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Using Eco-Friendly Adsorbent for Lead (II) and Cadmium (II) Removal from Industrial Waste Water and Simple Column Application

Alaa E. Ali, Gehan S. El-Assala, Essam M. Elmeleigy, Amany S. Abd-Elhamied

Abstract— **Sugarcane Bagasse was used as environment friendly adsorbents in the present study. This study focuses on the investigation of the adsorption ability of Lead Pb(II) and Cadmium Cd(II) from aqueous solution. The adsorption of heavy metals onto Sugarcane Bagasse was dependent on initial concentration, dose, solution pH, contact time, agitation speed and temperature. Kinetic data were tested using pseudo-first-order, pseudo- second order kinetic, Elovich rate equation and Intra particle difussion models. The best fit was obtained with the pseudo-second-order kinetic model. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) isotherm models have been applied to calculate adsorption data and the thermodynamic parameters; entropy (ΔS°), enthalpy (ΔH°), and the Gibbs free energy (ΔG°); were determined. The results suggests that the adsorption of heavy metals by the Sugarcane Bagasse are endothermic and a spontaneous process. Thus, it was concluded that Sugarcane Bagasse is promising adsorbents for the adsorption of heavy metals from aqueous solutions.**

Index Terms— **Heavy metals, Adsorption, Sugarcane Bagasse, aqueous solution, Isotherm, Kinetics, Thermodynamics, Pb(II) and Cd(II).**

I. INTRODUCTION

Clean water is an important matter in the modern society facing environmental problems such a pollution of water resources. Water pollution is a major global environmental problem which requires ongoing evaluation and revision of water resources policy at all levels [1, 2]. Rapid industrialization and population growth are the main causes of accumulation heavy metals in the environment [3]. Heavy metals have dangerous impact on human health. It can cause acute and chronic diseases, increase cancer incidence in the population area and leads to hair loss, liver cirrhosis, renal failure and neural disorder [4]. Cadmium contamination causes renal dysfunction, bone degeneration, liver and blood damage. The acute poisoning of Cd may cause pulmonary edema, headaches, nausea, vomiting, weakness, and diarrhea. Osteomalacia disease[5]. Pb contamination causes disruption of the biosynthesis of hemoglobin and anemia, high blood pressure, kidney damage, irritability, poor attention span, headaches, hallucinations, loss of memory, Disruption of nervous systems, Brain damage, Declined fertility of men through sperm damage and behavioural disruptions of children[6,7]. It is necessary to remove heavy metal ions from contaminated or wastewater before it can be discharge into the environment. Over the past decade, numerous methods have been investigated for removal of heavy metals from wastewater including, chemical precipitation, ion exchange, reverse osmosis, electrodialysis and adsorption. Most of methods have some disadvantages such as expensive chemicals, usually produce large amounts of sludge, high cost, time consuming and low efficiency, especially in removing lower concentration of heavy metals[8, 9]. Adsorption is known to be one of the greatest of the technologies applied for the wastewater treatment because it is an effective, economical and ecofriendly treatment technique. During the past few years, numerous studies were published reporting that Agricultural waste is one of the rich sources of adsorbent which can be used to remove toxic metal ions from wastewater due to its abundant availability [10, 11]. One of the promising adsorbents from agricultural wastes is Sugarcane Bagasse (SB). It is rich with lignin, cellulose and hemicelluloses that contain high amount of functional groups such as hydroxyl and carboxylic groups that are responsible for binding of divalent cations[12].

Therefore, the purpose of this study is to investigate the efficiency of using Sugarcane Bagasse for the removal of lead and cadmium ions from aqueous solution. The influence of physical parameters affecting the adsorption such as pH, contact time, M(II) concentration, agitation speed, temperature and adsorbent dose was studied. The adsorption is studied in terms of pseudo-first- and pseudo-second-order kinetics, Elovich rate equation and intra particle diffusion, and different isotherm models are applied to experimental data to obtain information on the interactio n of adsorbate- adsorbent.

II. MATERIALS AND METHODS

Adsorbent preparation and characterization

The bagasse was collected from local producers of sugarcane syrup at El Behera Governorate in Egypt, The bagasse was washed thoroughly under running tap water to remove dust and any adhering particles, then was washed by distilled water, then dried in sunlight for few days, then dried in oven at 70 ºC until it became crisp. The dried bagasse crushed to obtain homogenous particles, then washed by distilled water several times until washing are free from any colour and washed by diluted acid to remove any contamination and achieve further purity, then washed by distilled water and dried in oven at 70 ºC and stored in an airtight plastic for further use to avoid contact with moisture in atmosphere. Fourier transform infrared (FTIR) spectroscopy was used in order to give a qualitative analysis of the main functional

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Alaa E. Ali, Gehan S. El-Assala, Amany S. Abd-Elhamied, Chemistry department, Faculty of science, Damanhur univ. Egypt
Essam M. Elmeleigy, National food safety authority, Egypt

groups of the SB and responsible of the adsorption using a Perkin Elmersege (version 10.5.3) spectrophotometer. The materials were mixed with KBr powder and processed in pellets. The spectra were recorded in the range of 4000–500 cm^{-1}.

Adsorbate

Stock M(II) solutions (1000 mg/L) with which the experiments were conducted were prepared by dissolving Cadmium chloride ($CdCl_2$) and Pb(II) acetate [$(CH_3COO)_2Pb$] in distilled water. Then the required concentrations of experimental solutions were prepared by dilution. HCl and NaOH solutions (0.1 M) were used for the pH adjustment.

Batch adsorption experiments

The experimental tests were conducted in batch mode by varying pH from 3 to 7, temperatures (20, 25, 30, 35 and 40 °C), Sugarcane bagasse dose (0.1, 0.2, 0.3, 0.5 and 0.7 g), contact time (5, 10, 15, 30 and 60 min) and M(II) concentrations (25, 50, 100 and 200 mg/L). For each experiment, an accurate quantity of Sugarcane bagasse was added to 200 mL of M(II) solutions in conical flasks (250 mL), in constant magnetic stirrer speed (MS-H-PRO) of 400 rpm for 60 min at 25°C. The suspensions were filtered with Whatman 41 filter paper. The M(II) quantities before and after equilibrium were analyzed by atomic adsorption spectrometry (Pinnacle A A 900T), and the adsorbed amount (q_e) was calculated from the formula.

$$q_e = \frac{(C_o - C_e)\,V}{m} \qquad [1]$$

where, C_o and C_e are the initial and equilibrium concentrations (mg/L), m is the amount of adsorbent (g), and V is the volume of solution (ml). The removal efficiency percentage of metal (%R) was calculated as follows:

$$\%R = \frac{(C_o - C_e)}{C_o} * 100 \qquad [2]$$

Micro-Column extraction of metal ion application

Adsorption tests were performed in Micro column system using metal ions solution as the compound to be adsorbed by SB. The simple set up involved in the study, which were made of Perspex tubes 4.0 cm internal diameter and 90 cm in height. The adsorbent SB was packed with different concentrations of lead and cadmium ions at a fixed flow rate to the filled with known bed height of adsorbent. The metal ions solution of different concentrations was charged from the top of the column in a down flow method. Prior to each experiment, distilled water was passed through the column to get rid of the column impurities and air bubbles. The initial concentration of lead and cadmium ions (10, 100, 250, 500 and 1000ppm) were used at room temperature, and adsorption pH of (7.0), a fixed flow rate 5 ml/min, constant volume 1000ml and with a fixed quantity of SB dose (2.5g/l) to study the suitability of application of SB for removal this metal ions.

III. RESULTS AND DISCUSSION

Characterization of adsorbent

The FTIR spectra of Sugarcane Bagasse show a broad absorption band at 3414 cm^{-1} which is attributed to the stretching vibrations of O-H group of phenols, alcohols and carboxylic acid must be due to presence of hemicelluloses, cellulose and lignin. The 2918, 1733 cm^{-1} Peaks correspond to the stretching vibrations of aliphatic C-H and carbonyl groups of carboxylic acids, respectively. The band at 1250 cm^{-1} can be assigned to acetyl group present in hemicellulose; moreover, the 1053 cm^{-1} is attributed to C-O stretching vibration in hemicellulose, cellulose and lignin or C-O-C stretching vibration in hemicellulose, cellulose**.** The 609 cm^{-1} peak refer to aromatic compounds indicating presence of lignin[13, 14] (Fig. 1).

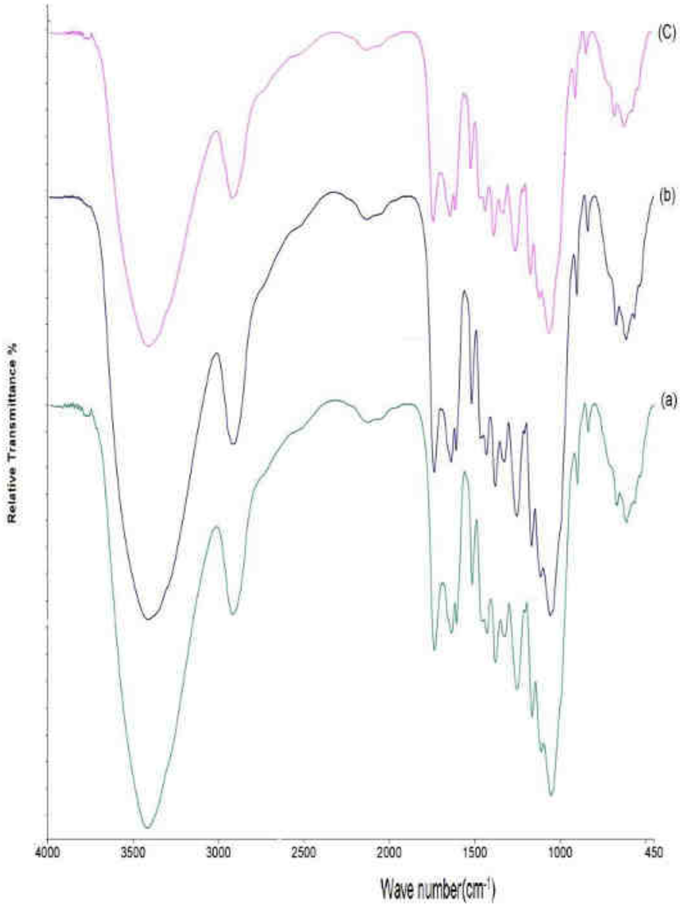

Fig. 1.The FTIR spectra of Sugarcane Bagasse (a) and after Pb(II) ions uptake (b) and Cd(II) ions uptake(c).

