Korean J. Chem. Eng., 33(9), 2716-2731 (2016)
DOI: 10.1007/s11814-016-0109-3

pISSN: 0256-1115
eISSN: 1975-7220

Influence of ultrasonication on preparation of novel material for heavy metal removal from wastewater

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(*Received 24 February 2016 • accepted 19 April 2016*)

Abstract−The present research introduces a new concept on rapid removal of Pb(II) ions from wastewater using novel agro-based material. The two types of materials such as sulfuric acid modified *Caryota urens* seeds (SMCUS) and ultrasonic assisted *Caryota urens* seeds (UACUS) were prepared and performance was compared for Pb(II) ions removal. The functional groups available on the *C. urens* were discussed by using FT-IR report. Adsorption influencing parameters such as initial metal ion concentration, pH, contact time, adsorbent dosage and temperature were studied to predict the optimum conditions. Several isotherm and kinetic models were applied to examine the experimental data. The present adsorption-adsorbate system best obeys the Freundlich and pseudo-first-order models. Langmuir monolayer capacity of the SMCUS and UACUS for Pb(II) ions was found to be 93.7 and 175.9 mg/g, respectively. Thermodynamic parameters explain that the adsorption of Pb(II) ions was spontaneous and exothermic.

Keywords: Heavy Metal Ions, *Caryota urens* Seeds, Ultrasonication, Equilibrium, Kinetics, Process Design

INTRODUCTION

Water resources have been severely affected because of anthropogenic activities which have become a global environmental concern. This contaminant is mostly comprised of heavy metals like lead, mercury, chromium, copper, cadmium, and zinc, which pose a serious threat to ecological balance and public health because of their toxicity, bioaccumulation, and non-biodegradation [1-4]. Among the various heavy metals present in the wastewater, Pb(II) ions contribute major pollution in the present age because of the tendency to last for a long period in an aqueous environment, with a half-life of at least 20 years; consequently, it has received a greater attention from the environmentalists [5]. This metal ion mostly exists in the effluents of various industrial processes such as metallurgy, electroplating, dyes, glass, storage battery, paint coating, electronics, petroleum refining industry, radiation shielding and construction industries, which causes serious potential impacts over the environment [6,7]. When humans are exposed to such heavy metals, even a trace level can cause serious health illness such as damage to kidneys, liver, reproduction system, mental retardation, irreversible brain damage, nervous system, poor muscle coordination, genital system, viscera and basic cellular processes which can cause several diseases like cancer, anemia, and intellectual disability [8]. Pb(II) ions, even present at low concentration in the aqueous environment, can cause a viral impact on human beings, animals and the ecosystem. Therefore, the US Environmental Protection Agency (USEPA) and Bureau of Indian Standards (BIS) have regulated the permissible limits for Pb(II) in drinking water as 0.015 mg L^{-1} and 0.1 mg L^{-1}, respectively [7]. Thus, it is very important to remove the excess metal ions from the wastewater before it is being discharged into the water bodies. Also, taking into account fast population growth, increasing demands for clean water, along with the continued environmental destruction, it is important to remove the heavy metal ions from wastewater before being released into the environmental ecosystems. Hence, several treatment technologies, including chemical precipitation [9], electrochemical treatment [10], ion exchange [11], adsorption [12] and membrane filtration process such as microfiltration [13], ultrafiltration [14], nanofiltration [15], reverse osmosis [16] and electrodialysis [17], have been developed to isolate the high concentration of Pb(II) ions from aqueous solution. However, many of these traditional technologies are restricted due to cost, complexity, removal efficiency and secondary waste (require additional treatment). Nowadays, adsorptive removal, i.e., binding of heavy metals over adsorbents has become an efficient technique for wastewater treatment. This treatment technique has more advantages such as low cost, fast removal rate and higher affinity towards the metal ions. Meanwhile, the exhausted adsorbents can be reactivated by using suitable desorption process in case of reversible adsorption process [18-20]. In recent years, various adsorbents have been employed for the removal of Pb(II) ions from aqueous environment and some of them include granular activated carbon [21], graphite oxide [22], coconut shell [23], tamarind seeds [24], cashew nut shell [25], grape seed [26], leaf ash [27] and wheat pulp [28]. Unfortunately, these adsorbents have some built-in disadvantages, such as low adsorption capacity, unsatisfactory in removing metal ions at very low concentration and being expensive. Hence, researchers have shown an interest in development of an efficient adsorbent with high adsorption capacity and regeneration at low cost. From these strategies, the agricultural waste biomass has been especially considered as a

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precursor for the preparation of an effective adsorbent material for the removal of toxic metal ions from water/wastewater. This waste biomass consists of several compounds such as simple sugars, starch, hemicellulose, lignin and lipids, which enhances the adsorption capacity of the biomass. Adsorbents derived from naturally occurring agricultural biomass such as fishtail palm *Caryota urens* seeds, can be utilized to isolate the organic and inorganic contaminants because of its greater active sites, light mass density and highly porous in structure. *C. urens* seeds consist of simple sugars such as glucose, sucrose and fructose which facilitate the removal of toxic metal ions from aqueous solution in an effective manner [29].

The main objective of the present research was to prepare novel effective adsorbents from *C. urens* seeds for the removal of Pb(II) ions from aqueous solution. The adsorption of Pb(II) ions onto the raw *C. urens* seeds is slightly inspected because of its low surface area, porosity and crystallinity. Because of these drawbacks, the sulfuric acid modified and the ultrasonic assisted methodologies have been adopted to modify the surface of the adsorbent material (*C. urens* seeds). The sulfuric acid treatment was used to improve the surface properties of the adsorbent. This surface property was further improved by ultrasonication treatment. The surface modified materials have adequate surface properties for the sequestration of toxic metal ions from aqueous solution. The surface modified *C. urens* seeds were characterized by Fourier transform infrared spectroscopic (FT-IR) analysis. Experimental studies on Pb(II) ions removal by surface modified *C. urens* seeds were performed in a batch mode operation. The effects of operational parameters such as initial Pb(II) metal ion concentration, solution pH, adsorbent dose, temperature and contact time were studied. The results from the influencing parameter studies were used to investigate the isotherm, kinetic and thermodynamics of the process. The adsorption equilibrium data were tested by using several adsorption isotherm models, such as two-parameter Langmuir and Freundlich, three-parameter Langmuir-Freundlich, Fritz-Schlunder, Radke-Prausnitz, Toth, Redlich-Peterson and Sips model, four-parameter: Fritz-Schlunder and Baudu, and five-parameter Fritz-Schlunder model. A single stage batch adsorber was designed by using the best fitted adsorption isotherm model. The adsorption kinetic data were analyzed by using pseudo-first order, pseudo-second order and Elovich kinetic models. The effect of temperature data was used to examine the thermodynamic parameters such as changes in Gibbs free energy (ΔG^o), changes in entropy (ΔS^o) and changes in enthalpy (ΔH^o), which gives valuable information about the nature of adsorption process (either endothermic or exothermic).

MATERIALS AND METHODS

1. Collection and Preparation of Adsorbents

1-1. RCUS Synthesis

The fishtail palm *C. urens* seeds were collected from SSN College of Engineering Campus, Chennai, Tamil Nadu, India. In the preparation stage, the raw seeds were washed thoroughly with tap water to remove dirt and other impurities. This washed material was dried at room temperature to remove the moisture. The dried samples were ground in a steel mill to give a uniform particle size of 0.354 mm [30]. The obtained fine solid is referred to as raw *C. urens* seed (RCUS). The resulting material was used as a precursor for the preparation of the adsorbent (sulfuric acid modification and ultrasonic treatment).

1-2. Modification of RCUS using Concentrated H_2SO_4

The RCUS was modified by treating it with concentrated H_2SO_4 in the ratio of 1 : 2 by weight for about 24 h. The excessive acid present in the dehydrated *C. urens* seeds powder was rinsed with double distilled water until the pH turned nearly neutral. Afterwards, the sample was dried in hot air oven at 80 °C for about 3 h and then ground to fine particles. Particles of different sizes were separated by using sieve analysis and the required size of 0.354 mm were collected [30]. The resultant material was titled as sulfuric acid modified *C. urens* seeds (SMCUS) and it was stored in an air-tight plastic container. This prepared material was used as an adsorbent for the removal of Pb(II) ions from the aqueous solution. Also, this SMCUS was further utilized as a precursor for the preparation of UACUS.

1-3. Modification of SMCUS using Ultrasonication

The ultrasonic assisted *C. urens* seeds was synthesized by dispersing 4 g of SMCUS in 50 mL of deionized water by using an ultrasonicator for about 1 h. The sonication of above mixture was performed in an ultrasonicator accompanied with mechanical agitation at a speed of 500 rpm under working frequency of 24 kHz. The final solution containing *C. urens* seed slurry was filtered off and then dried at 40 °C for 24 h [31]. Finally, this material was reported as ultrasonic assisted *C. urens* seeds (UACUS). This ultrasonication treatment was used to improve the surface properties of the adsorbent towards the removal of Pb(II) ions from aqueous solution.

2. Instrumentation

The characteristics of surface modified adsorbents such as SMCUS and UACUS were studied in before and after adsorption of Pb(II) ions using FT-IR analysis. The concentration of Pb(II) ions in the feed solution and residual solutions was measured by using an atomic adsorption spectrophotometer (AAS) (SL 176 Model, Elico Limited, Chennai, India). A digital pH meter equipped with combined glass electrode was used for the analysis of pH of the wastewater solution.

3. Preparation of Pb(II) Ion Solution and Analysis

All the chemicals used in this study were analytical grade purchased from E. Merck, India. The aqueous solutions were prepared by using double-distilled water. A stock solution of Pb(II) ion solution (1,000 mg/L) was prepared in a 1 L volumetric flask by dissolving 1.598 g of lead nitrate ($Pb(NO_3)_2$) salt with an adequate amount of double-distilled water. The solution was shaken well and made up to 1,000 mL by using double-distilled water. And it was further diluted in suitable proportion to obtain desired concentration of Pb(II) ion solution (i.e., working solution: 100-500 mg/L). The pH of the working solution was maintained to the required value with either 0.1 M NaOH or 0.1 M HCl. The concentration of Pb(II) ions in the solutions before and after the adsorption was measured by AAS.

