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Adsorptive removal of Pb^{2+} and Cu^{2+} from aqueous solution using an acid modified glucuronoxylan-based adsorbent

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ABSTRACT

This article reported the isolation of glucuronoxylan (GX) from seeds of *Cydonia oblonga* and conversion of GX to GX-succinate (SGX) and GX-succinate-Na, that is, Na-SGX. The Na-SGX was then used for the removal of Pb^{2+} and Cu^{2+} from aqueous solution. Fourier-transform infrared spectroscopic analysis confirmed the successful linkage of succinate moieties onto GX. Point-zero charge pH ($pH_{ZPC} = 5.2$) was determined to monitor the charge on Na-SGX surface with change in pH. The metal ion sorption aptitude of Na-SGX was found to be strongly depended on pH of aqueous solution (2–8), initial concentration of Pb^{2+} and Cu^{2+} in aqueous solution (50–450 mg L^{-1}), dose of sorbent (20–80 mg), time of contact between sorbent and sorbate (5–120 min), and operational temperature (298–343 K). To the available experimental sorption data, Langmuir isothermal, pseudo-second-order kinetic, and ion-exchange models were fitted nicely. Maximum theoretical sorption capacity (Q_{max}) as-calculated from Langmuir model was noted to be 555.55 and 294.11 mg g^{-1} for Pb^{2+} and Cu^{2+}, respectively. Moreover, the sorption process was spontaneous and exothermic. The re-generation and competitive metal sorption studies indicated that Na-SGX is an efficient supersorbent for the uptake of Pb^{2+} and Cu^{2+} ions from aqueous solution and could equally be used to stimulate galvanic waste water.

Keywords: Chemisorption; Glucuronoxylan, Ion-exchange; Succinylation; Langmuir isotherm; Regeneration

1. Introduction

The discharge of heavy metals into water bodies through industrial and agriculture activities poses lot of serious hazards to the living organisms [1]. Both lead (Pb^{2+}) and copper (Cu^{2+}) are very vital elements as they offer longstanding benefits to human beings. Pb^{2+} is most widely used in the preparation of batteries, plastic water pipes, beverages, ointments, etc. whereas Cu^{2+} is an essential precursor of electrical equipment [2–5]. Besides, it also uses as heat exchanger in industrial machinery [6]. In spite of their versatile applications, both of these heavy metals are tedious and causes failure of kidney, liver, reproductive system, and central nervous system once their concentration in drinking water exceed from permissible limits, that is, 0.05 mg L^{-1} Pb^{2+} and 1.3 mg L^{-1} Cu^{2+} as standardized by Word Health Organization (WHO) [7,8].

Thereby, to protect public health, aquatic life, and environment, the removal of these toxic heavy metals from

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aqueous solutions is imperative. For this purpose, many approaches, such as membrane filtration, nanofiltration, reverse osmosis, coagulation/flocculation [9–11], etc. have been proposed and applied by the researchers. However, all of these treatments suffer problems of pricing, mechanical loss of products, toxicity, slow kinetics and inadequate sorption capacities.

Hence, keeping in view the aforesaid problems of physical and chemical techniques, the use of adsorption involving ion-exchange deserve particular attention. Previously chemically treated activated carbon and some low cost cellulosic materials have been extensively used as adsorbents for removal of toxic pollutant from aqueous bodies [12–15]. However, these cellulosic materials contain different functional groups and it is difficult to assign that which type of functional group is responsible for metal uptake. Chemical modification of these materials might offer single types of functional groups which might provide ion-exchange sites for removal of toxic metal ions [16]. Glucuronoxylan isolated from *Mimosa pudica* was proved as an efficient adsorbent after its chemical modification for the uptake of cadmium (Cd^{2+}) from distilled water and ground water [17]. Therefore, there is an utmost need to introduce more efficient and selective sorbents with a single kind of functional group to obtain a defined and higher sorption capacity.