Effect of pH

The pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It can change the surface charge on the adsorbent and also affect speciation of the metal ions and the degree of ionization. The adsorption of both cadmium and lead SB were found to increase with increasing pH from 3 to 7 having the maximum removal at pH 7 (Fig. 2), In this context, The adsorption capacity of M(II) increases with increasing pH (Fig. 3); the minimal adsorption at pH 3 is due to high competition between the hydronium ions and (Pb(II), Cd(II)) ions present in the solution surrounding the adsorbent is established so protonated adsorption sites were incapable of binding Pb(II) and Cd(II) ions due to electrostatic repulsion between positively charged heavy metal ions and positive charged sites. When the pH value increases, the competition between hydronium ions and the (Pb(II, Cd(II)) ions decreases, the adsorbent surface becomes deprotonated and more negatively charged, surface sites become available. Therefore, The Pb(II) and Cd(II) ions uptake increases by electrostatic attraction, thus improving the adsorption capacity[15, 16].

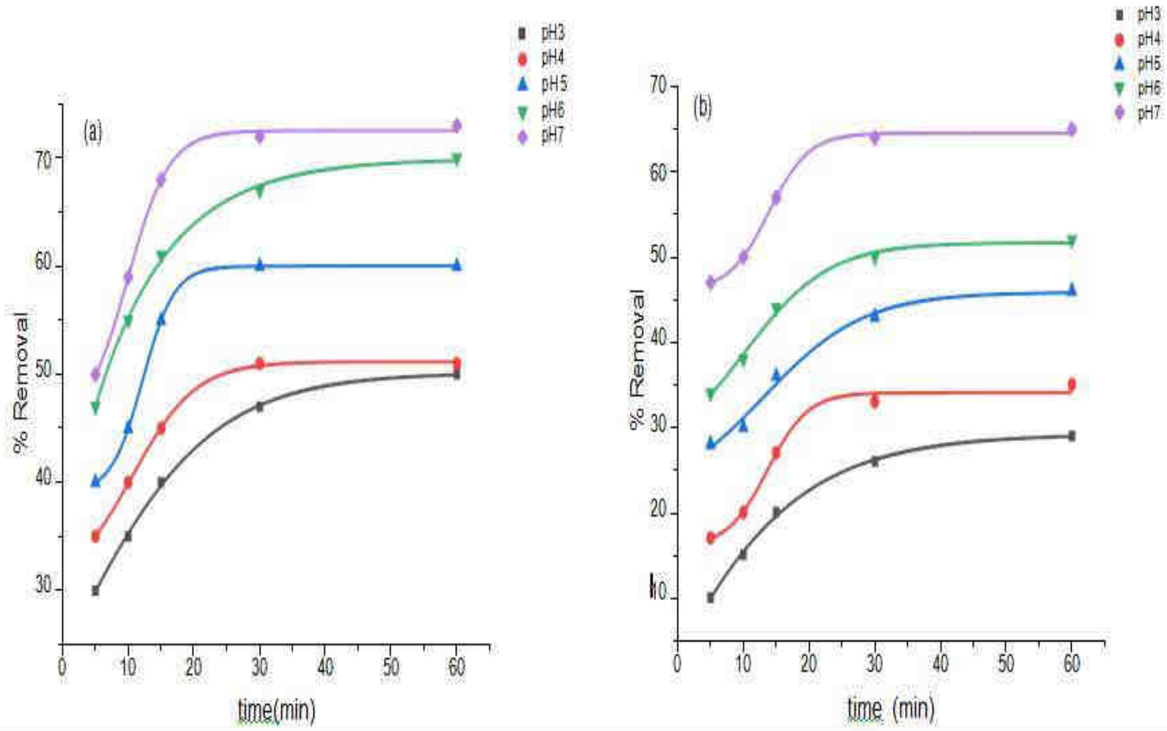

Fig.2 Effect of %removal of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different pH.

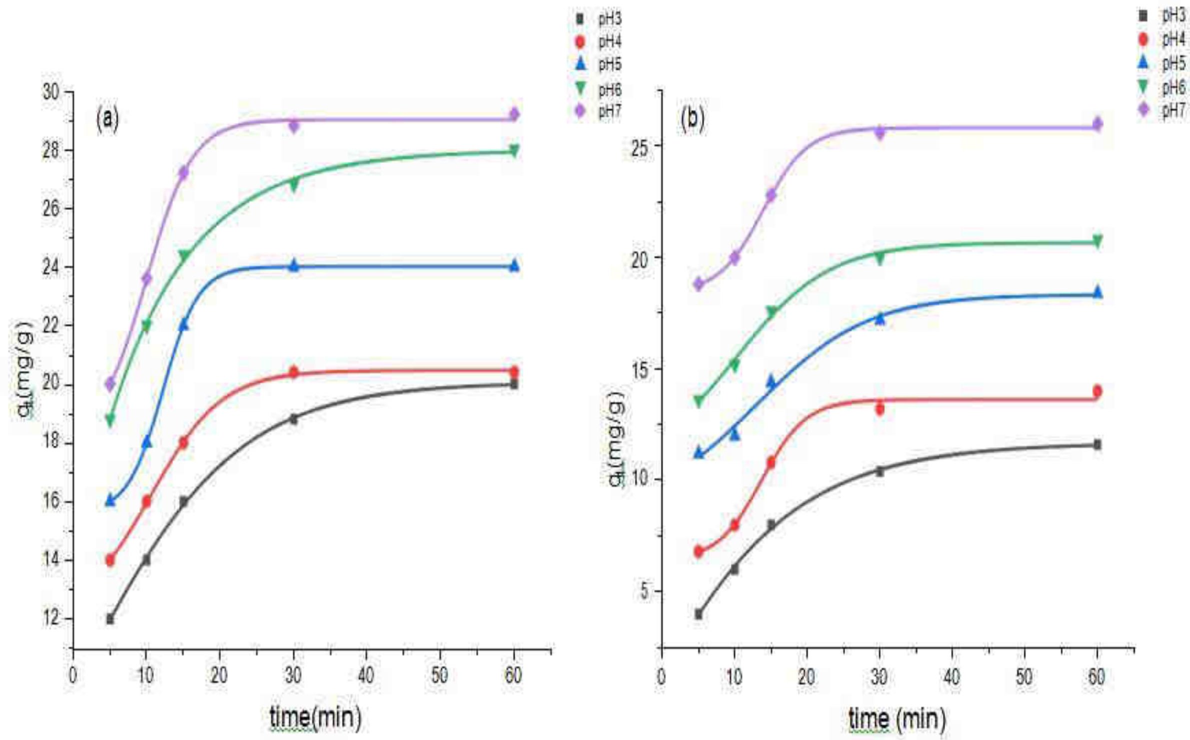

Fig.3 Effect of uptake (mg/g) of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different pH

Effect of adsorbent dose

Lead and Cadmium removal increased with increased adsorbent dosage reaching maximum removal percentage at dose (0.5g and 0.7g) of SB plant, respectively, removal of lead ion increase from (77% to 85%) then decrease to 75%, also removal of cadmium ions increase from (36% to 81%) (Fig.4). Such behavior is obvious because with an increase in adsorbent dosage, the number of active sites available and adsorbent surface area for lead and cadmium adsorption would be more. It is known that as the amount of adsorbent is increased, the adsorption sites remain unsaturated during the adsorption reaction causing to decrease in adsorption capacity (Fig.5) due to crowdedness of the adsorbent particles at higher dosage. This lead to decrease in the total surface area of the adsorbent particles available for the metal ions, thereby leading to decrease in amount of metal ions removed from the aqueous solution [17].

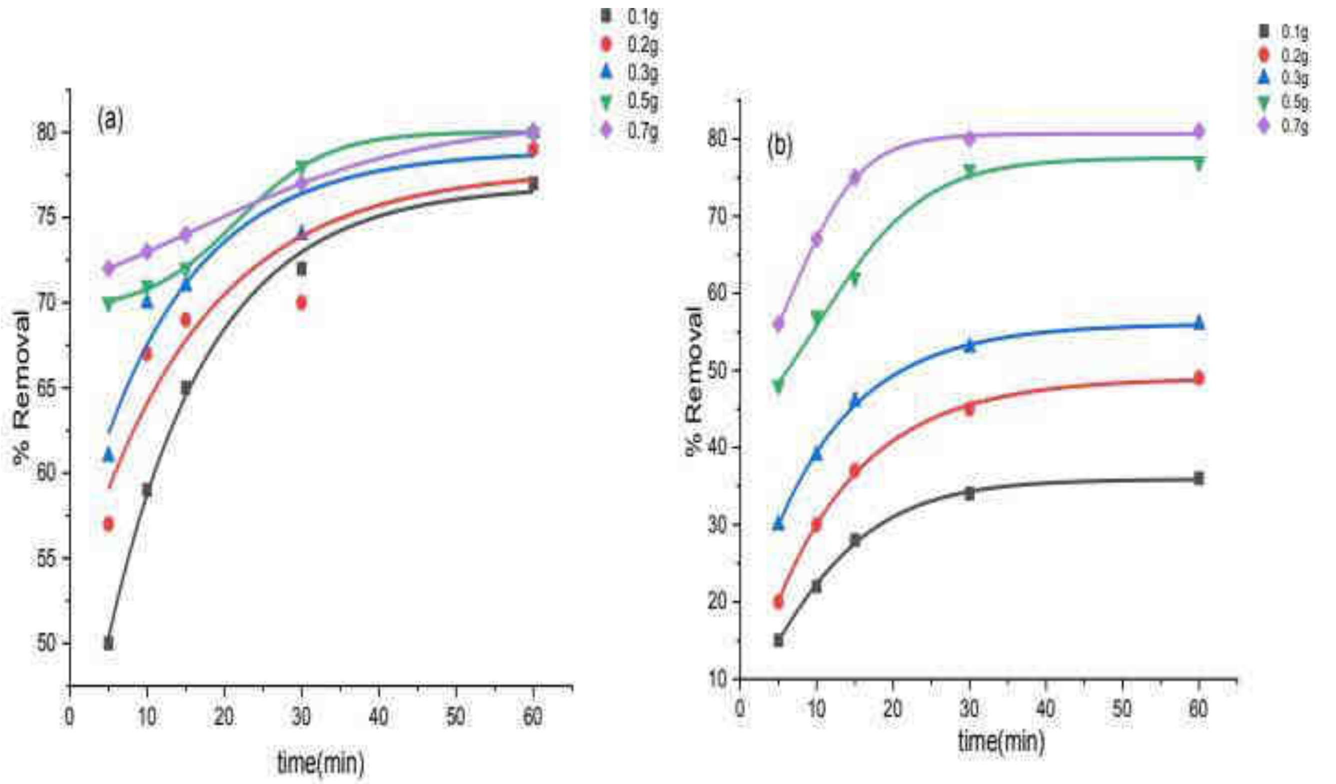

Fig.4 Effect of %removal of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different adsorbent dose.