4. Batch Adsorption Experiments

The adsorption experiments were performed under batch mode operation to investigate the Pb(II) ions removal by the surface modified adsorbents (SMCUS and UACUS). This experiment was studied by using an Erlenmeyer flask of 100 mL capacity which acts as a batch adsorber, under the effect of various operational parameters such as adsorbent dose (0.1 to 0.8 g/L for SMCUS and 0.05 to 0.45 g/L for UACUS), initial Pb(II) ion concentration (100 to 500 mg/L), temperature (30 to 60 °C), contact time (5 to 60 min for SMCUS and 5 to 45 min for UACUS), and solution pH (2.0 to 7.0). Prior to the experiments, the pH of the solution was adjusted to the required level by using either 0.1 M NaOH or 0.1 M HCl. A series of Erlenmeyer flasks were filled with 100 mL of Pb(II) ion solution of varying concentrations (100-500 mg/L). Afterwards, an optimum quantity of adsorbent (SMCUS or UACUS) was added into each individual sample of conical flasks. This adsorption system was operated in a temperature controlled incubation shaker (80 rpm). After the prescribed contact time, the liquid samples were withdrawn from the shaking incubator, the mixtures were centrifuged to separate supernatant which was then analyzed by using AAS. The removal of Pb(II) ions from aqueous solution can be calculated by using the following mass balance relationship:

$$\%\ \text{Removal of Pb(II) ion} = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where C_o and C_e are the initial and final Pb(II) ions concentrations (mg/L) in the sample, respectively. Precision of the results was achieved by running all the experiments in triplicate.

5. Influence of the Operating Parameters

5-1. Effect of Initial Pb(II) Ion Concentration

The effect of initial Pb(II) ions concentration on the removal of Pb(II) ions was studied by varying the initial Pb(II) concentration and by keeping all other operating parameters constant. The optimum dose of adsorbent was mixed with the 100 mL of Pb(II) ion solution with a varying initial concentration range from 100 to 500 mg/L in a series of conical flasks. This adsorption system was operated under optimum condition in a temperature controlled incubation shaker (60 for SMCUS and 45 min UACUS). After the system attained equilibrium condition, the samples were centrifuged, and the supernatant was examined using AAS.

5-2. Effect of Solution pH

The pH of the solution is an important key parameter for the adsorption process. In this case, the pH of the solution was varied from 2.0 to 7.0 and by keeping all other parameters at constant. The operating conditions used for the present study were: initial Pb(II) ions concentration of 100 mg/L, contact time 60 min for SMCUS and 45 min for UACUS, temperature of 30 °C, SMCUS dose of 0.5 g and UACUS dose of 0.3 g. The known concentration of Pb(II) ions solution with an optimum adsorbent dose was taken in a series of conical flasks. These conical flasks were kept in a temperature controlled incubation shaker at 80 rpm. After preset time, the samples were centrifuged and analyzed for Pb(II) ion concentration in the aqueous solution as mentioned previously.

5-3. Effect of Temperature

The temperature influence on the removal of Pb(II) ions was studied by varying the temperature ranging from 30 to 60 °C and by keeping all other parameters constant. The operating conditions used for the present study were: initial Pb(II) ions concentration of 100-500 mg/L, contact time 60 min for SMCUS and 45 min for UACUS, pH of 5.0, SMCUS dose of 0.5 g and UACUS dose of 0.3 g. A similar experimental and analysis procedure was carried out as mentioned above.

5-4. Effect of Contact Time

The effect of contact time on the removal of Pb(II) ions was determined by varying the contact time from 5 to 60 min for SMCUS and 5 to 45 min for UACUS. Other operating parameters were kept constant. The operating conditions used for the present study were: initial Pb(II) ions concentration of 100-500 mg/L, temperature of 30 °C, pH of 5.0, SMCUS dose of 0.5 g and UACUS dose of 0.3 g. The known concentration of Pb(II) ions solution with an optimum adsorbent dose was taken in a series of conical flasks. These conical flasks were kept in a temperature controlled incubation shaker at 80 rpm. At predetermined time intervals, the samples were taken and centrifuged. The supernatant was analyzed for Pb(II) ion concentration in the aqueous solution by using AAS.

5-5. Effect of Adsorbent Dosage

The study on the influence of adsorbent dose is not restricted to calculating the adsorption capacity alone but also for the economical aspects. The effect of adsorbent dose for the removal of Pb(II) ions was studied by varying the adsorbent dose (from 0.1 to 0.8 g/L for SMCUS and 0.05 to 0.45 g/L for UACUS) and by maintaining all other parameters to be kept constant. The operating conditions used for the present study were: initial Pb(II) ions concentration of 100 mg/L, temperature of 30 °C, pH of 5.0, contact time of 45 min for SMCUS and 30 min for UACUS. The known concentration of Pb(II) ions solution and adsorbent dose was taken in a series of conical flasks. These conical flasks were kept in a temperature controlled incubation shaker at 80 rpm. After preset time, the samples were taken and centrifuged. The supernatant was analyzed for Pb(II) ion concentration in the aqueous solution by using AAS.

6. Adsorption Equilibrium Experiments

The data obtained from the effect of initial concentration studies were used to examine the adsorption equilibrium models. The quantity of Pb(II) ion adsorbed over the adsorbent at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_e is the concentration of Pb(II) ion in the solution at equilibrium (mg/L), V is the volume of Pb(II) ion solution (L), m is the mass of adsorbent (g).

Adsorption equilibrium data were applied to the different adsorption isotherm models such as two-parameter Langmuir and Freundlich, three-parameter Langmuir-Freundlich, Fritz-Schlunder, Radke-Prausnitz, Toth, Redlich-Peterson and Sips model; four-parameter Fritz-Schlunder and Baudu, and five-parameter Fritz-Schlunder model to study the behavior between the aqueous solution and the adsorbents. Nonlinear regression analysis was done by using MATLAB R2009a software to simulate the parameters, coefficient of correlation (R^2), and error values. Based on the results obtained from aforementioned analysis, the appropriate adsorption isotherm model was chosen.

Two parameter model

Langmuir adsorption isotherm model is given by [32]:

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

where q_e is the adsorption capacity at equilibrium (mg/g), q_m is the maximum monolayer adsorption capacity (mg/g), C_e is the concentration of the metal ions in the solution at equilibrium (mg/L) and K_L is the Langmuir equilibrium constant (L/mg).

The Freundlich adsorption model is given by [33]:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant [(mg/g)(L/mg)$^{(1/n)}$] related to the bonding energy and n is a measure of deviation from the linearity of adsorption (g/L). The significance of 'n' is as follows: n=1 (linear), n>1 (physical process) and n<1 (chemical process).

Three-parameter model

Langmuir-Freundlich isotherm model equation is given by [34]:

$$q_e = \frac{q_{mLF}(K_{LF}C_e)^{mLF}}{1+(K_{LF}C_e)^{mLF}} \tag{5}$$

where q_{mLF} is the Langmuir-Freundlich maximum adsorption capacity (mg/g), K_{LF} is the equilibrium constant and mLF is the Freundlich heterogeneity parameter between 0 to 1.

Fritz-Schlunder model equation is given by [35]:

$$q_e = \frac{q_{mFS}K_{FS}C_e}{1+q_{mFS}C_e^{\alpha}} \tag{6}$$

where q_{mLS} is the Fritz-Schlunder maximum adsorption capacity (mg/g), K_{FS} is the Fritz-Schlunder equilibrium constant (L/mg) and mFS is the Fritz-Schlunder model exponent.

Radke-Prausnitz model equation is given by [36]:

$$q_e = \frac{q_{mRP}K_{RP}C_e}{(1+K_{RP}C_e)^{mRP}} \tag{7}$$

where q_{mRP} is the Radke-Prausnitz maximum adsorption capacity (mg/g), K_{RP} is the Radke-Prausnitz equilibrium constant and mRP is the Radke-Prausnitz model exponent.

Toth model equation is given by [37]:

$$q_e = \frac{q_{mT}C_e}{(1/K_T + C_e^{mT})^{1/mT}} \tag{8}$$

where q_{mT} is the Toth maximum adsorption capacity (mg/g), K_T is the Toth equilibrium constant and mT is the Toth model exponent.

Redlich-Peterson isotherm model is given as follows [38]:

$$q_e = \left(\frac{K_{RP}C_e}{1+\alpha_{RP}C_e^{\beta_{RP}}}\right) \tag{9}$$

where β_{RP} is the exponent which lies between 0 and 1, K_{RP} is the Redlich-Peterson isotherm constant (L/g), α_{RP} is the Redlich-Peterson isotherm constant (L/mg)$^{1/\beta}{}_{RP}$ The significance of β is as given as: β=1 (Langmuir adsorption isotherm model is a preferable adsorption isotherm model); β=0 (Freundlich adsorption isotherm model is a preferable adsorption isotherm model).

The Sips adsorption isotherm model is given as follows [34]:

$$q_e = \left(\frac{K_S C_e^{\beta_S}}{1+\alpha_S C_e^{1/\beta_S}}\right) \tag{10}$$

where K_s is the Sips model isotherm constant (L/g)$^{\beta S}$ and α_s is the Sips model constant (L/g)$^{1/\beta S}$, β_S is often regarded as the heterogeneity factor, with values close to 1 indicating a homogeneous binding site, and values greater than 1 indicating a heterogeneous adsorption system.

Four-parameter model

The Fritz-Schlunder model is given by [35]:

$$q_e = \frac{AC_e^{\alpha}}{(1+BC_e^{\beta})} \tag{11}$$

where A and B are the Fritz-Schlunder parameters, α and β are the Fritz-Schlunder equation components.

