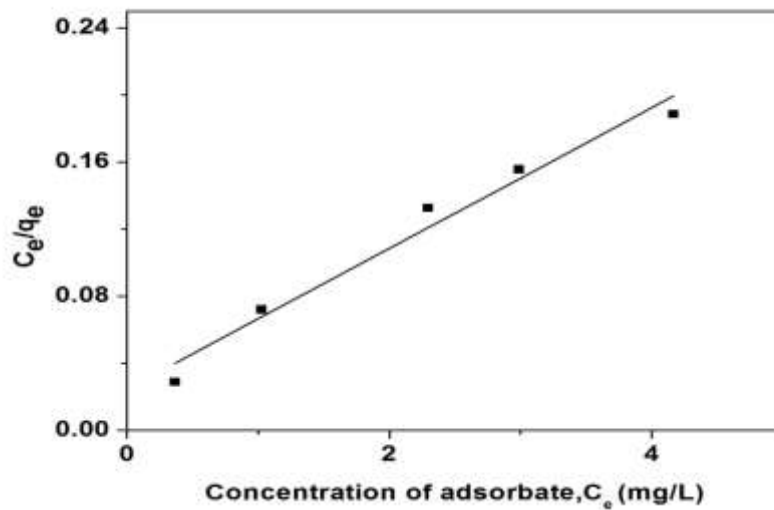


Fig.7. (a) Langmuir isotherm model for the Pb (II) adsorption onto SDAC

(b) Langmuir isotherm model for the Pb (II) adsorption onto CCSDAC

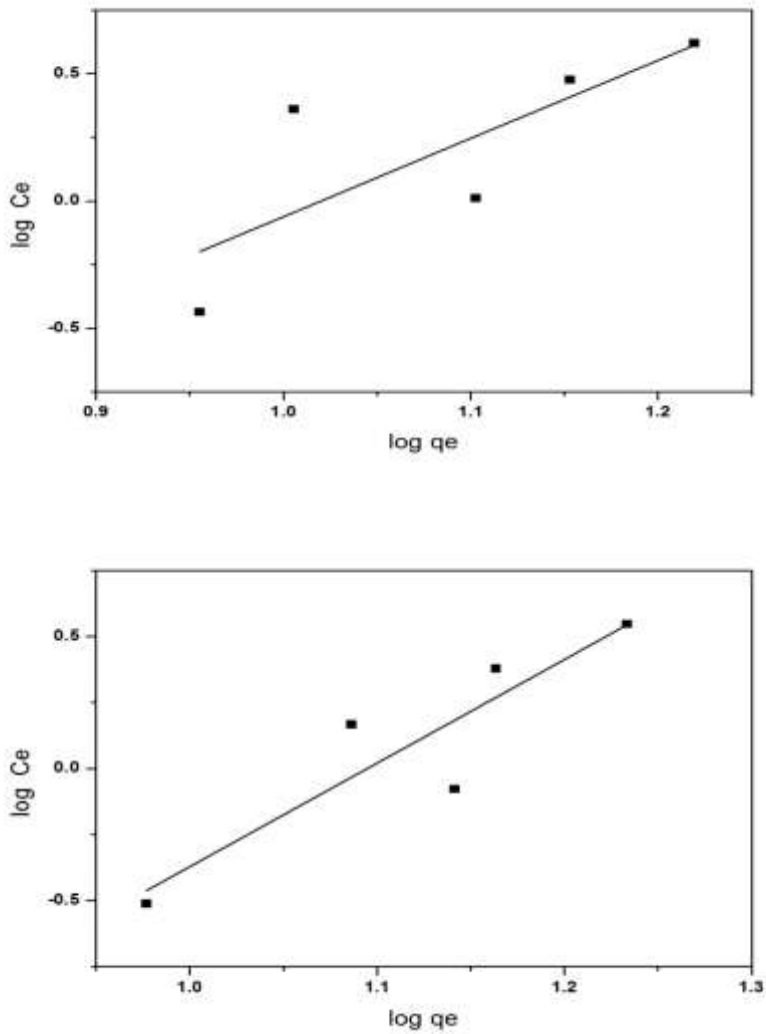
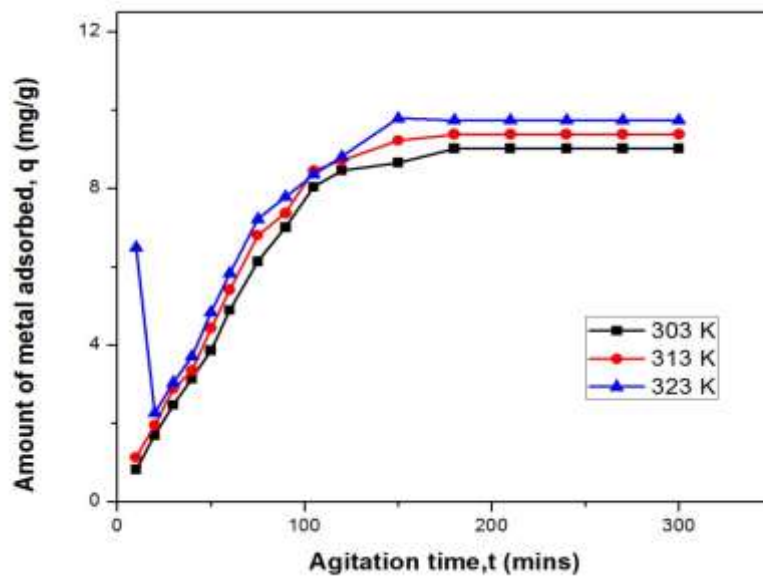