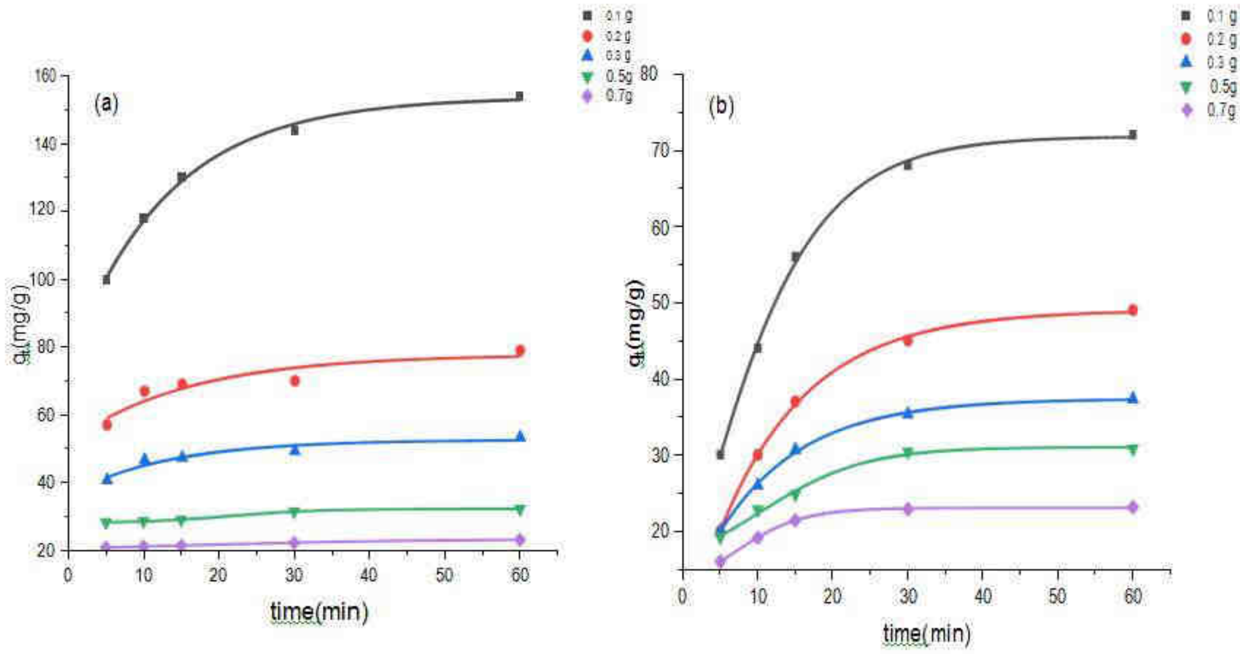

Fig.5 Effect of uptake (mg/g) of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different adsorbent dose.

Effect of the initial concentration of heavy metals

The percentage adsorption of the Lead and Cadmium ions increases with increasing the initial concentration from 25 mg/L to 50 mg/L as shown in (Fig.6). It is obvious that at low concentrations of Pb(II), Cd(II) ions, the percentage of adsorption was high because of the availability of more vacant sites on the surface of SB. On the other hand, further increase in concentrations from 50 mg/L to 200 mg/L resulted in decrease the percentage removal of metal ions. This could be associated with the number of metal ions was much higher than the number of active sites available for adsorption and may be attributed to the increase of driving force and reduces the mass transfer resistance between the liquid and solid phases with increasing heavy metal ions concentration. A significant amount of metal ions adsorbed at high initial metal concentration can be related to two main factors, namely high probability of collision between metal ions with the adsorbent surface and high rate of metal ions diffusion onto adsorbent surface, Therefore, with the increase of metal concentration in the solution, the adsorption capacity of metal increased [18] (Fig.7).

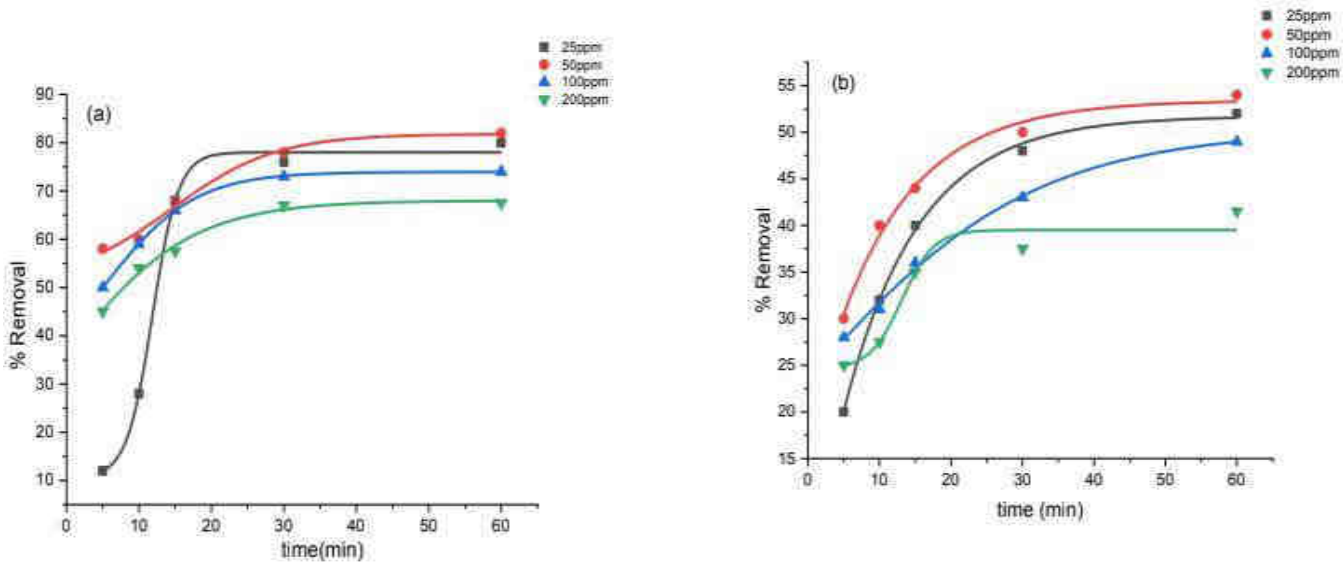

Fig.6 Effect of %removal of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different initial metal ion concentration.

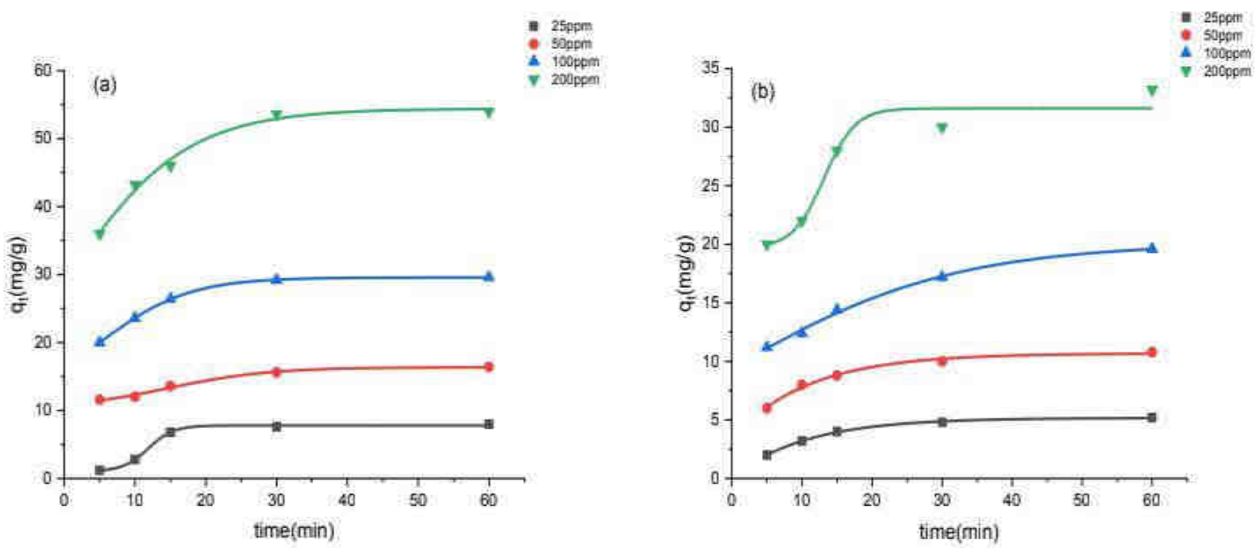

Fig.7 Effect of uptake (mg/g) of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different initial metal ion concentration.

Effect of the contact time

In order to control the effect of the contact time on the metal adsorption and to estimate the time sufficient to achieve equilibrium, the experiments were carried out at pH ~ 7, a biomass dose of 0.5 g, an initial M(II) concentration of 100 mg/L and a temperature of 25 °C. The concentration of M(II) in solution was determined at regular time intervals (Fig.6). Removal efficiency of lead and cadmium ions has increased rapidly with the increase of shaking time 60 min. There was no significant increase in adsorption from 30 min to 60 min for lead and cadmium, indicating the attainment of equilibrium conditions occurred at around 60 min. The rate of adsorption is fast at the beginning of adsorption because most of the active sites on the adsorbent's surface were ready to bind with lead and cadmium ions. As time increases, more amount of lead and cadmium ions get adsorbed onto the surface of the adsorbent due to vander waal forces of attraction. and becomes less efficient during the second stage (30–60min) to reach a saturation; this can be explained by adsorption sites become saturated with adsorbate ions at the end of the adsorption reaction so this lead to a decrease in the available surface area of the adsorbent particles(19).

Effect of speed of agitation

The removal of lead(II) and Cd(II) metals ion increase by increasing speed of agitation, reaching the highest percentage of removal 80% and 69%, respectively for SB plant at speed of agitation 500 rpm (Fig.8). The amount of metal ions adsorbed increased when speed of agitation changed from 100 rpm to 500 rpm (Fig.9).When increasing the agitation speed, the metal ions diffusion from the bulk liquid to the liquid boundary layer surrounding adsorbent particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer around adsorbent particles and decreases the resistance in the liquid solid interface phase which leads to better removal efficiency and lower equilibrium time(20).