Baudu model is given by [39]:

$$q_e = \frac{q_m b_o C_e^{(1+x+y)}}{1+b_o C_e^{(1+x)}} \tag{12}$$

where q_m is the Baudu maximum adsorption capacity (mg/g), x and y are the Baudu parameters and b_o is the equilibrium constant.

Five-parameter model

The Fritz-Schlunder model is given by [35]:

$$q_e = \frac{q_{mFSS}K_1C_e^{m_1}}{1+K_2C_e m_2} \tag{13}$$

where q_{mFSS} is the Fritz-Schlunder maximum adsorption capacity (mg/g). K_1, K_2, m_1 and m_2 are the Fritz-Schlunder parameters.

7. Adsorption Kinetic Experiments

The data obtained from the effect of contact time studies were used to examine the adsorption kinetic models. The quantity of Pb(II) ion adsorbed onto adsorbent at predetermined time intervals (q_t) was determined by:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{14}$$

where q_t is the amount of Pb(II) ions adsorbed onto the adsorbent at any time t (mg/g), m is the mass of the adsorbent (g), V is the volume of the Pb(II) ions solution (L) and C_t is the concentration of Pb(II) ions measured at a particular time 't' (mg/L).

Sorption kinetics was performed to study the rate-controlling steps, mechanism and characteristics of sorption. Hence adsorption kinetics data of Pb(II) ions were simulated by using pseudo-first order, pseudo-second order and Elovich kinetic models.

Pseudo-first order kinetic model equation is provided below [40]:

$$q_t = q_e(1-\exp(-k_1t)) \tag{15}$$

where k_1 is the pseudo-first order kinetic rate constant (min^{-1}), t is the time (min).

Pseudo-second order kinetic model equation is given as [41]:

$$q_e = \frac{q_e^2 k_2 t}{1+q_e k_2 t} \tag{16}$$

where t is the time (min), k_2 is the pseudo-second order kinetic rate constant (g/mg·min).

The Elovich kinetic model equation is given as follows [42]:

$$q_t = (1+\beta_E)\ln(1+\alpha_E\beta_E t) \tag{17}$$

where β_E (g/mg) is the desorption constant related to the activation energy of chemisorption and α_E is the initial adsorption rate mg/(gmin).

8. Thermodynamic Study

Thermodynamic studies were performed to calculate the thermodynamic parameters such as Gibbs free energy change (ΔG^o, kJ mol^{-1}), enthalpy change (ΔH^o, kJ mol^{-1}), and entropy change (ΔS^o, kJ mol^{-1}) to predict whether the adsorption process was spontaneous or not. These parameters were calculated using the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{18}$$

$$\Delta G^o = -RT \ln K_c \tag{19}$$

$$\text{Log}K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{20}$$

where C_e is the equilibrium concentration in solution (mg/L), C_{Ae} is the amount of Pb(II) ion adsorbed on the adsorbent per litre of solution at equilibrium (mg/L), R is the gas constant (8.314 J/mol/K), T is the temperature (K) and K_c is the equilibrium constant. The values of ΔH^o and ΔS^o were calculated using the slope and the intercept obtained from van't Hoff's plot of log K_c versus 1/T.

RESULTS AND DISCUSSION

1. Material Characterization - FTIR Studies

The surface chemistry of the adsorbent material plays an important role in determining the adsorption mechanism. The functional groups present on the surface of the adsorbent material (*C. urens*) were illustrated by FT-IR analysis. FT-IR spectra can be used to find the interaction between the Pb(II) ion and the adsorbent material (SMCUS and UACUS). Fig. 1(a)-(d) shows that the FT-IR spectra of surface modified adsorbent SMCUS and UACUS before and after the adsorption process. Fig. 1(a) shows that the FT-IR spectra of SMCUS before the adsorption. The intense peak at 2,922.31 cm^{-1} in the SMCUS is corresponding to the C-H vibrations in methylene groups. The band vibrations at 1,697.38 and 1,602.87 cm^{-1} relate to the ketone group and aromatic ring stretch C=C-C^a. The peak vibrations at 1,135.30 and 1,037.05 cm^{-1} indicate that secondary amine of C-N and aromatic ring (aryl) group of aromatic C-H in plane bend. Fig. 1(b) shows that the FT-IR spectra of UACUS before the adsorption. The intense peaks at 3,355.16 and 2,917.90 cm^{-1} represent the hydroxyl compound group of H-bonded OH stretch and alkane group of asymmetric stretching of methylene C-H, respectively. The strong peak at 1,610.72, 1,517.95, 1,437.40, 1,319.92, 1,241.34, 1,142.55, 1,031.27, 939.01 and 760.19 cm^{-1} relates to the aromatic ring stretch of C=C-C^a, hetero-oxy compounds of aromatic nitro compounds, carbonate ion, acetylenic compounds of C-C stretch, aromatic ethers, aryl-O stretch, C-O stretch, silicon-oxy compounds, silicate ion and OH alcohol groups, respectively.

Fig. 1(c) shows that the FT-IR spectra of SMCUS after the adsorption process. The peak vibration at 3,722.14, 1,725.60 and 686.75 cm^{-1} corresponds to hydroxyl group, aldehyde, and thioether CH_2-S. The FT-IR spectra of UACUS after the adsorption process are shown in Fig. 1(d). The intense peak at 3,696.44 cm^{-1} s indicates the chemisorptions of water molecules on the surface of the adsorbent material that lead to the formation of hydroxyl group OH stretch. The peaks at 800.96, 795.99, 786.09 cm^{-1} correspond to the formation of aliphatic-chloro compounds, C-Cl stretch and aromatic C-H out-of-plane bend, respectively. The peak value of 703.66 and 698.18 cm^{-1} represents the presence of aryl thioether. The FT-IR analysis clearly repors that the alcoholic groups (1,037.05 and 760.19 cm^{-1}) in the SMCUS and UACUS (before the adsorption) get converted into ether (686.75 and 698.18 cm^{-1}) in the SMCUS and UACUS (after the adsorption). This alteration demonstrates the formation of matrix with a cross linked network. After the adsorption process, the peak observed at 1,437.40 cm^{-1} (UACUS) indicates the presence stretching vibration of ionic groups (carbonate ion).

The thioether was observed at 686.75 cm^{-1} in the SMCUS (after adsorption). Similarly, aliphatic-chloro compounds, C-Cl stretch and aromatic C-H out-of-plane bend were observed at the peaks of 800.96, 795.99, 786.09 cm^{-1} in the UACUS (after adsorption), respectively. These bands were not observed in the SMCUS and UACUS

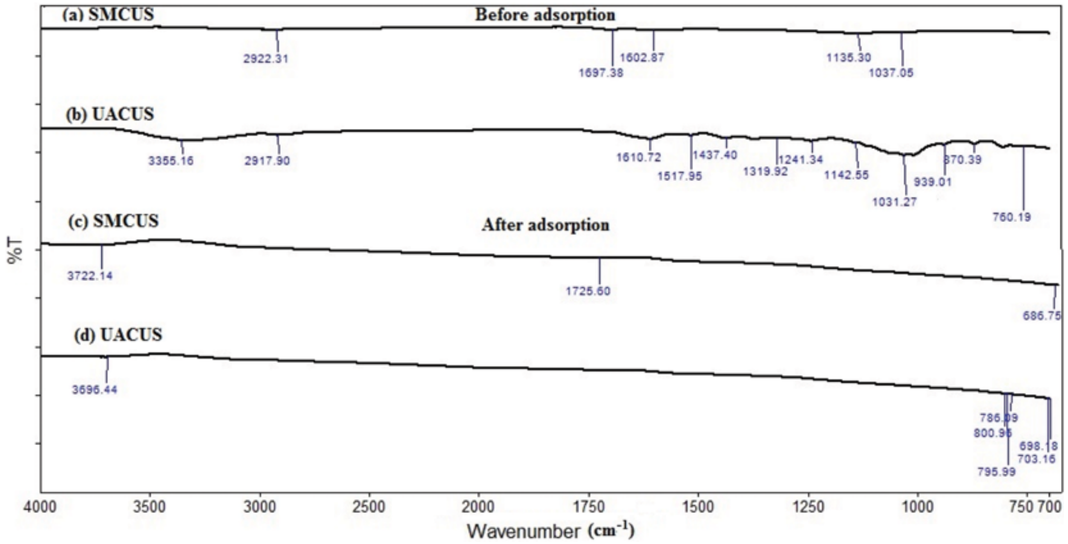

Fig. 1. FTIR analysis of SMCUS and UACUS before and after adsorption.

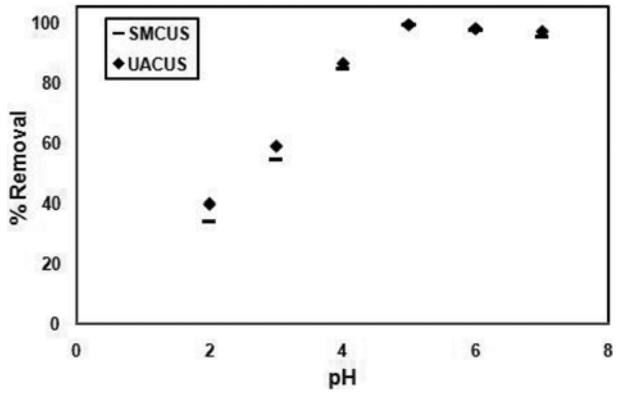

Fig. 2. Effect of pH on the adsorption of Pb(II) ions onto the SMCUS and UACUS (Pb(II) ions concentration=100 mg/L, volume of sample=100 mL, temperature 30 °C, adsorbent dose=0.5 g for SMCUS and 0.3 g for UACUS, time=45 min for SMCUS and 30 min for UACUS).