Fig. 8. (a) Freundlich isotherm model for the Pb(II) adsorption onto SDAC
 (b) Freundlich isotherm model for the Pb(II) adsorption onto CCSDAC



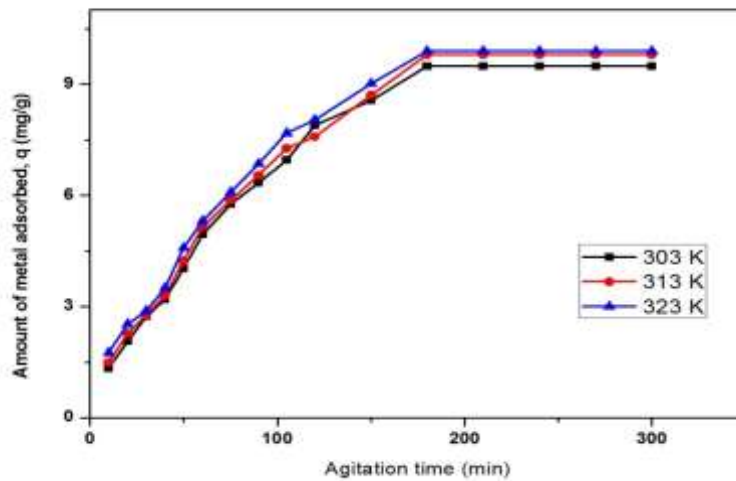


Fig. 9. (a) Effect of temperature on Pb(II) uptake by SDAC
(b) Effect of temperature on Pb(II) uptake by CCSDAC

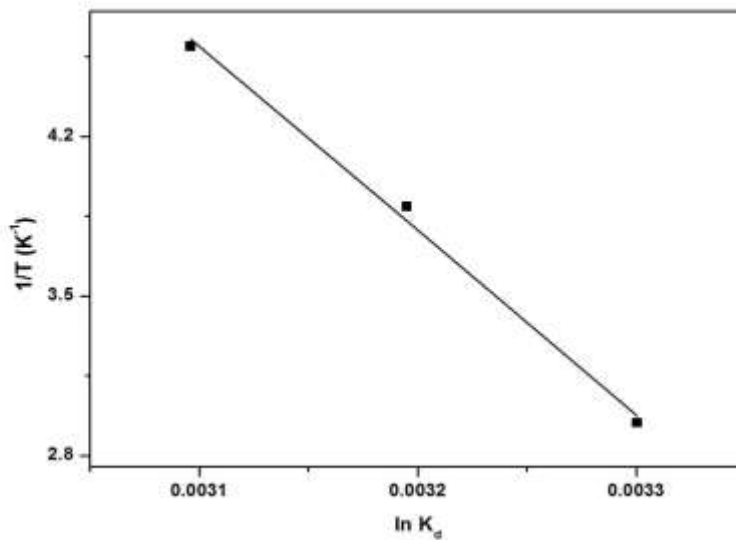
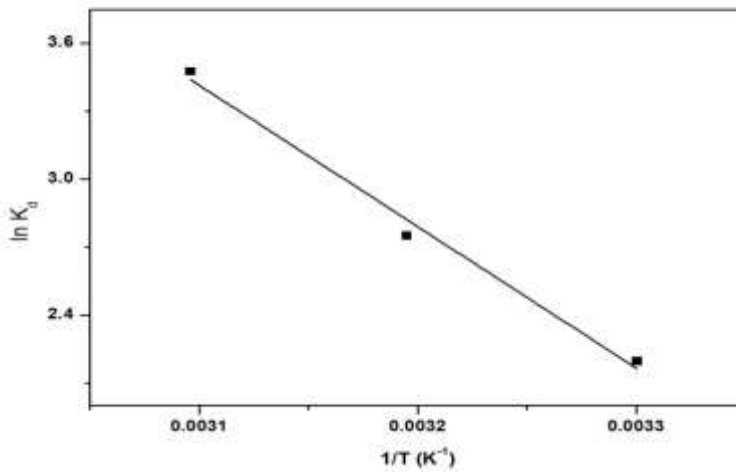


Fig. 10. (a) Plot of $\ln K_d$ versus $1/T$ for estimation of thermodynamic parameters for the biosorption of Pb(II) on SDAC

(b) Plot of $\ln K_d$ versus $1/T$ for estimation of thermodynamic parameters for the biosorption of Pb(II) on CCSDAC