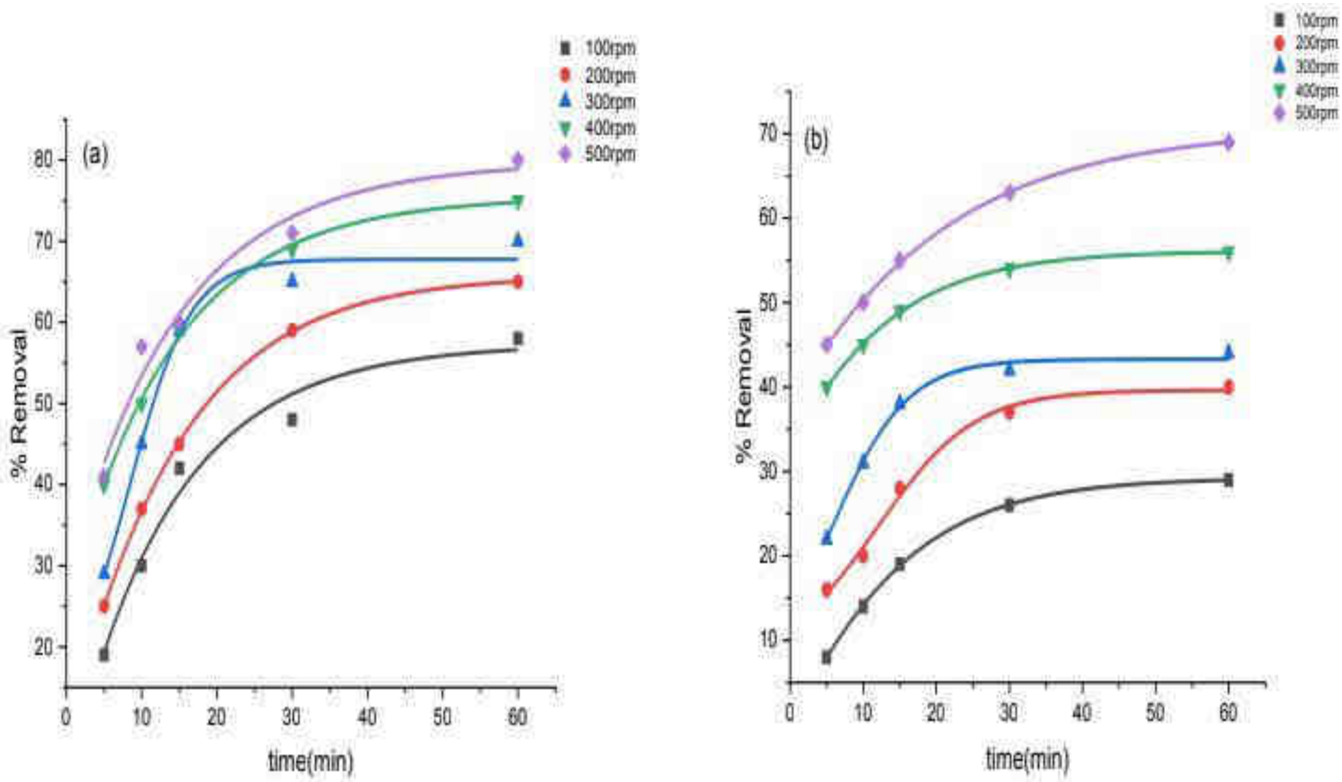

Fig.8 Effect of %removal of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different agitation speed.

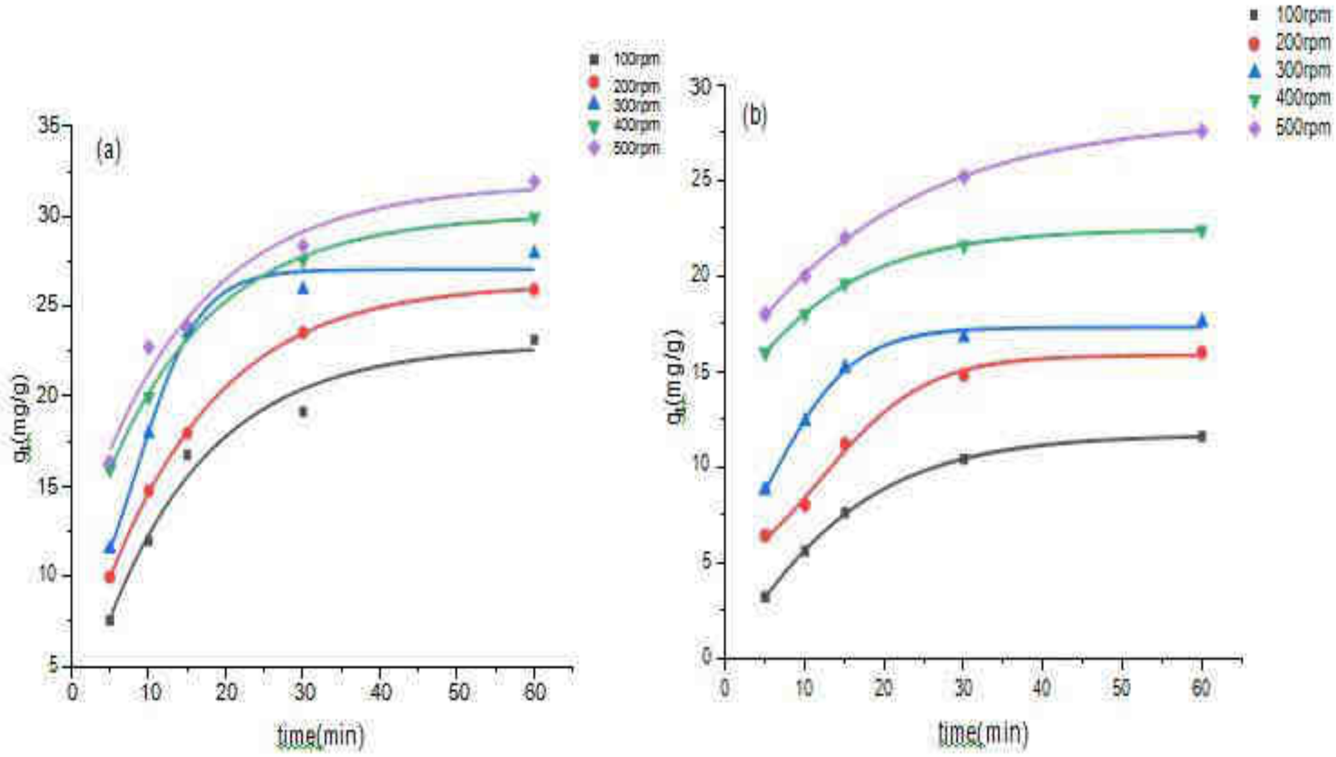

Fig.9 Effect of uptake (mg/g) of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different agitation speed.

Effect of Temperature

To determine the effect of temperature, the adsorption of Pb(II) and Cd(II) on SB was also studied at temperatures of 20, 25, 30, 35 and 40 °C. It is found the removal efficiency increases by increasing the temperature for both lead and cadmium ions, when the temperature was raised from 20 °C to 40°C (Fig.10). The increase may be due to the rise in the kinetic energy of adsorbent particles and increasing the mobility of the metal cations. Thus, the collision frequency between adsorbent and adsorbate increases; which results in the enhanced adsorption on to the surface of the adsorbent and higher metal uptake (Fig.11) at higher temperatures which may be attributed to the availability of more active sites on the surface of the adsorbent by expansion of the pores(21).

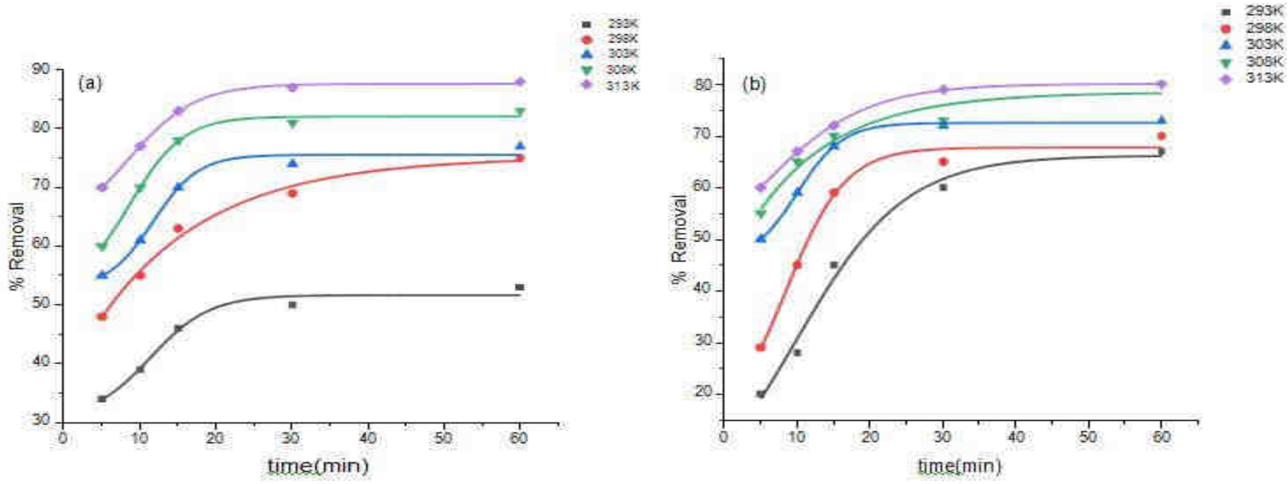

Fig.10 Effect of %removal of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different temperature.