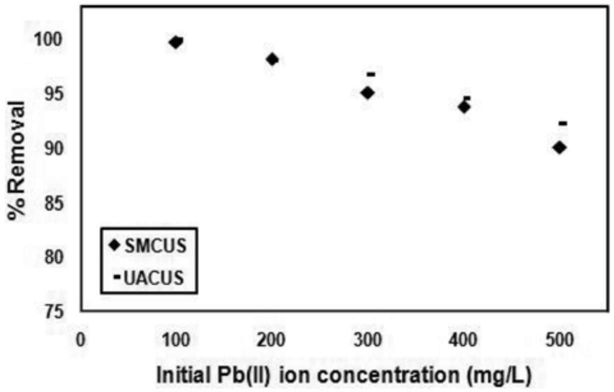

Fig. 3. Effect of initial Pb(II) ion concentration on the adsorption of Pb(II) ions (solution pH=5.0, volume of sample=100 mL, temperature 30 °C, adsorbent dose=0.5 g for SMCUS and 0.3 g for UACUS, time=45 min for SMCUS and 30 min for UACUS).

(before the adsorption). These ionic groups form the covalent bond between the surface of the adsorbent material and the Pb(II) ion. The comparison peak between the before and after the adsorption process of SMCUS and UACUS shows that the presence of hydroxyl, ether groups, covalent bridge and matrix formation (after the adsorption), which confirms that adsorbent material (SMCUS and UACUS) has superior potential for the adsorption of heavy metal ions from the wastewater.

2. Effect of pH

The solution pH is the main important process parameter for the adsorption process; it affects the chemical speciation of metal ions and the ionization state of the functional groups present on the surface of the adsorbent material. Fig. 2 shows the influence of the solution pH on the adsorption of Pb(II) ions onto the adsorbent material (SMCUS and UACUS). Adsorption experiments were performed in the pH range of 2.0 to 7.0 for an initial Pb(II) ion concentration of 100 mg/L, temperature of 30 °C, contact time of 45 min for SMCUS and 30 min for UACUS and the adsorbent dose of 0.5 g for SMCUS and 0.3 g for UACUS. The adsorption of Pb(II) ion increased with an increase in the value of pH from 2.0 to 5.0, and the maximum adsorption amount of Pb(II) ion onto the adsorbent was at pH 5.0. At acidic conditions, several functional groups present on the surface of the adsorbent (fishtail palm *C. urens* seeds) become protonated. This indicates that the numbers of positively charge on *C. urens* seeds have been increased. Less removal was observed at low pH because of the electrostatic repulsion between the positively charged active sites and the positively charged Pb(II) ions. The removal of Pb(II) was increased with the increase in solution pH because of the electrostatic attraction between the negatively charged active sites and the positively charged Pb(II) ions. Beyond the pH of 5.0, metal hydroxide complexes were formed due to the presence of hydroxyl ions which gradually decreased the adsorption capacity of the adsorbent. Consequently, the percentage removal of Pb(II) ions was decreased gradually.

3. Effect of Initial Pb(II) Ion Concentration

The initial metal concentration in the liquid phase plays an important role and significantly affects the adsorption process. The effect of Pb(II) ion concentration on the adsorption of Pb(II) ions and isotherm studies was examined by changing the Pb(II) concentration in the range of 100 to 500 mg/L at a temperature of 30 °C and the adsorbent dosage of 0.5 g for SMCUS and 0.3 g for UACUS (Fig. 3). From Fig. 3, the maximum adsorption amount of Pb(II) ions onto the SMCUS (99.72%) and UACUS (99.88%) was obtained at 100 mg/L. The experimental results clearly show that the percentage removal of Pb(II) ions decreased from 99.72% to 90.05% for SMCUS, 99.88% to 92.28% for UACUS with the increase of initial feed solution concentration from 100 to 500 mg/L. It has been shown that removal of Pb(II) ions decreased with an increase in the initial Pb(II) ions concentration, due to the saturation of available active sites present on the surface of the adsorbent. In addition, at low Pb(II) ion concentration, the ratio of the available active sites to the initial Pb(II) ion concentration was higher, which indicates that percentage removal of Pb(II) ions was high. On the other hand, at high Pb(II) ion concentration, more metal ions were available in liquid phase for adsorption process, but the available active sites got saturated, i.e., the ratio of the available active sites to the initial Pb(II) ion concentration was low. The equilibrium adsorption capacity was increased with an increase in the initial Pb(II) ion concentration maybe due to the increased rate of mass transfer, which shows the increased concentration of driving force. Therefore, the percentage removal of Pb(II) ions was higher at low Pb(II) ion concentration and lower at high Pb(II) ion concentration.

4. Construction of Adsorption Isotherm

The adsorption isotherm was performed with the data obtained from the effect of initial Pb(II) ion concentration studies. Adsorption isotherm model affords the basic information about the capacity of the adsorbent and the characterization of the adsorption process [43]. Additionally, the adsorption isotherm model describes the single stage adsorption design system. It gives the specific interaction between the adsorbate in the liquid solution and the adsorbate in the solid adsorbent at equilibrium. In this study, the adsorption isotherms were employed by using different adsorption isotherm models such as two-parameter Langmuir and Freundlich, three-parameter Langmuir-Freundlich, Fritz-Schlunder, Radke-Prausnitz, Toth, Redlich-Peterson and Sips model, four-parameter Fritz-Schlunder and Baudu, five-parameter Fritz-Schlunder model to fit the adsorption equilibrium data of the adsorption of Pb(II) ions onto the adsorbent materials (SMCUS and UACUS). The adsorption isotherm model parameters, correlation coefficient values (R^2) and error function values [SSE (sum of squared errors), RMSE (root mean squared values)] were evaluated by using the MATLAB R2009a software by applying the experimental data (C_e and q_e) to the isotherm models; these values are listed in Tables 1 and 2. The best fitted adsorption isotherm model was identified based on the higher correlation coefficient (R^2) and low error values. The Langmuir adsorption isotherm parameters q_m, K_L, R_L, SSE and RMSE were estimated from the plot of C_e and q_e (Fig. 4) and the results shown in Tables 1 and 2. The nature of the adsorption process (favorable or unfavorable or linear or irreversible) was identified from the values of separation factor (R_L). The significance of R_L values was as follows: $R_L=0$ (irreversible), $0<R_L<1$ (favorable), $R_L=1$ (linear), $R_L>1$ (unfavorable). The calculated values from the Langmuir

Table 1. Adsorption isotherm results for the adsorption of Pb(II) ions onto SMCUS

Isotherm model	Parameters	R^2	SSE	RMSE	Equation
Two parameter model					
Langmuir	$q_m=93.7$ (mg/g) $K_L=0.169$ (L/mg)	0.9302	400.4	10.01	$q_e=\frac{93.7*0.169*C_e}{1+0.169*C_e}$
Freundlich	$K_F=26.37$ ((mg/g) (L/mg)$^{(1/n)}$) $n=3.193$ (g/L)	0.9965	21.7	2.115	$q_e=26.37*C^{1/3.193}$
Three parameter model					
Langmuir-Freundlich	$q_{mLF}=100.3$ (mg/g) $K_{LF}=0.1762$ (L/mg) $m_{LF}=0.6521$	0.9594	233	7.632	$q_e=\frac{100.3*(0.1762*C_e)^{0.6521}}{1+(0.1762*C_e)^{0.6521}}$
Fritz-Schlunder	$q_{mF}=22.34$ (mg/g) $K_{FS}=6.383$ (L/mg) $\alpha=0.6177$	0.9792	119.4	4.887	$q_e=\frac{22.34*6.383*C_e}{1+(22.34*C_e)^{0.6177}}$
Radke-Prausnitz	$q_{mRP}=12.95$ (mg/g) $K_{RP}=12.63$ $m_{RP}=0.7004$	0.9916	48.13	3.469	$q_e=\frac{12.95*12.63*C_e}{(1+12.63*C_e)^{0.7004}}$
Toth	$q_{mT}=23.3$ (mg/g) $K_T=1.126$ $m_T=0.2736$	0.9796	116.9	4.836	$q_e=\frac{23.3*C_e}{\left(\frac{1}{1.126}+C_e^{0.2736}\right)^{1/0.2736}}$
Redlich Peterson	$\alpha_{RP}=3.349$ (L/mg)$^{1/\beta_{RP}}$ $\beta_{RP}=0.7013$ $K_{RP}=65.3$ (L/g)	0.9826	100.1	5.003	$q_e=\frac{65.3*C_e}{1+3.349*C_e^{0.7013}}$
Sips	$\alpha_s=3.575$ (mg/g) $K_S=26.8$ (L/mg) $\beta_S=0.3044$	0.9947	30.36	3.181	$q_e=\frac{26.8*C_e^{0.3044}}{1+3.575*C_e^{1/0.3044}}$
Four parameter model					
Fritz-Schlunder	$A=146$ $B=0.979$ $\alpha=0.1543$ $\beta=0.00238$	0.9959	23.45	2.425	$q_e=\frac{146*C_e^{0.1543}}{1+0.979*C_e^{0.00238}}$
Baudu	$q_{m0}=66$ $b_0=0.0392$ $x=17.09$ $y=19.56$	0.9909	52.36	5.117	$q_e=\frac{66*0.0392*C_e^{(1+17.09+19.56)}}{1+0.0392*C_e^{(1+17.09)}}$
Five parameter model					
Fritz-Schlunder	$q_{mFSS}=18.23$ $K_1=19.82$ $K_2=12.7$ $m_1=0.382$ $m_2=0.07355$	0.9944	31.94	5.652	$q_e=\frac{18.23*19.82*C_e^{0.382}}{1+12.7*C_e^{0.07355}}$

Table 2. Adsorption isotherm results for the adsorption of Pb(II) ions onto UACUS