Seeds of *C. oblonga* (Syn: Bahidana/Quince) release mucilage/glucuronoxylan (GX) upon soaking in deionized water. The structure of glucuronoxylan is mainly composed of 4-*O*-methyl-α-D-glucupyranosyluronic acid and α-D-glucupyranosyluronic acid fractions. Both of these residues are connected through position 2 of a (1→4)-β-D-xylan [18]. It has been utilized as a material of descent choice for drug delivery and wound healing applications both in native and chemically modified form [19,20]. The GX isolated from *C. oblonga* (an economical, commercially available material) have never been used for removal of toxic pollutants from aqueous solution. The GX might offer single types of functionalities for efficient and selective removal of heavy metal ions from aqueous solution after its chemical modification.

Keeping in view the significant applications of glucuronoxylan (GX) isolated from different plant seeds, GX isolated from seeds of *C. oblonga* was chemically modified and then used as a novel material for water purification in this study. After isolation and purification, GX was then converted to sodium salt (Na-SGX) by treating it with succinic anhydride and followed by saponification with backing soda. The Na-SGX will be characterized by Fourier-transform infrared spectroscopy (FTIR) and pH_{ZPC} analyses. Batch studies will be carried out to monitor the influence of pH, initial metal ion concentration, sorbent dosage, time of contact, and temperature on Pb^{2+} and Cu^{2+} capturing tendency of Na-SGX. The results obtained by these batch experiments were then fitted to different sorption isotherms models, uptake-kinetics models, thermodynamics of sorption, and ion-exchange models. Furthermore, the effectiveness of Na-SGX for competitive removal of Pb^{2+} and Cu^{2+} from aqueous solution is also aimed. Regeneration studies will be carried out over five cycles of sorption and desorption.

2. Materials and methods

2.1. Materials

Seeds of fruit *C. oblonga* were purchased from the local market of District Sargodha, Sargodha Pakistan, and screened thoroughly from redundant materials prior to extrude mucilage (QH = GX). Solvents and reagents used to prepare sorbent and performed sorption experiments were of analytical grade (>99% pure). Succinic anhydride (SAn) was afforded by Alfa Aesar, Kandel Germany. *N,N*-dimethylacetamide (DMAc), and 4-dimethylaminopyridine (DMAP) was received as a gift from Riedel-de-Haën, Germany. Backing soda, HCl, NaOH, acetone, *n*-hexane, $NaNO_3$, $AgNO_3$, $Pb(NO_3)_2$ and $CuSO_4$ were obtained from Sigma-Aldrich, USA. Deionized water (DI) was used to prepare necessary solutions, dilutions, and to wash glassware's.

2.2. Isolation of hydrogel

After proper screening and sieving, *C. oblonga* seeds (150 g) were allowed to swell in deionized water (500 mL) for 2 h at ambient temperature and then warmed at 70°C for 15 min followed by stirring magnetically for a time period of 6 h. The mucilage extruded from seeds (QH = GX) was isolated using cotton cloth by squeezing with hand. Washing of resulted GX was carried out with *n*-hexane in replicates to get freedom from non-polar substances. GX thus obtained was further isolated in pellet form after centrifugation at 4,000 rpm for 2 h, dried in vacuum oven at 50°C for 48 h, passed through 60 mesh sieve, ground to finely divided powdered form, and stored in an airtight jar in a vacuum desiccator [14].

2.3. Synthesis of SGX and sorbent Na-SGX

SGX and Na-SGX were synthesized using already reported strategy [12]. Accordingly, the dried GX (2.0 g) was suspended in *N,N*-dimethylacetamide (DMAc, 30 mL) for 2 h at 80°C under continuous magnetic stirring at 150 rpm. The reaction was carried out under inert nitrogenous environment to homogenize the suspension of GX and DMAc. In the reaction mixture succinic anhydride (7.40 g) was added and stirred for next 8 h at 80°C and then cooled at room temperature. Glucoronoxylan-based succinate of *C. oblonga* hydrogel (SGX) was obtained by precipitating the reaction mixture in ethanol (200 mL). The precipitates were further purified in ethanol (250 mL) to eradicate unreactive succinic acid and succinic anhydride. SGX was dried under vacuum in an oven at 50°C for 1 h and ground to homogenize it in powder form.