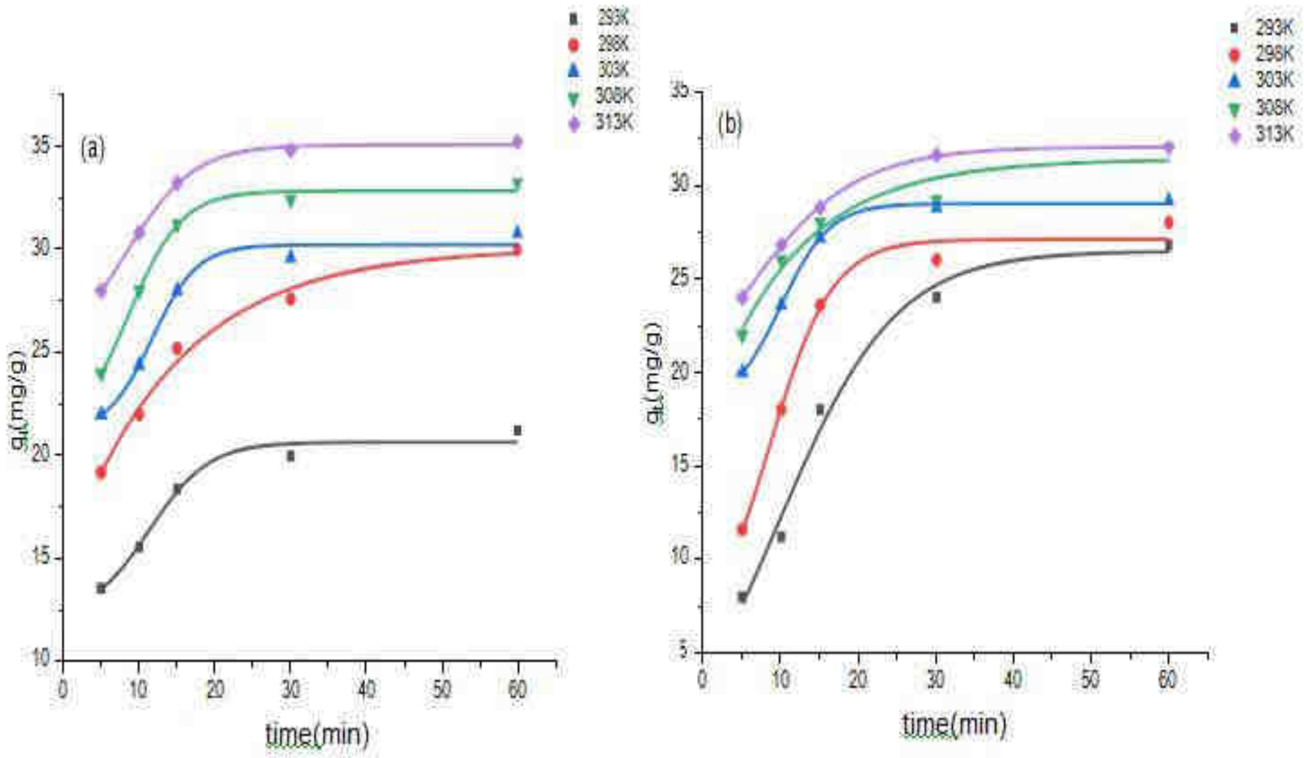

Fig.11 Effect of uptake (mg/g) of lead(II)(a) and Cadmium(II)(b) against time onto sugarcane bagasse at different temperature.

Isotherm, kinetic and thermodynamic analysis of adsorption data

Isotherm studies

Adsorption isotherms studies were conducted with varying initial Pb(II) and Cd(II) concentrations (25, 50, 100, 200 mg/l) and analyzed by four isotherm models, namely, Langmuir, Freundlich, Dubinin - Radushkevich (D-R), and Temkin isotherms. These models are currently used to identify the adsorption performance and adsorption mechanism of adsorbents or adsorbates(19). The correlation coefficient and parameter values for all the four isotherm models are presented in Table1. The correlation coefficient (R^2) values for Freundlich, Langmuir, Temkin and Dubinin - Radushkevich (D-R) models indicated the adequate equipping of data for adsorption with R^2 values (22, 23). However, The correlation coefficient of Freundlich was closer to unity (R^2 0.98) when compared with others which correlate to the multilayer adsorption on heterogeneous active sites of adsorbent and model is more satisfying to fit the equilibrium adsorption data of Pb (II) and Cd(II).

Langmuir isotherm model

The Langmuir isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no transmigration of adsorbate in the plane of the surface (24). The linear form of the Langmuir equation is rendered as Eq. (3)

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \quad [3]$$

Ce (mg/L) is the equilibrium concentration; q_e is the amount of ion adsorbed on SB at equilibrium, q_m and b are Langmuir constants related to capacity and energy of adsorption respectively. A plot of Ce/qe vs Ce indicates a straight line of slope 1/qm and intercept of 1/bqm as shown in (Fig. 12).

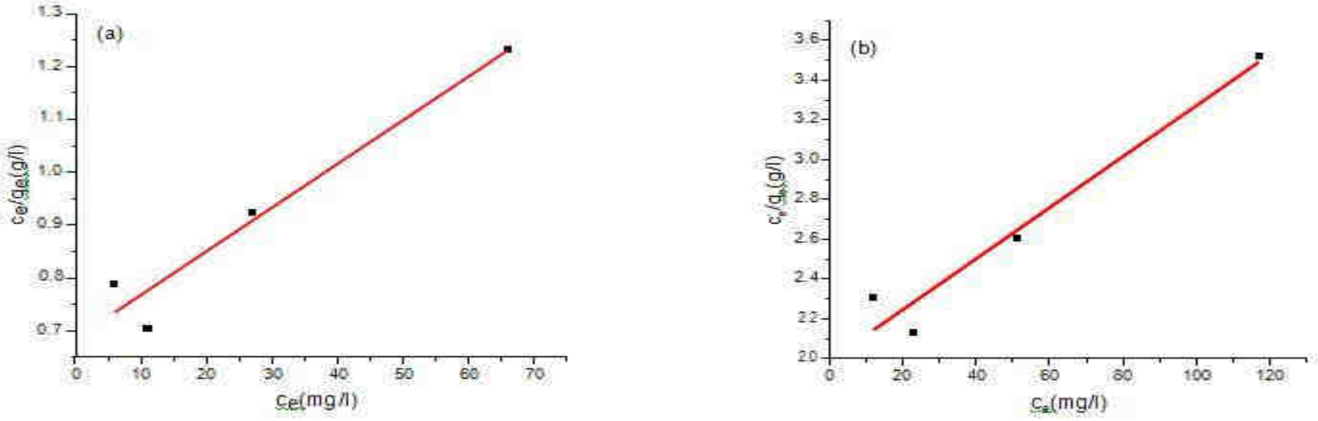

Fig.12 The linear Langmuir adsorption isotherm for lead (II) ions (a) and Cadmium(II) ions (b) with SB at 298 K.

Freundlich isotherm model

Freundlich isotherm model is an empirical equation based on adsorption on a multilayer heterogeneous surface, with adsorption sites of different energies [25]. It is given as eq. (4)

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad [4]$$

k_f is the Freundlich constant related to the adsorption capacity of the metal ions, 1/n is a constant that indicates the surface heterogeneity of an adsorbent, n indicates the adsorption intensity. The equilibrium constants are determined from the plot log q_e versus log C_e as shown in (Fig.13).

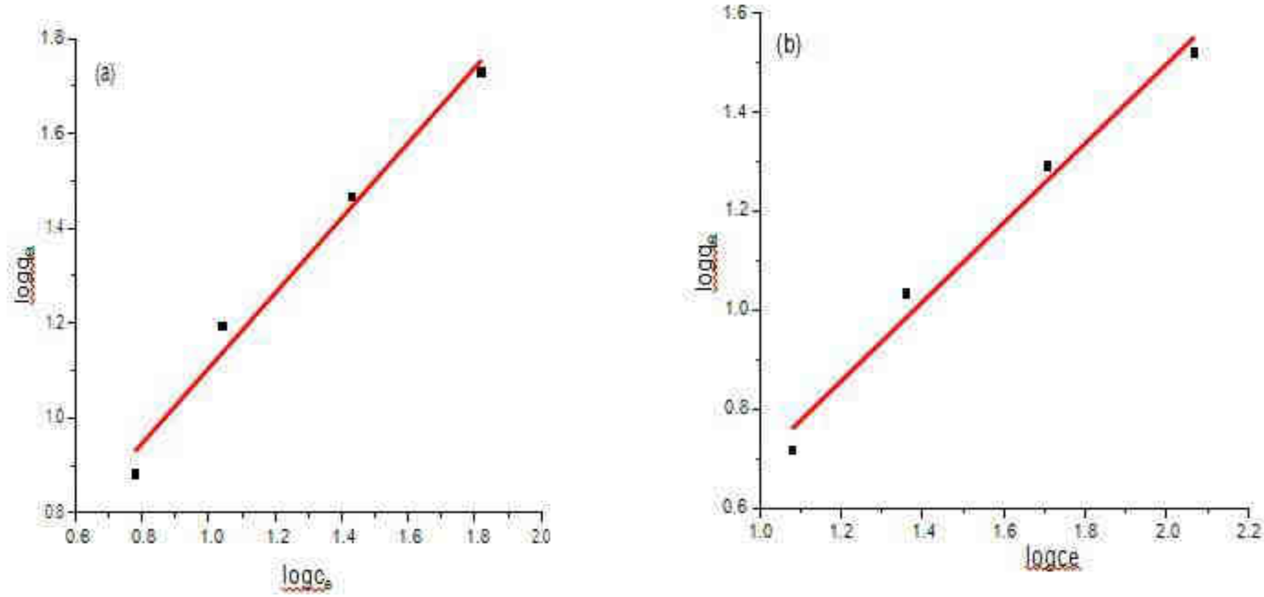

Fig.13 The linear Freundlich adsorption isotherm for lead (II) ions (a) and Cadmium(II) ions (b) with SB at 298 K.

The Tempkin Isotherm

Temkin model has a factor which can explain adsorbent-adsorbate interactions. It describes the behaviour of adsorption on heterogenous surfaces [26]. It is given by (5)

$$q_e = B\ln A_T + B\ln C_e \qquad [5]$$

Where: AT = Temkin isotherm equilibrium binding constant, b = Temkin isotherm constant, R=
b
universal gas constant, T= Temperature at 25 c, B = Constant related to heat of sorption. The fitting was carried out by plotting the quantity adsorbed q_e against $\ln C_e$ as shown in (Fig.14).

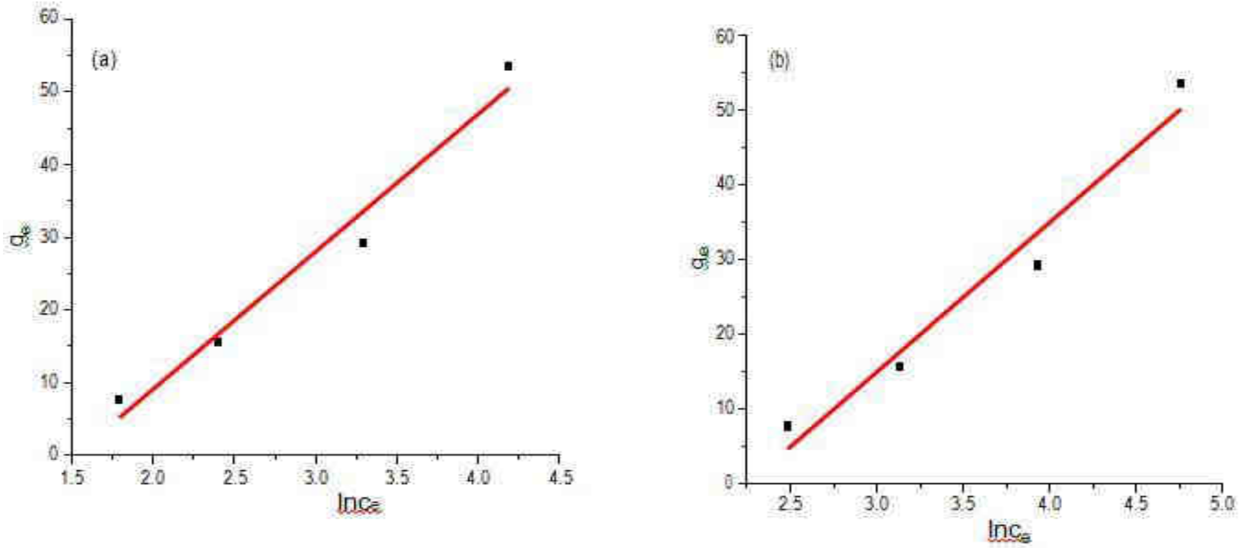

Fig.14 The linear Tempkin adsorption isotherm for lead (II) ions (a) and Cadmium(II) ions (b) with SB at 298 K.