Isotherm model	Parameters	R^2	SSE	RMSE	Equation
Two parameter model					
Langmuir	q_m=175.9 (mg/g) K_L=0.1376 (L/mg)	0.9386	1022	15.98	$q_e=\frac{175.9*0.1376*C_e}{1+0.1376*C_e}$
Freundlich	K_F=43.77 ((mg/g)(L/mg)$^{(1/n)}$) n=2.921 (g/L)	0.9897	71.05	3.847	$q_e=43.77*C^{1/2.921}$
Three parameter model					
Langmuir-Freundlich	q_{mLF}=3503 (mg/g) K_{LF}=1.32 (L/mg) m_{LF}=0.3148	0.9891	172.3	6.543	$q_e=\frac{3503*(1.32*C_e)^{0.3148}}{1+(1.32*C_e)^{0.3148}}$
Fritz-Schlunder	q_{mF}=469 (mg/g) K_{FS}=1.866 (L/mg) α=0.6347	0.9866	223.6	8.634	$q_e=\frac{469*1.866*C_e}{1+(4691*C_e)^{0.6347}}$
Radke-Prausnitz	q_{mRP}=95.57 (mg/g) K_{RP}=0.336 m_{RP}=0.7975	0.9464	891.7	14.93	$q_e=\frac{95.57*0.336*C_e}{(1+0.336*C_e)^{0.7975}}$
Toth	q_{mT}=4.325 (mg/g) K_T=1.568 m_T=0.088	0.9835	275.4	9.581	$q_e=\frac{4.325*C_e}{\left(\frac{1}{1.568}+C_e^{0.088}\right)^{1/0.088}}$
Redlich peterson	α_{RP}=1.005 (L/mg)$^{1/\beta_{RP}}$ β_{RP}=0.7529 K_{RP}=65.85 (L/g)	0.9563	727.7	13.49	$q_e=\frac{66.85*C_e}{1+1.005*C_e^{0.7529}}$
Sips	α_s=1.337 (mg/g) K_S=85.01 (L/mg) β_S=0.9967	0.9592	679.3	13.03	$q_e=\frac{85.01*C_e^{0.9967}}{1+1.337*C_e^{1/0.9967}}$
Four parameter model					
Fritz-Schlunder	A=25.34 B=0.0066 α=0.6158 β=1.225	0.9512	812.3	16.45	$q_e=\frac{25.34*C_e^{0.6158}}{1+0.0066*C_e^{1.225}}$
Baudu	q_{m0}=56.52 b_0=1.221 x=4.278 y=0.2757	0.9476	872.8	14.77	$q_e=\frac{56.52*1.221*C_e^{(1+4.278+0.2757)}}{1+1.221*C_e^{(1+4.278)}}$
Five parameter model					
Fritz-Schlunder	q_{mFSS}=22.528 K_1=2.13 K_2=0.8718 m_1=0.1038 m_2=0.0206	0.9865	58.64	4.658	$q_e=\frac{22.528*2.13*C_e^{0.1038}}{1+0.8718*C_e^{0.0206}}$

adsorption isotherm parameter showed that R_L=0<1, which relates that adsorption process, was favorable adsorption. The Freundlich adsorption parameters K_F, n, R^2, SSE and RMSE were estimated from the plot of C_e and q_e (Fig. 4) and the results shown in Tables 1 and 2. The Freundlich exponent (n) value can be used to find the nature of the adsorption process (physical or chemical). Tables 1 and 2 show that n value was attained between 1 to 10, which indicates that the adsorption of Pb(II) ions onto the adsorbent material (SMCUS and UACUS) is a physical adsorption process. Furthermore, three-, four- and five-parameter model parameters, R^2, SSE and RMSE, were estimated from the plot of C_e and q_e (Fig. 4) and the results are shown in Tables 1 and 2. Among these, the two-parameter Freundlich adsorption isotherm model provided the higher correlation coefficient values (R^2=0.9965 and 0.9897 for SMCUS and UACUS) and low error values (SSE=21.7 and RMSE=2.115 and SSE=71.05 and RMSE=3.847 for SMCUS and UACUS), which suggests that the adsorption of Pb(II) ions onto the adsorbent was of multilayer adsorption. This further indicates that the

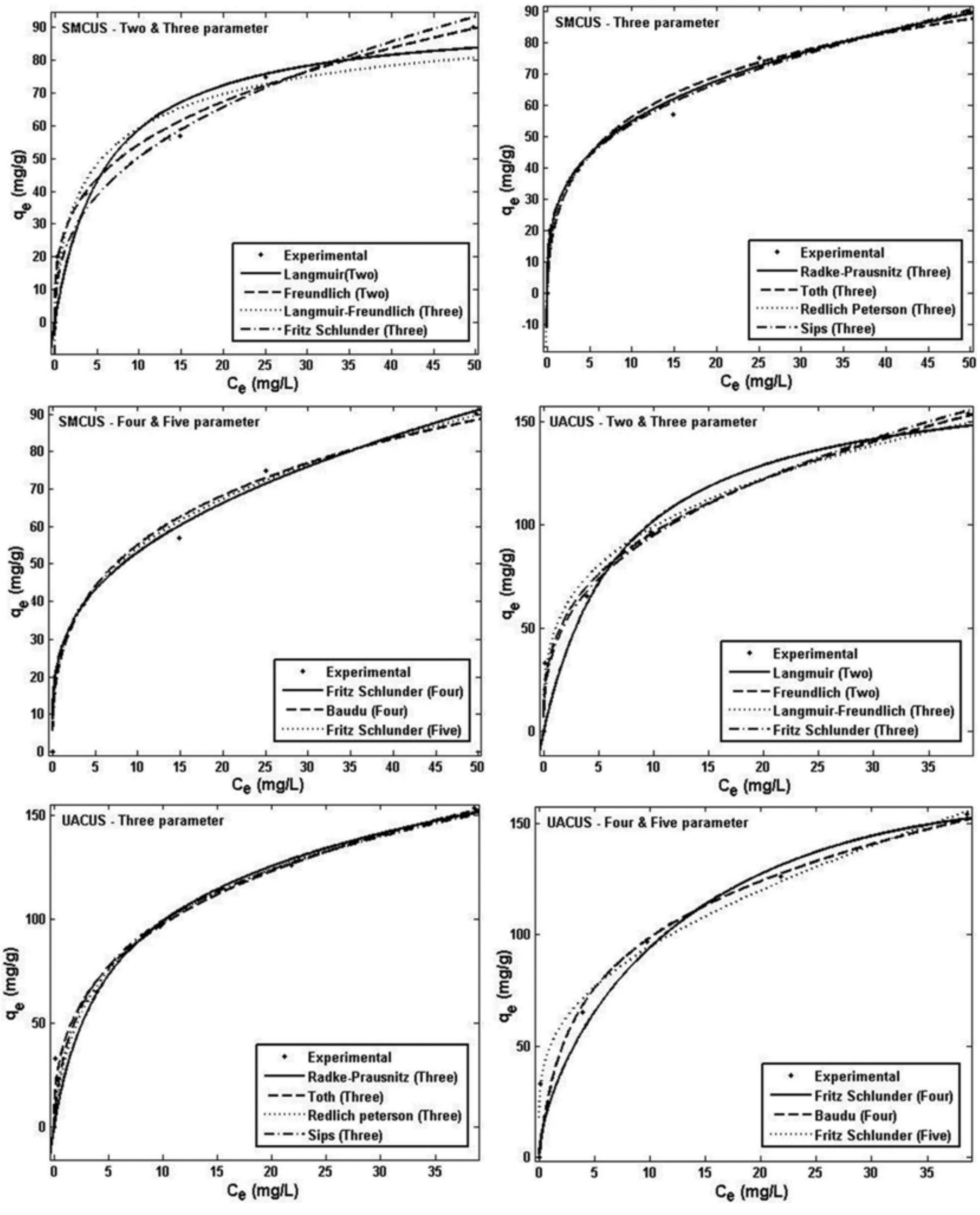

Fig. 4. Adsorption isotherm study on the adsorption of Pb(II) ions onto the SMCUS & UACUS.

adsorbent possesses heterogeneous surface properties. The Freundlich model gave an empirical expression representing the isothermal variation of adsorption of Pb(II) ions adsorbed per unit mass of adsorbent (SMCUS and UACUS), which shows that adsorption process was of physical nature. The maximum monolayer adsorption capacity of the SMCUS and UACUS was found to be 93.7 and 175.9 mg/g, respectively.

5. Effect of Adsorbent Dosage

Adsorbent dose is an important process parameter for the adsorption of Pb(II) ions from the aqueous solution, which determines the adsorption capacity of an adsorbent material (SMCUS and UACUS). The results of the effect of adsorbent dose studies are shown in Fig. 5(a)-(b). From Fig. 5(a)-(b), the removal of Pb(II) ions increased with an increase of adsorbent dosage. It might be possibly due to the availability of more binding sites on the surface of the adsorbent material and the available active sites [44]. The maximum percentage removal of Pb(II) ions was attained at 0.5 g (99.15%) and 0.3 g (99.22%) for SMCUS and UACUS, respectively. As further boost up in the adsorbent dosage, the percentage removal was maintained as constant. This indicates that the 0.5 g of SMCUS and 0.3 g of UACUS were found to be an optimum adsorbent dose for the present adsorption system.

6. Effect of Temperature

The effect of temperature on the adsorption of Pb(II) ions was

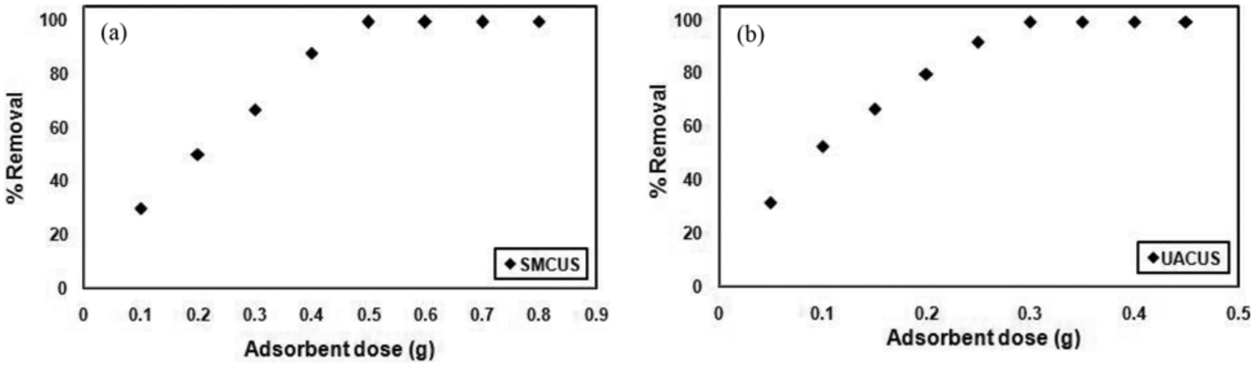

Fig. 5. (a) Effect of adsorbent dose on the adsorption of Pb(II) ions onto the SMCUS (Pb(II) ions concentration=100 mg/L, solution pH=5.0, volume of sample=100 mL, temperature 30 °C, time=45 min). (b) Effect of adsorbent dose on the adsorption of Pb(II) ions onto the UACUS (Pb(II) ions concentration=100 mg/L, solution pH=5.0, volume of sample=100 mL, temperature=30 °C, time=30 min).