Yield: 1.45 g (72%)

FTIR (KBr): 3,371 (–OH), 1,730 (C=Oester), 1,043 (–COC–) cm^{-1}

The saturated solution of backing soda ($NaHCO_3$) was prepared in DI and filtered to get its clear solution. The succinylated glucronoxylan (SGX) was added in this saturated solution and stirred for 1 h at room temperature to convert it into its sodium salt, that is, Na-SGX. The as-formed precipitates containing Na-SGX were filtered and washed with DI till the neutralization of filtrate.

Ultimately, the Na-SGX was dried in an oven under vacuum at 60°C and kept in an air-tight jar to characterize it and to use it as adsorbent for the uptake of Pb^{2+} and Cu^{2+} from aqueous solution [12].

FTIR (KBr): 3,371 (–OH), 1,730 (C=Oester), 1,043 (–COC–) cm^{-1}, 1,557 ($-COO^-$) cm^{-1}.

2.4. Determination of degree of succinylation value

The degree of succinylation value (DS) onto GX was determined using a standard acidimetric titration method after saponification [21]. Seeking to this connection, SGX (100 mg) was stirred in a solution of $NaHCO_3$ (0.02 M, 100 mL) at ambient temperature for 2 h. After that, the mixture was filtered and a known volume of $NaHCO_3$ solution was acquired to titrate it against HCl solution (0.02 M). To carry out this titration phenolphthalein was used as indicator. The net amount (V_{HCl}) of HCl consumed during its titration against $NaHCO_3$ (V_{NaHCO_3}) was put in Eq. (1) to calculate the total number of moles of free carboxylic acid moieties (n_{suc}) onto GX which were then put in Eq. (2) to determine the DS value.

$$n_{suc} = V_{NaHCO_3} \times M_{NaHCO_3} - V_{HCl} \times M_{HCl} \tag{1}$$

$$DS = \frac{162.14 \times n_{suc}}{m_{SGX} - 100 \times n_{suc}} \tag{2}$$

where M_{NaHCO_3} and M_{HCl} denoted the molarity of $NaHCO_3$ and HCl, respectively while m_{SGX} was taken as the mass of conjugate SGX in g. The factor 162.14 g mol^{-1} was grasped as the molar mass of an anhydrous glucose unit (AGU) presumed for every substituted succinyl moiety, and 100 g mol^{-1} is the overall increase in the mass of an AGU.

2.5. Calculation of yield

The theoretical yield of the esterification reaction between GX and succinic anhydride was calculated by putting the pre-calculated DS value of SGX in Eq. (3) [22]:

$$\text{Theoretical Yield} = m_{GX} + \left[\frac{m_{SGX}}{M_{SGX}} \times DS \times M_{Suc}\right] \tag{3}$$

where m_{GX} and m_{SGX} are the masses of repeating unit of GX and acidic sorbent, that is, SGX, respectively. These masses were measured in g. M_{SGX} and M_{Suc} embodies the molar masses of SGX and succinic anhydride, respectively and was taken in g mol^{-1}.