Dubinin-Radushkevich isotherm

The isotherm of Dubinin-Radushkevich (D-R isotherm) is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. It has been applied to distinguish the physical and chemical adsorption of metal ions(27), and its non-linear expression is presented in Eq. (6)

$$\ln q_e = \ln q_m - K_{ad}\,\varepsilon^2 \qquad [6]$$

Where q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g); q_m = theoretical isotherm saturation capacity (mg/g); K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2 /kJ^2) related to the mean free energy of adsorption per mol of the adsorbate, and ε is the Polanyi's potential, which is given by Eq. [7]:

$$\varepsilon = RT\ln\left(1+\frac{1}{ce}\right) \qquad [7]$$

Where R is the gas constant (8.314 J $K^{-1}mol^{-1}$) and T (K) is the absolute temperature. This parameter was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy as shown in Eq.(8)

$$E(\,kJ/mol\,) = 1/\sqrt{2k} \qquad [8]$$

From the linear plot $\ln q_e$ against ε^2 of D-R model (Fig.15) and table1, q_m was determined to be 37.44 mg/g, 36.6 mg/g and the mean free energy, E = 0.206 kJ/mol, E = 0.108 kJ/mol(24) indicating a physio-sorption process for lead and cadmium, respectively.

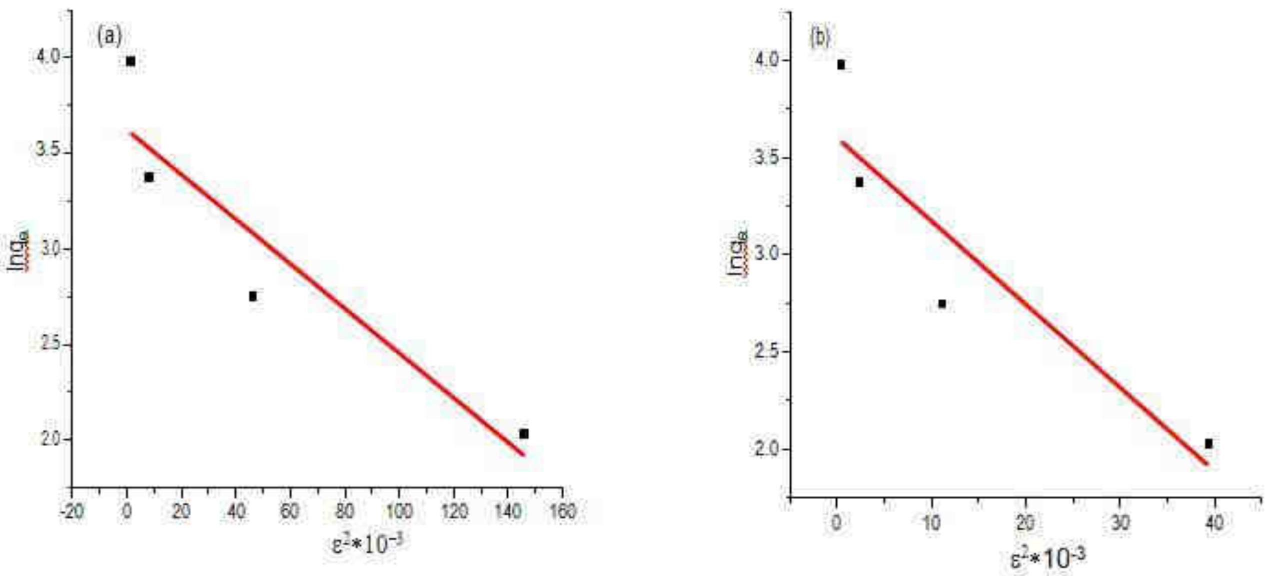

Fig.15 The linear Dubinin-Radushkevich adsorption isotherm for lead (II) ions (a) and Cadmium(II) ions (b) with SB at 298 K.

Kinetics studies

Adsorption kinetics supply significant information about the reaction pathways and controlling mechanism of adsorption process. The adsorption kinetic depends on the physical and chemical properties of adsorbent and adsorbate, pH of medium, temperature, contact time and mass transport process that affect adsorption mechanism. In this study, the kinetic data obtained from batch studies was analyzed by using pseudo first- order, pseudo second-order, Elovich rate equation and Intra particle Diffusion model [29] as shown in table 2.

Pseudo-first order kinetic model

The linear form of pseudo first-order kinetic model is generally expressed by Lagergren[30] as follows [9]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad [9]$$

Where, q_e and q_t (mg/g) are the amount of metal ions adsorbed per unit mass of the adsorbent at equilibrium and time t, respectively and K_1 is the adsorption rate constant. As it is showed in Fig.(16) for Pb(II) and Cd(II) the value of q_e and K_1 were obtained from the slope and intercept of the plot of log (q_e−q_t) vs. t. The values of q_e, K_1 and R^2 determined in the current study were found in Table (2, 3) for lead and cadmium. The correlation coefficients (R^2) for the pseudo first-order kinetic model are low and a difference of equilibrium adsorption capacity (q_e) between the experimental and the calculated data was observed, indicating a poor pseudo first-order fit to the experimental data[31].

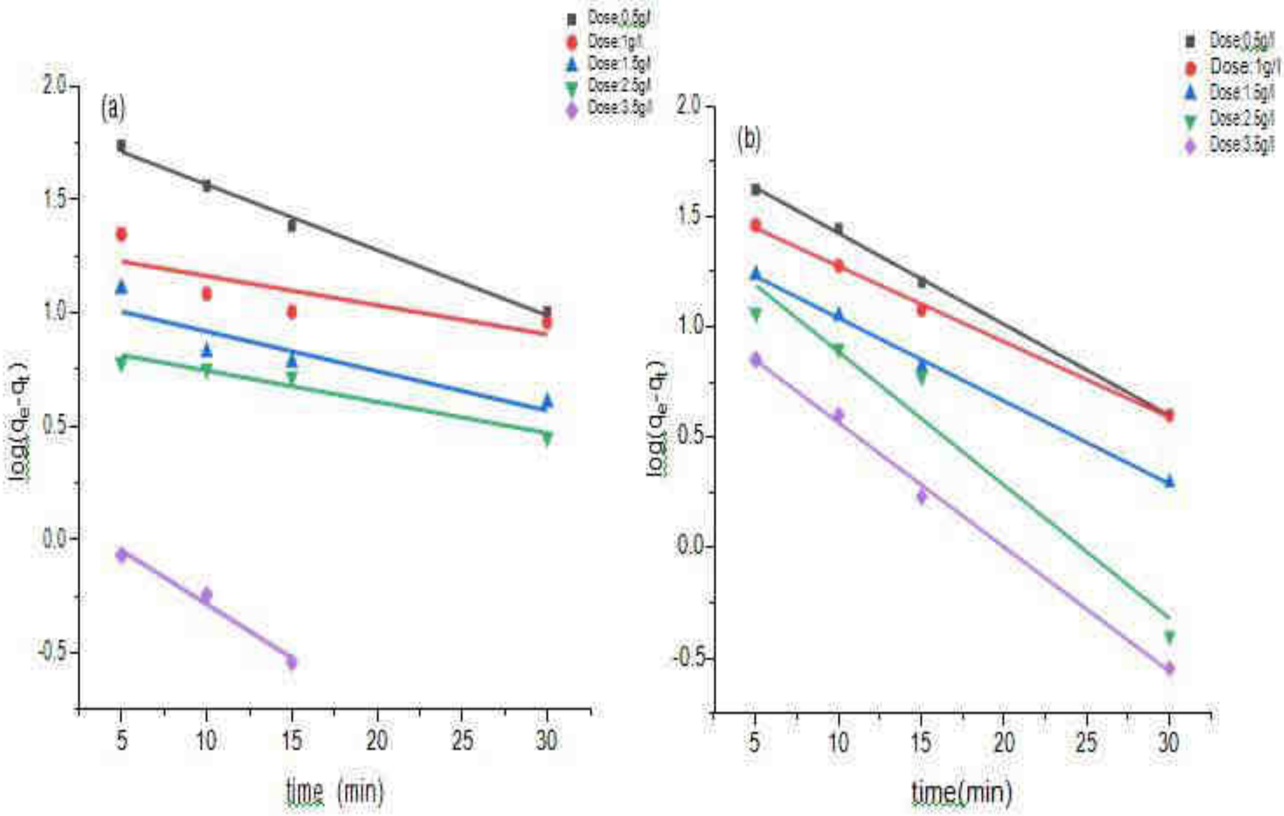

Fig.16: Pseudo-first order kinetic fit for adsorption of lead(II)(a) and cadmium(II) onto SB at different adsorbent, The initial concentration=100mg/l, 400 rpm and 298°K.

Pseudo-second order kinetic model

A pseudo-second order model is also one of the most common models to explain the kinetic of adsorption reactions, proposed by Ho and McKay, is based on the assumption that the adsorption follows second-order. The linear form can be expressed as follows [10][32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad [10]$$

Where, ‗q_e‘ and ‗q_t‘ are the amount of nickel adsorbed (mg/ g) at equilibrium and at time t, respectively, and k_2 is the rate constant of pseudo-second-order kinetics. The plots between t/q_t versus t were drawn and are shown in.(17) for lead and cadmium. As can be seen from Table (2, 3) for lead and cadmium that the theoretical q_e(cal) values close well to the experimental uptake values q_e(exp) in case of pseudo-second- order model. Further, the correlation coefficient (R^2) for the pseudo-second-order kinetic model was 0.998 suggesting that the present adsorption system Fig can be described more favorably by pseudo-second-order process[33, 18].