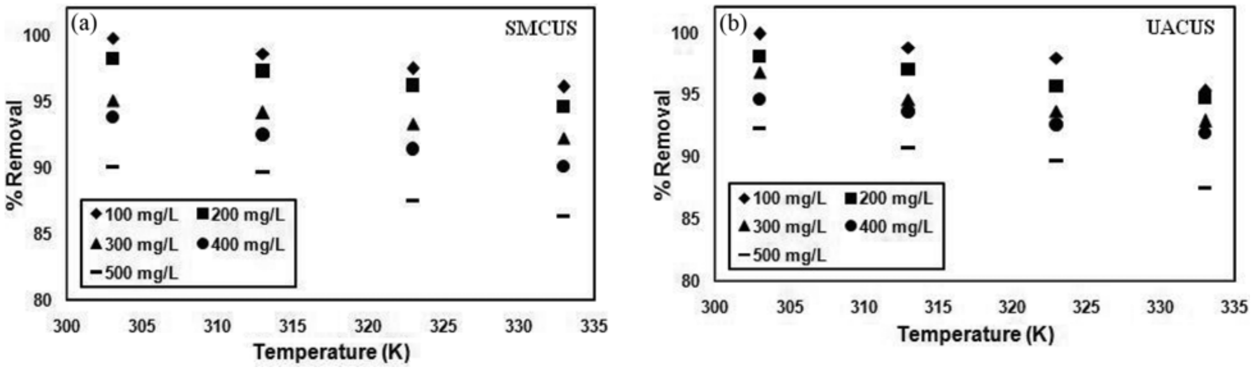

Fig. 6. (a) Effect of temperature on the adsorption of Pb(II) ions onto the SMCUS (Pb(II) ions concentration=100 mg/L, adsorbent dose=0.5 g, solution pH=5.0, volume of sample=100 mL, time=45 min). (b) Effect of temperature on the adsorption of Pb(II) ions onto the UACUS (Pb(II) ions concentration=100 mg/L, adsorbent dose=0.3 g, solution pH=5.0, volume of sample=100 mL, time=30 min).

studied and the results are shown in Fig. 6(a)-(b). From Fig. 6(a)-(b), the removal of Pb(II) from aqueous solution was decreased with an increase in the temperature, which indicated that the adsorption process was exothermic in nature. Temperature is directly related to the kinetic energy of the metal ions in the liquid solution. As temperature increases, physical damage may occur on the adsorbent material and reduce its adsorption capacity; this might be possibly due to the weakening of adsorptive forces between the metal ions and the adsorbent material. The maximum removal of Pb(II) ions was attained at 30 °C for both SMCUS (99.72%) and UACUS (99.88%).

7. Thermodynamic Study

Thermodynamic behavior of the adsorption of Pb(II) ions onto the adsorbent (SMCUS and UACUS) was investigated by plotting the graph between the log K_c and 1/T [Fig. 7(a)-(b)], which gives valuable information about the nature of adsorption process such

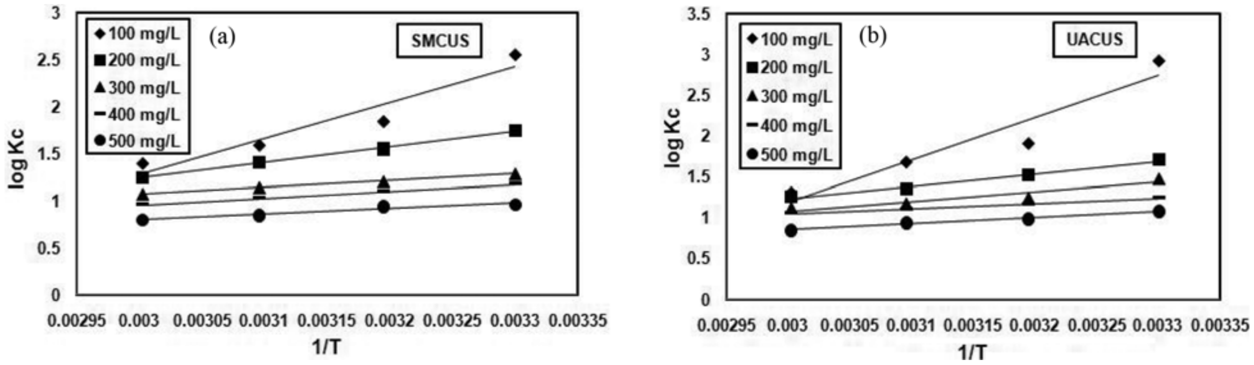

Fig. 7. (a) Thermodynamic study on the adsorption of Pb(II) ions onto the SMCUS. (b) Thermodynamic study on the adsorption of Pb(II) ions onto the UACUS.

Table 3. Thermodynamic parameters for the adsorption of Pb(II) ions onto adsorbents

			SMCUS				
Metal ions	Conc of Pb(II) ion solution (mg/L)	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)	ΔG^o (kJ/mol)			
				30 °C	40 °C	50 °C	60 °C
Pb(II)	100	−73.123	−194.92	−14.800	−10.997	−9.772	−8.834
	200	−31.420	−70.61	−10.060	−9.249	−8.656	−7.910
	300	−13.533	−20.12	−7.444	−7.211	−7.049	−6.830
	400	−13.977	−23.68	−6.821	−6.519	−6.333	−6.098
	500	−11.007	−17.73	−5.549	−5.626	−5.213	−5.088
			UACUS				
Metal ions	Conc of Pb(II) ion solution (mg/L)	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)	ΔG^o (kJ/mol)			
				30 °C	40 °C	50 °C	60 °C
Pb(II)	100	−98.799	−273.61	−16.939	−11.413	−10.370	−8.313
	200	−29.276	−64.45	−9.842	−9.063	−8.292	−7.970
	300	−22.479	−46.89	−8.549	−7.426	−7.226	−7.094
	400	−12.202	−16.64	−7.193	−6.968	−6.766	−6.713
	500	−14.489	−27.21	−6.250	−5.911	−5.806	−5.374

as endothermicity or exothermicity, randomness and spontaneity [45]. Table 3 shows the thermodynamic parameters such as changes in free energy (ΔG^o), changes in entropy (ΔS^o) and changes in enthalpy (ΔH^o) for the adsorption of Pb(II) ions onto the adsorbent. The entropy change (ΔS^o) and the enthalpy change (ΔH^o) can be calculated from the slope and intercept value of van't Hoff plot of ln K_c vs 1/T. As illustrated from Table 3, the negative value of Gibbs free energy (ΔG^o) indicated that the adsorption process was spontaneous. If the Gibbs free energy (ΔG^o) value is more negative with decreasing temperature, it makes the adsorption process easier. If the Gibbs energy value (ΔG^o) is in the range of −80 to −400 kJ mol^{-1} it indicates that chemical adsorption is involved in the process. But in this study, the value of Gibbs free energy (ΔG^o) was less than −20 KJ mol^{-1}; therefore, the adsorption of Pb(II) ions on the adsorbent was a physical adsorption process. The negative value of entropy (ΔS^o) at different temperature indicates that the decrease in the degree of freedom of the adsorbed Pb(II) ions and advises the decrease in the Pb(II) ion concentration in the liquid-solid interface, which shows the increase in the Pb(II) ion concentration on the adsorbent material. The negative value of enthalpy (ΔH^o) corresponds to the adsorption of Pb(II) ions onto the adsorbent is an exothermic process.

8. Effect of Contact Time

The contact time between the metal ions (liquid phase) and the surface of the adsorbent material (solid phase) is an important parameter for the adsorption process. The effect of contact time on the adsorption of Pb(II) ions onto the adsorbent was investigated and the results are shown in Fig. 8(a)-(b). It can be seen from Fig. 8(a)-(b), the removal of Pb(II) ions was highly increased at the initial stage of contact time and attained the maximum removal of Pb(II) ions at 45 min (99.72%) for SMCUS and 30 min (99.88%) for UACUS. It might be possibly due to the availability of large

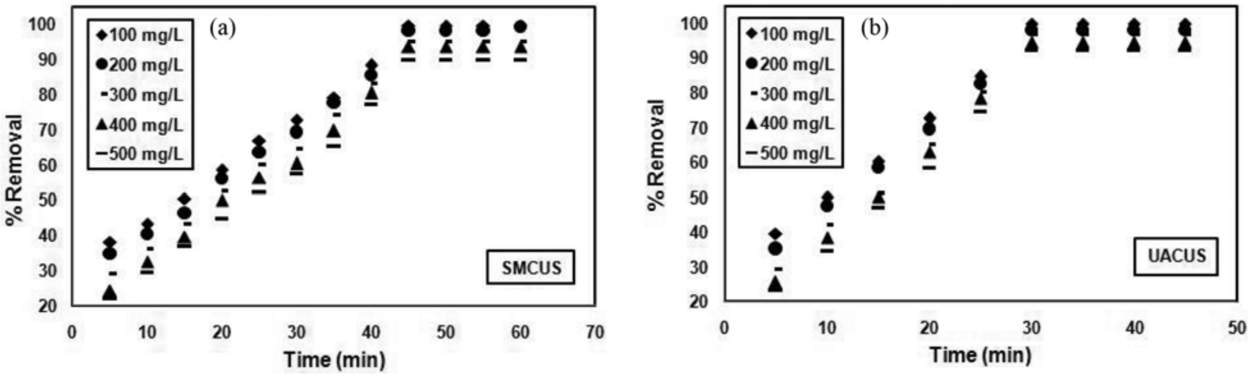

Fig. 8. (a) Effect of contact time on the adsorption of Pb(II) ions onto the SMCUS (Pb(II) ions concentration=100 mg/L, adsorbent dose=0.5 g, solution pH=5.0, temperature=30 °C, volume of sample=100 mL). (b) Effect of contact time on the adsorption of Pb(II) ions onto the UACUS (Pb(II) ions concentration=100 mg/L, adsorbent dose=0.3 g/L, solution pH=5.0, temperature=30 °C, volume of sample=100 mL).