2.6. Characterization

Various analytical approaches were used to characterize the surface of GX before and after chemical modification to SGX and Na-SGX. FTIR (KBr) spectra of samples were recorded on FTIR Prestige-21 spectrophotometer (Shimadzu, Japan) to confirm the attachment of functional group, that is, carboxylic acid onto GX backbone. After each sorption experiment, the supernatant layer was collected and residual Pb^{2+} and Cu^{2+} concentrations were determined using optical radiation of fixed wavelength, that is, 327.70 for Pb^{2+} and 283.3 for Cu^{2+} at 228.8 nm using a flame (air-acetylene) atomic absorption spectrophotometer (FAAS, AA 6300, Shimadzu, Japan). The concentration of analyte was measured using Beer-Lambert law whereas the radiation flux was measured using the detectors of corresponding metals. Sorbent surface charge is one of the imperative parameter to judge the capabilities of sorbents for metal uptake. So, to determine point of zero charge pH (pH_{ZPC}), solid addition method as described by [23] was employed with necessary modification. Briefly, DI (100 mL) was taken in separate beakers and sodic form of sorbent (Na-SGX, 50 mg) was added in each beaker. The pH of solution was adjusted from 2–8 using HNO_3 (0.1 M) or NaOH (0.1 M) solutions. This pH corresponds to initial pH and designated as pH_i. These solutions were then shaken in shaking incubator for 2 h at ambient temperature and final pH (pH_f) of each solution was noted. The difference between pH_i and pH_f (pH_i–pH_f) was taken and plotted against pH_i. The point at which the plot intersect the *X*-axis corresponds to pH_{ZPC}.

2.7. Sorption studies

For the optimization of the experimental parameters, that is, the effect of pH, initial metal ion concentration, sorbent dosage, contact time, and temperature on the sorption of Pb^{2+} and Cu^{2+} ions, a batch series of experiments were performed at ambient temperature. FAAS was employed to assess the concentration of Pb^{2+} and Cu^{2+} before and after the experiment. A 1,000 ppm (1,000 mg L^{-1}, 1,000 mL) standard stock solution of both Pb^{2+} and Cu^{2+} was prepared separately by adding 1.60 g of $Pb(NO_3)_2$ and 1.855 g of $CuSO_4$ in DI to a 1-L Erlenmeyer volumetric flask. For proper and homogeneous mixing, solutions of both the tested metals were stirred magnetically and the pH of the solutions was adjusted using 0.1 M HCl or 0.1 M NaOH. The stock solutions of both the metals were further diluted as per requisites.

Solution containing metal ions of known concentration, that is, 250 mg L^{-1} for Pb^{2+} and 150 mg L^{-1} for Cu^{2+} were taken in Erlenmeyer flasks having 100 mL DI and shaken well in orbital shaking incubator (Orbital Shaking Incubator, PA-42/250R, PAMICO Equipment's, Faisalabad, Pakistan) for 30 min at ambient temperature followed by the addition of sorbent Na-SGX (50 mg). After that, solutions were filtered to separate the sorbent and the residual concentrations of Pb^{2+} and Cu^{2+} was measured by FAAS at 327.70 and 283.3 nm wavelengths, respectively in supernatant layer. The quantity of Pb^{2+} and Cu^{2+} captured by Na-SRG in mg g^{-1} and in % age was calculated using Eqs. (4) and (5):

$$q_e = \frac{C_i - C_e}{m} \times V \tag{4}$$

$$\text{Percentage uptake} = \frac{C_i - C_e}{C_i} \times 100 \tag{5}$$

where the q_e (mg g^{-1}) denoted the equilibrium sorption capacity of Na-SRG. C_i and C_e represented the initial and residual concentration of Pb^{2+} and Cu^{2+} in mg L^{-1}, respectively. V (L) referred to the volume of the aqueous solution used for sorption studies and m (g) is the used mass of sorbent.

2.7.1. Effect of pH

To interpret the effect of pH, the pH of Pb^{2+} and Cu^{2+} based aqueous solutions was adjusted in the range 2.0–8.0 using HNO_3 (1 M) and NaOH (1 M) solution. Other sorption conditions were maintained at optimum level, that is, sorbent dosage 50 mg/100 mL, concentration of metal ions (250 mg L^{-1} for Pb^{2+} and 150 mg L^{-1} for Cu^{2+}), agitation speed 150 rpm, time of contact 30 min, and temperature 298 K. After filtration, the equilibrium concentrations of Pb^{2+} and Cu^{2+} were assessed by FAAS at their particular wavelengths.