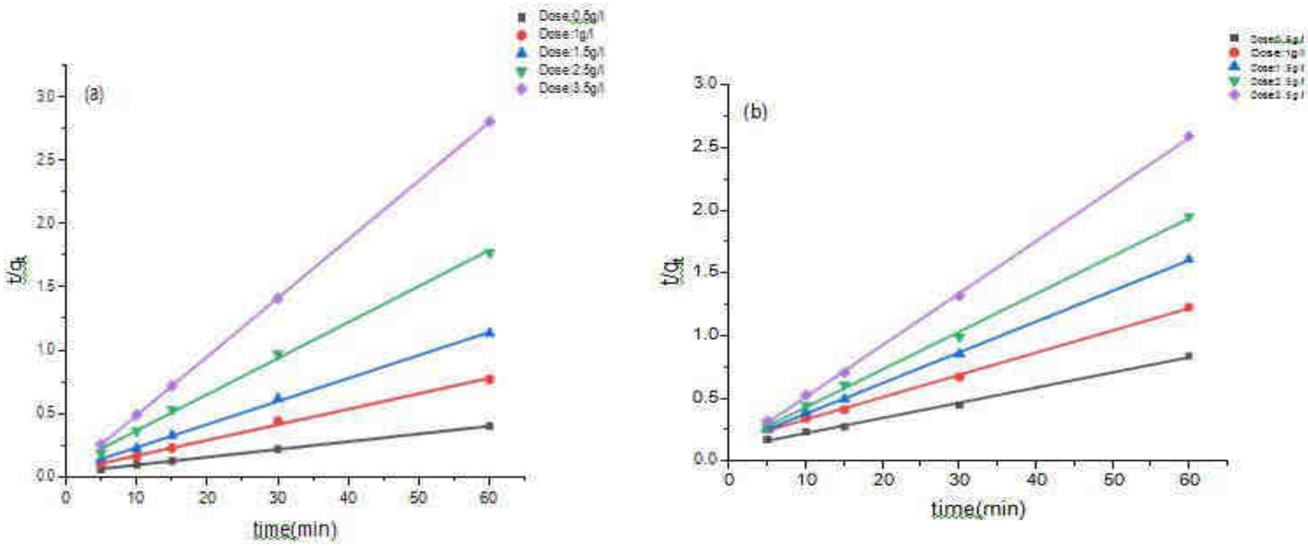

Fig.17: Pseudo- second order kinetic fit for adsorption of lead(II)(a) and cadmium(II)(b) onto SB at different adsorbent, The initial concentration=100mg/l, 400 rpm and 298°K.

Elovich rate equation

The Elovich equation based on the adsorption capacity; used for general application to chemisorption. The Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage, respectively. The linearized form is given in Eq. (11) [34]:-

$$q_t = [1/\beta]\ln [\alpha\beta] + [1/\beta]\ln t \qquad [11]$$

Where, α (mg/g/min) is the initial adsorption rate and β (g/mg) is the de-sorption constant during any experiment. The Elovich constants are determined from the linear plot of q_t versus lnt Fig.(18) for Pb(II) and Cd(II) and presented in table (4, 5). The regression R^2 value is ranged between 0.894 and 0.982 for lead and ranged between 0.883 and 0.968 for cadmium. This indicate that applicapility of this model to the experimental data obtained for the adsorption of Pb(II) and Cd(II) onto SB[35].

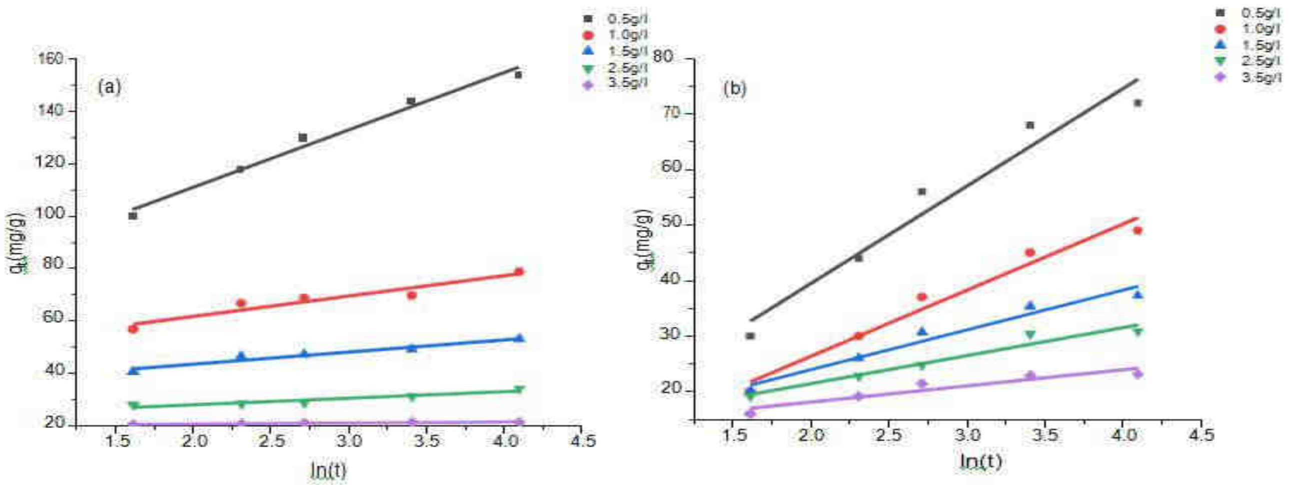

Fig.18: Elovich model plot for adsorption of lead(II)(a) cadmium(II)(b) onto SB at different adsorbent, The initial concentration=100mg/l, 400 rpm and 298°K.

Intra particle diffusion model

The intra particle diffusion describes the diffusion controlled adsorption processes, where the adsorption rate is dependent on the speed of adsorbate diffusion towards adsorption. This model is characterized by the relationship between specific adsorption and the square root of time. The kinetic results were further analyzed by using Weber and Morris [36]. Intra particle diffusion model is described as in Eq. (12)

$$q_t = k_{dif}\, t^{1/2} + I \qquad [12]$$

Where, k_{dif} ($mg/g.min^{0.5}$) is the inter-particle diffusion rate constant, and *I*(mg/g) is the intercept and reflect the boundary layer effect as illustrated in Fig.19 and table (4, 5) for lead and cadmium. Intra-particle diffusion is the sole rate controlling step if the plot of q_t vs $t^{1/2}$ is linear and passes through the origin. In case the plot does not pass through the origin, some degree of boundary layer control is considered to exist. This indicates that intra particle diffusion is not the only rate-limiting step and then other surface phenomena are involved. The regression values for lead and cadmium were both less than unity. The linear plots for lead and cadmium did not pass through the origin. This deviation from origin is due to differences in the rate of mass transfer in the initial and final stages of the bio-sorption. This also reveals possible involvement of some other mechanism along with intra particle diffusion in controlling the rate of sorption process [37].

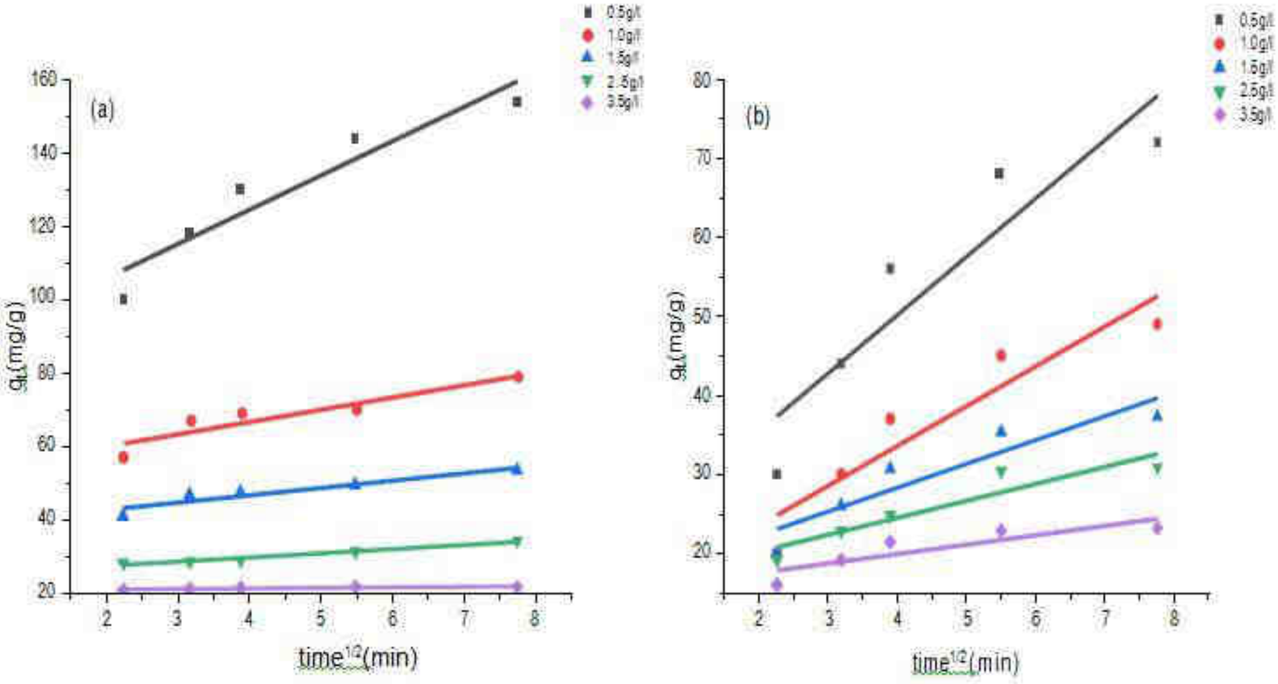

Fig.19: Intra particle Diffusion model plot for adsorption of lead(II) and cadmium(II) onto SB at different adsorbent, The initial concentration=100mg/l, 400 rpm and 298°K.