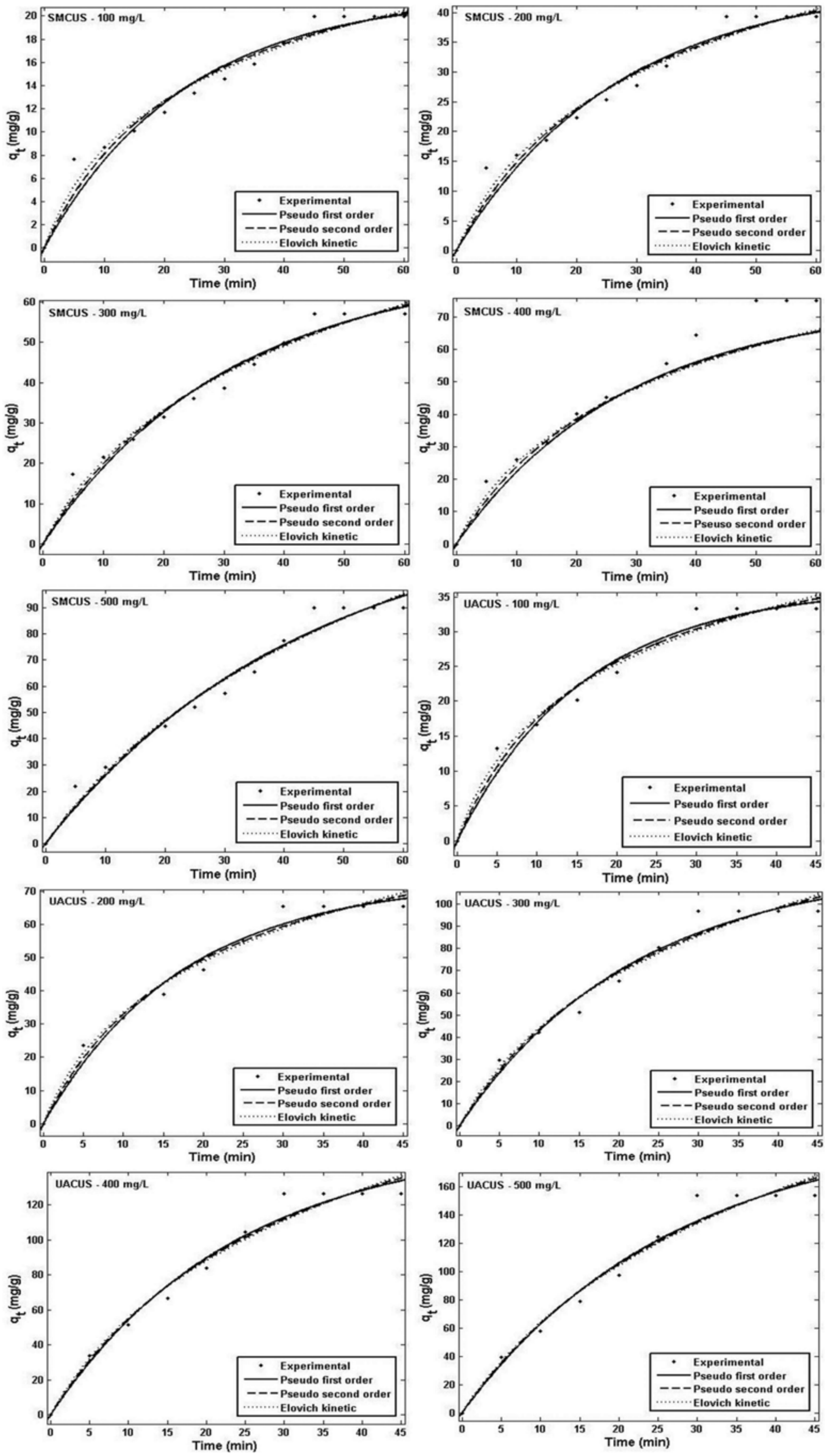

Fig. 9. Adsorption kinetic fit on the adsorption of Pb(II) ions onto the SMCUS & UACUS.

Table 4. Adsorption kinetic results for the adsorption of Pb(II) ions onto adsorbents

Adsorption kinetics	SMCUS				
	100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
Pseudo first order	$q_{e,exp}$ (mg/g)=19.982 $q_{e,cal}$ (mg/g)=21.8 k_1 (min^{-1})=0.0423 R^2=0.9791 SSE=11.52 RMSE=1.032	$q_{e,exp}$ (mg/g)=39.6902 q_e (mg/g)=44.9 k_1 (min^{-1})=0.0369 R^2=0.9721 SSE=67.79 RMSE=2.483	$q_{e,exp}$ (mg/g)=57.082 q_e (mg/g)=68.7 k_1 (min^{-1})=0.0322 R^2=0.9782 SSE=110.1 RMSE=3.163	$q_{e,exp}$ (mg/g)=75.047 q_e (mg/g)=74.12 k_1 (min^{-1})=0.035 R^2=0.8874 SSE=3486 RMSE=17.8	$q_{e,exp}$ (mg/g)=90.088 q_e (mg/g)=126.8 k_1 (min^{-1})=0.023 R^2=0.9791 SSE=255.4 RMSE=4.818
Pseudo second order	q_e (mg/g)=29.11 k_2 (g/mg·min)=0.0013 R^2=0.9645 SSE=15.79 RMSE=1.198	q_e (mg/g)=61.85 k_2 (g/mg·min)=0.0005 R^2=0.9674 SSE=58.37 RMSE=2.303	q_e (mg/g)=98.21 k_2 (g/mg·min)=0.00026 R^2=0.9748 SSE=99.81 RMSE=3.012	q_e (mg/g)=101 k_2 (g/mg·min)=0.00030 R^2=0.8726 SSE=3420 RMSE=17.63	q_e (mg/g)=196.3 k_2 (g/mg·min)=0.00007 R^2=0.9764 SSE=215.7 RMSE=4.783
Elovich kinetic	α_E (mg/g·min)=0.069 β_E (g/mg)=2.601 R^2=0.9725 SSE=12.22 RMSE=1.054	α_E (mg/g·min)=0.018 β_E (g/mg)=7.138 R^2=0.9707 SSE=48.83 RMSE=2.107	α_E (mg/g·min)=0.0071 β_E (g/mg)=12.83 R^2=0.9774 SSE=89.38 RMSE=2.851	α_E (mg/g·min)=0.01004 β_E (g/mg)=12.39 R^2=0.879 SSE=3368 RMSE=17.5	α_E (mg/g·min)=0.0015 β_E (g/mg)=30.3 R^2=0.9769 SSE=246.3 RMSE=4.732
Adsorption kinetics	UACUS				
	100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
Pseudo first order	$q_{e,exp}$ (mg/g)=33.303 q_e (mg/g)=36.48 k_1 (min^{-1})=0.062 R^2=0.9855 SSE=21.48 RMSE=1.653	$q_{e,exp}$ (mg/g)=65.3891 q_e (mg/g)=73.22 k_1 (min^{-1})=0.0572 R^2=0.9811 SSE=88.5 RMSE=3.326	$q_{e,exp}$ (mg/g)=96.793 q_e (mg/g)=116.9 k_1 (min^{-1})=0.045 R^2=0.9777 SSE=233.2 RMSE=5.399	$q_{e,exp}$ (mg/g)=126.105 q_e (mg/g)=157.4 k_1 (min^{-1})=0.042 R^2=0.9801 SSE=367.1 RMSE=6.774	$q_{e,exp}$ (mg/g)=153.8622 q_e (mg/g)=202.7 k_1 (min^{-1})=0.0379 R^2=0.9761 SSE=672.4 RMSE=9.168
Pseudo second order	q_e (mg/g)=48.47 k_2 (g/mg·min)=0.00115 R^2=0.9774 SSE=25.34 RMSE=1.78	q_e (mg/g)=99.56 k_2 (g/mg·min)=0.00049 R^2=0.9802 SSE=88.33 RMSE=3.323	q_e (mg/g)=168.8 k_2 (g/mg·min)=0.00021 R^2=0.9756 SSE=254.6 RMSE=5.641	q_e (mg/g)=233 k_2 (g/mg·min)=0.00013 R^2=0.9771 SSE=421.2 RMSE=7.256	q_e (mg/g)=309.6 k_2 (g/mg·min)=0.00008 R^2=0.9734 SSE=748.6 RMSE=9.673
Elovich kinetic	α_E (mg/g·min)=0.0518 β_E (g/mg)=5.012 R^2=0.9784 SSE=24.29 RMSE=1.742	α_E (mg/g·min)=0.0172 β_E (g/mg)=11.93 R^2=0.9796 SSE=91.06 RMSE=3.374	α_E (mg/g·min)=0.00516 β_E (g/mg)=23.32 R^2=0.9737 SSE=274.5 RMSE=5.858	α_E (mg/g·min)=0.00289 β_E (g/mg)=34.05 R^2=0.9744 SSE=471.8 RMSE=7.68	α_E (mg/g·min)=0.00159 β_E (g/mg)=47.79 R^2=0.971 SSE=816.9 RMSE=10.11

number of binding sites on the surface of the adsorbent material initially. Beyond the contact time of 45 min for SMCUS and 30 min for UACUS, the removal of Pb(II) ions increased slowly until equilibrium was reached, because the accessibility of binding active sites was steadily tapered and damage of driving force.