Thermodynamic studies

To study the effect of thermal on the M(II) adsorption by *SB*, the temperature was varied from 20 to 40°C using constant parameters at equilibrium. Three thermodynamic parameters were studied (1) Gibb's free energy change (ΔG°), (2) enthalpy change (ΔH°) and (3) entropy change (ΔS°) which is given in Table (4, 5) Accordingly, all of the calculated adsorption enthalpies for of Pb(II) and Cd(II) adsorption are positive, indicating endothermic processes. he standard Gibbs free energy change ΔG^o at all temperatures was negative for Pb-SB and Cd-SB confirming that the adsorption of Lead and Cadmium onto Sugarcane Bagasse was spontaneous and thermodynamically favorable. The more negative the ΔG^o, the stronger driving force of adsorption reaction and vice versa.

he thermodynamic parameters (ΔG°, ΔH° and ΔS°) were determined from the following Eq.(13):

$$\Delta G^o = -RT \ln K_e \qquad [13]$$

where R is the universal gas constant. The thermodynamic equilibrium constant K_e is determined by Eq.(14):

$$K_e = \frac{q_e}{C_e} \qquad [14]$$

where q_e(mg/g) is the amount of Cd(II) or Pb(II) ions adsorbed onto the SB at equilibrium, C_e (mg/l) the equilibrium concentration of heavy metals ions in the solution. The thermal effect on thermodynamic constant is determined [38] by Eq. (15)

$$\log K_e = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \qquad [15]$$

Where ΔH° and ΔS° are calculated from the slope and intercept of the linear plot, of log(q_e/c_e)versus 1/T as shown in Fig.20. The free energy is given by Eq.(16):

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad [16]$$

he free energy (ΔG°) is negative and increases with temperature (Table 6), indicating that the best adsorption is obtained at higher temperature and confirmed the feasibility and spontaneity of adsorption process while the positive enthalpy ΔH° suggests the endothermic nature of the adsorption process. The positive value of ΔS° corresponds to increase in the degree of freedom of adsorption of metal ions. The physical adsorption was confirmed by values of thermodynamic parameters[39].

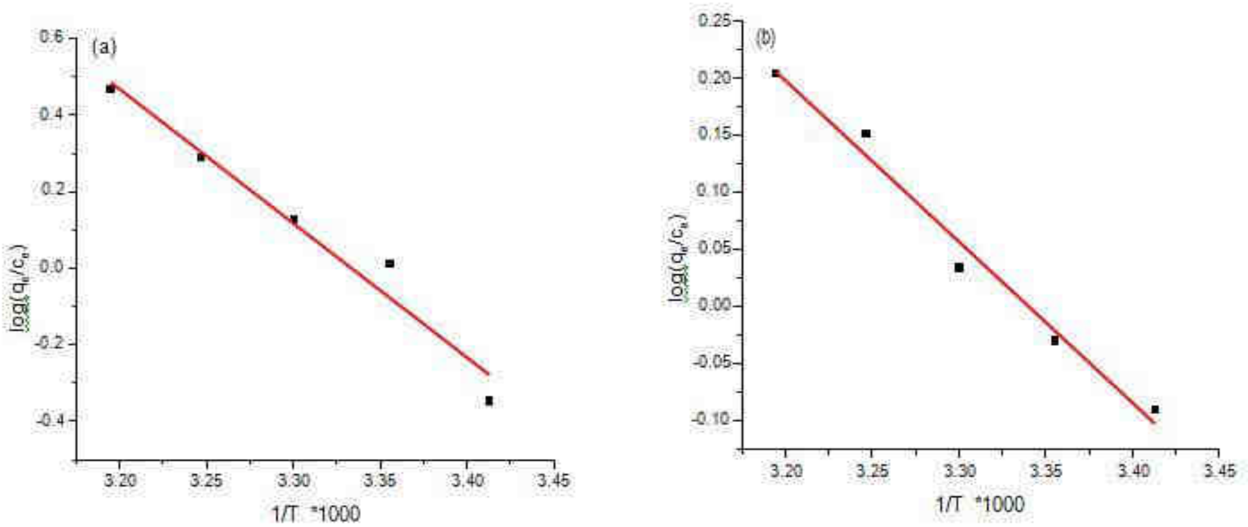

Fig.20: Relationship between log (q_e/c_e) and reciprocal of temperature, at constant initial concentration of 100 mg/l, 2.5g/l of SB and 400 rpm for lead(II) (a) and cadmium(II)(b).

Table (1): Adsorption isotherm constants for the adsorption of lead (II) and cadmium (II) onto SB at 298K.

Heavy metal	adsorbent	Langmuir isotherm				Freundlich isotherm			
		q_m (mg/g)	B	R_l	R^2	K_f (mg/g)	N	1/n	R^2
Lead	SB	120.9	0.01207	0.292-0.768	0.949	2.051	1.261	0.792	0.988
Cadmim		77.8	0.006	0.436-0.860	0.9533	0.785	1.247	0.801	0.983

Heavy metal	adsorbent	Temkin isotherm				Dubinin–Radushkevich isotherm			
		A_T (L/mg)	b_T	B(J/mol)	R^2	q_m (mg/g)	k_{ad} (mol^2/kJ^2)	E (KJ/mol)	R^2
Lead	SB	0.218	130.8	18.92	0.970	37.4	$8.32*10^{-5}$	0.206	0.863
Cadmim		0.104	123.5	20.05	0.964	36.6	$4.28*10^{-5}$	0.108	0.843

Table (2): Kinetic models Pseudo-first order, Pseudo-second order equations and other parameters for adsorption of lead(II) onto SB at different adsorbent dose of metal ions, initial concentration=100mg/l, 400 rpm and 301K.

Kinetic models	Parameters	Dose of adsorbent				
		0.5 (g/l)	1(g/l)	1.5(g/l)	2.5(g/l)	3.5(g/l)
	q_e(Exp) (mg/g)	154	79	53.33	34	21.42
Pseudo-first order equation	q_e (Calc.) (mg/g)	70.8	19.36	12.26	7.56	1.55
	$k_1(min^{-1})$	0.06648	0.02966	0.040256	0.03173	0.10987
	R^2	0.99201	0.64256	0.82845	0.95228	0.7765
Pseudo-second order equation	q_e (Calc.) (mg/g)	160	81.2332	54.7945	35.00175	21.53316
	k_2 (g/mg. min)	0.001699	0.00448	0.008464	0.011694	0.181844
	R^2	0.99979	0.99688	0.99898	0.99798	0.9999

Table (3): Kinetic models Pseudo-first order, Pseudo-second order equations and other parameters for adsorption of cadmium(II) onto SB at different adsorbent dose of metal ions, initial concentration=100mg/l, 400 rpm and 301K

Kinetic models	Parameters	Dose of adsorbent				
		0.5 (g/l)	1(g/l)	1.5(g/l)	2.5(g/l)	3.5(g/l)
	q_e(Exp) (mg/g)	72	49	37.33	30.8	23.14
Pseudo-first order equation	q_e (Calc.) (mg/g)	60.2	41.6	26.1	25.7	13.5
	$k_1(min^{-1})$	0.09499	0.07887	0.08654	0.139032	0.129682
	R^2	0.9987	0.99755	0.99748	0.9558	0.9963
Pseudo-second order equation	q_e (Calc.) (mg/g)	75.44	56.27	40.68	33.10	24.125
	k_2 (g/mg. min)	0.00159	0.002114	0.004789	0.007442	0.018437
	R^2	0.99744	0.99901	0.99963	0.99825	0.99961

Table (4): Kinetic models Elovich model, Intra particle Diffusion model and other parameters for adsorption of lead(II) onto SB at different adsorbent dose of metal ions, initial concentration=100mg/l, 400 rpm and 301K.

Kinetic models	**Parameters**	**Dose of adsorbent**				
		0.5 (g/l)	1(g/l)	1.5(g/l)	2.5(g/l)	3.5(g/l)
Elovich model	β (g/mg)	0.4562	0.1283	0.2152	0.4039	2.704
	α (mg/g/min)	0.3697	0.0550	0.0081	$3.39*10^{-5}$	$4.58*10^{23}$
	R^2	0.982	0.911	0.943	0.894	0.912
Intra particle Diffusion model	k_{dif} ($mg/g.min^{0.5}$)	9.338	3.365	1.990	1.147	0.1533
	I(mg/g)	87.18	53.25	38.51	24.91	20.39
	R^2	0.904	0.861	0.878	0.974	0.796

Table (5): Kinetic models Elovich model, Intra particle Diffusion model and other parameters for adsorption of cadmium(II) onto SB at different adsorbent dose of metal ions, initial concentration=100mg/l, 400 rpm and 301K.

Kinetic models	**Parameters**	**Dose of adsorbent**				
		0.5 (g/l)	1(g/l)	1.5(g/l)	2.5(g/l)	3.5(g/l)
Elovich model	β (g/mg)	0.0569	0.0839	0.1396	0.198	0.3438
	α (mg/g/min)	0.915	0.916	0.504	0.248	0.019
	R^2	0.951	0.968	0.957	0.947	0.883
Intra particle Diffusion model	k_{dif} ($mg/g.min^{0.5}$)	7.370	5.032	3.010	2.144	1.186
	I(mg/g)	20.83	16.55	16.32	15.95	15.17
	R^2	0.851	0.877	0.857	0.868	0.7454

Table (6): Thermodynamic parameters of lead (II) and cadmium(II) onto SB at constant initial concentration of 100 mg/l.

Heavy metal		Thermodynamic parameters		
	T (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol. K)
	293	1.559288		
Lead	298	0.441498		

	303	-0.67629	67.06	0.223
	308	-1.79408		
	313	-2.91187		
Cadmium				
	293	0.575664		
	298	0.124093	27.03	0.090
	303	-0.32748		
	308	-0.77905		
	313	-1.23062		

Micro-Column extraction of metal ion application

Simple micro-column was packed with the dried powder of SB sample of synthetic industrial wastewater was applied in order to test suitability of application of plant for removal of lead and cadmium metal ions(40).

Table (7): Micro-Column application for lead(II) extraction

ppm spiked	ppm detected	% Removal
922	722	21.6
460	320	30.4
225	190	15.5
93	80	13.9
8	7	12.5

Table (8): Micro-Column application for cadmium(II) extraction.

ppm spiked	ppm detected	% Removal
760	45	94
470	20	95.7
250	43	82.8
82	16	80.4
9.5	2	78.9

The obtained data from micro column reported that the percentage removal of cadmium ions more than percentage removal of lead ions. This may be due to the packing effect of the Sugarcane Bagasse in the micro column which due to large ionic radius of lead ions than cadmium ions.

CONCLUSION

The present study showed that Sugarcane Bagasse is low cost adsorbent available abundantly in Egypt. The adsorption relied on pH, initial concentration, speed of agitation, adsorbent dose, temperature, and contact time. The maximum removal for lead (II) and cadmium (II) from the liquid phase succeeded at pH 7.0. The equilibrium data was analyzed with Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models and Freundlich model order is the best fitted isotherm model. The kinetics models for the adsorption of lead and cadmium ions on SB confirms better applicability of Pseudo-second order rate equation according to regression coefficient. The spontaneous and endothermic adsorptions of the metals were evidenced from the negative free energy ($\Delta G°$) and positive enthalpy ($\Delta H°$). Hence, the Sugarcane Bagasse can be used as adsorbent for the removal of heavy metal ions from aqueous solutions.

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