9. Exploration of Adsorption Kinetics

The adsorption kinetics for the removal of Pb(II) ions from the aqueous solution was performed to establish the adsorption rate and the controlling mechanism for the adsorption process. In this study, the adsorption kinetics of the adsorption of Pb(II) ions onto the adsorbents (SMCUS and UACUS) was examined by using different adsorption kinetic models, such as pseudo-first order, pseudo-second order and Elovich kinetic model and the results are presented in Fig. 9. The adsorption kinetic parameters, correlation coefficient values (R^2) and error values [SSE (sum of squared errors), RMSE (root mean squared values)] are listed in Table 4. The best fitted adsorption kinetic model was identified based on the correlation coefficient value (R^2) and the comparison between the calculated adsorption capacity (q_e, cal) and experimental equilibrium adsorption capacity (q_e, exp) [46]. The results showed that the calculated adsorption capacity (q_e, cal) values of the pseudo-first order kinetic model were closer to the experimental adsorption capacity (q_e, exp) values and Table 4 shows that the pseudo-first order kinetic model has higher correlation coefficient values (R^2=0.9791 and 0.9855 for SMCUS and UACUS) and low error values (SSE=11.52 and RMSE=1.032 and SSE=21.48 and RMSE=1.653 for SMCUS and UACUS) when compared to other models. This suggests that the adsorption of Pb(II) ions onto the adsorbent (SMCUS and

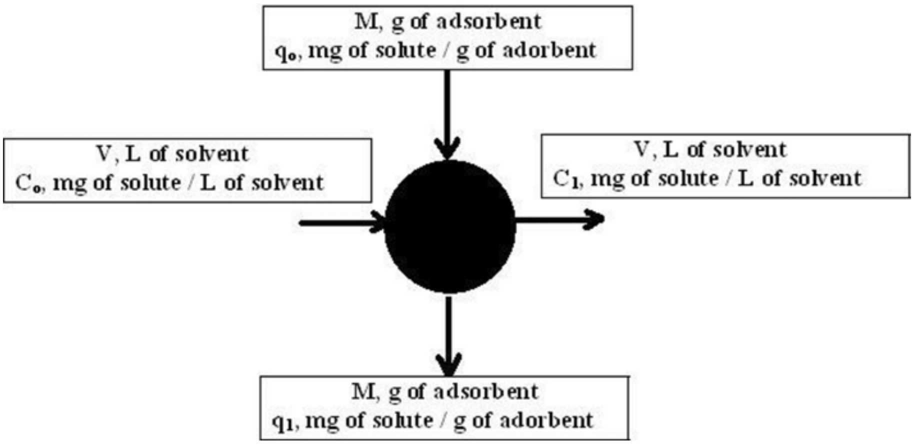

Fig. 10. Schematic diagram of a single-stage batch adsorber.

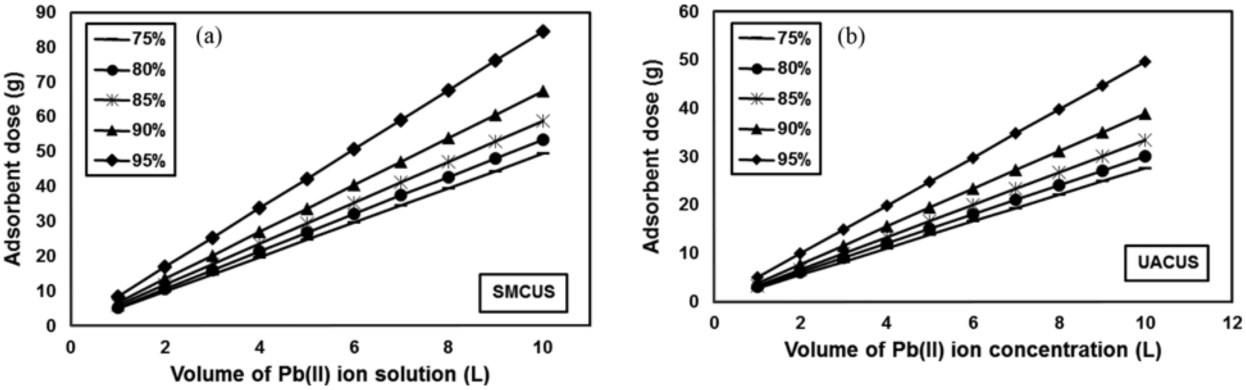

Fig. 11. (a) Design results of a single stage batch adsorber for SMCUS-Pb(II) ions system. (b) Design results of a single stage batch adsorber for UACUS-Pb(II) ions system.

UACUS) was fitted well with pseudo-first order kinetic model. The pseudo-first order kinetic model can be used to describe the kinetic process of liquid - solid phase adsorption. It describes the kinetic process based on adsorption capacity from solution concentration. The value of k_1 depends on the initial concentration of the adsorbate that varies from one system to another system, which indicates that the adsorption process is directly proportional to Pb(II) ion concentration involved in the process. The rate of process decreases linearly with an increase in the Pb(II) ion concentration.

10. Design of a Single Stage Batch Adsorber

The best fitted adsorption isotherm model, i.e., Freundlich model (for SMCUS and UACUS), was used to design the single stage batch adsorber for the treatment of Pb(II) ions wastewater. A schematic diagram for a single stage batch adsorber design is shown in Fig. 10. This design was used to determine the amount of adsorbent needed to treat the known volume of the desired Pb(II) ions concentration in the aqueous solution. The main intention of this proposed design is to reduce the Pb(II) concentration from C_o (mg/L) to C_e (mg/L) of solution volume V (L). The amount of adsorbent material (SMCUS and UACUS) used is M (g), and the Pb(II) ions adsorbed onto the adsorbent (SMCUS and UACUS) was changed from q_o (mg/g) to q_e (mg/g).

The mass balance for the single-stage batch adsorption system at equilibrium condition can be given as follows (at time t=0, q_o=0):

$$V(C_o-C_e)=M(q_e-q_o)=Mq_e \tag{21}$$

Freundlich isotherm model is the best fitted adsorption isotherm model for the Pb(II) ions onto the adsorbent (SMCUS and UACUS). The single-stage batch adsorber was designed by using the Freundlich adsorption isotherm model. Rearranging the Eq. (21) can be given as follows

$$M=\frac{(C_o-C_e)}{q_e}V=\frac{(C_o-C_e)}{K_F C_e^{1/n}}V \tag{22}$$

Fig. 11(a)-(b) shows that the linear plot of the amount of adsorbent (g) versus volume of the solution of initial Pb(II) ions concentration (L) of 300 mg/L for 75, 80, 85, 90 and 95% of removal at different solution volumes (1-10 L).

11. Performance Comparison Studies

The performance of the synthesized adsorbents (SMCUS and UACUS) was compared with the other studied materials for the removal of Pb(II) ions. The comparison results are shown in Table 5. The results show that the Langmuir monolayer capacity of the UACUS was found to be higher when it was compared with the other adsorbent materials.

Table 5. Performance comparison of adsorbents for Pb(II) ions removal

Adsorbent	Langmuir Monolayer adsorption capacity (mg/g)	References
GO-SBA	255.10	[48]
Ligand doped conjugate	188.67	[51]
UACUS	**175.9**	**This study**
Oak activated carbon	137	[54]
MHC/OMCNTs	116.3	[2]
Microwave assisted functionalized lignin	106	[50]
Sol-gel derived $MgO\text{-}SiO_2$	102.02	[8]
Manganoxide mineral	98	[53]
CARL	97.19	[47]
SMCUS	**93.7**	**This study**
y-Alumina	65.67	[6]
$MHNTs@MnO_2$	59.9	[52]
Magnetic ion-imprinted polymer	51.8	[49]
VAAC	17.77	[55]
Cedar leaf ash	7.23	[27]

CONCLUSION

From the experimental results we concluded that the surface modified fishtail palm *C. urens* seeds (SMCUS and UACUS) had sufficient adsorption properties for the removal of Pb(II) ions from aqueous solution in a batch adsorption process. Adsorption of Pb(II) ions onto the adsorbents (SMCUS and UACUS) was influenced by several process parameters, such as initial solution pH, initial Pb(II) ion concentration, temperature, contact time and biosorbent dosage. The maximum removal of Pb(II) ions for SMCUS (99.72%) and UACUS (99.88%) for an initial Pb(II) ion concentration of 100 mg/L occurred at the best working conditions: initial solution pH of 5.0, temperature of 30 °C, contact time of 45 min for SMCUS and 30 min for UACUS and adsorbent dosage of 0.5 g for SMCUS and 0.3 g for UACUS. The adsorption isotherm studies were examined by different adsorption isotherm models. Among the several models, the two-parameter Freundlich isotherm model was identified as a well suitable adsorption isotherm model for the adsorption of Pb(II) ions onto the adsorbents. The maximum monolayer adsorption capacity of the SMCUS and UACUS was found to be 93.7 and 175.9 mg/g, respectively. The adsorption kinetic study showed that the pseudo-first order kinetic was the best adsorption kinetic model, which afforded the best coefficient of determination values compared to other models, and the calculated adsorption capacity ($q_{e,cal}$) was very close to the experimental adsorption capacity ($q_{e,exp}$). The thermodynamic parameters indicated that adsorption was feasible, spontaneous, and exothermic. The single-stage batch adsorber was designed by using the two-parameter Freundlich isotherm data to determine the amount of adsorbent needed to treat the known volume and concentration of Pb(II) ions. From these observations, it can be concluded that *C. urens* seeds is an effective and low cost adsorbent for the removal of Pb(II) ions from aqueous solutions.

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