2.7.2. Effect of initial metal ion concentration

Different amounts ranging from 50–450 mg L^{-1} in 100 mL of Pb^{2+} and 50–350 mg L^{-1} in 100 mL of Cu^{2+} concentration were used in batch experiments to study the influence of initial metal ion concentration on the sorption capacity of sorbent Na-SGX. The value of remaining key factors was kept constant, that is, pH 6.0 for Pb^{2+} and 5.5 for Cu^{2+}, dosage of sorbent (50 mg), temperature (298 K), contact time (30 min), and agitation speed (150 rpm). The data acquired from this parameter was fitted to Freundlich and Langmuir isothermal models to study the mechanism of sorption.

2.7.3. Effect of sorbent dose

To investigate the effect of sorbent dosage on the sorption Pb^{2+} and Cu^{2+} from aqueous solution, batch equilibrium sorption studies were conducted out over a sorbent dosage range of 20–80 mg/100 mL. The solution containing optimum concentrations of metal ions (250 mg L^{-1} for Pb^{2+} and 150 mg L^{-1} for Cu^{2+}) was stirred at a speed of 150 rpm at 298 K for 30 min.

2.7.4. Effect of contact time

An optimum amount of sorbent (50 mg) was suspended in 100 mL aqueous solutions containing 250 mg L^{-1} Pb^{2+} and 150 mg L^{-1} Cu^{2+}. The pH and temperature of metal-based solutions were maintained at 6.0 for Pb^{2+} and 5.5 for Cu^{2+} at 298 K, prior to stirring for 5–120 min at 150 rmp and the residual concentration of tested metals were determined on FAAS. The sorption data obtained from this effect was further fitted to pseudo-first-order and pseudo-second-order kinetic models to establish the sorption kinetics.

2.7.5. Effect of temperature

Sorption data acquired from temperature effect on any sorption process can be used to study the thermodynamic of sorption process. Therefore, to note the effect of temperature on the removal of Pb^{2+} and Cu^{2+} by Na-SGX, the temperature of solution was changed from 298–343 K followed by the stirring of 50 mg of sorbent in 100 mL solution containing 250 and 150 mg L^{-1} of Pb^{2+} and Cu^{2+}, respectively at a speed of 150 rpm at pre-optimized conditions of pH (6.0 for Pb^{2+} and 5.5 for Cu^{2+}) and time (30 min). The uptake capacity was measured by calculating percentage uptake of metal ions. To confirm the spontaneous and exothermic mode of sorption experimental data furnished after conducting experiments on different temperature was used as supportive data.

These experiments were also performed on acidic sorbent (SGX) to establish ion-exchange mechanism after comparing its sorption capacity with sodic sorbent (Na-SGX). Moreover, results were statistically verified by applying t-test.

2.8. Sorption/desorption tests

A regenerable sorbent is more economical and efficient in nature. Therefore, tests regarding sorption/desorption and sorbent regeneration were conducted at pre-optimized sorption conditions. In general, sodic sorbent, that is, Na-SGX (50 mg) was first suspended in Pb^{2+} (250 mg L^{-1}) and Cu^{2+} (150 mg L^{-1}) containing aqueous solutions for 30 min at 298 K. Suspension was then filtered, and centrifuged. Filtrate was run on FAAS and solid residues were allowed to cool at ambient temperature prior to treat with saturated solution of sodium chloride (brine, NaCl). Same protocol was applied again on regenerated sorbent and repeated for five cycles.

2.9. Competitive metal uptake

A binary solution containing both the tested metals, that is, Pb^{2+} and Cu^{2+} was prepared by mixing 250 mg L^{-1} Pb^{2+} based-aqueous solution having pH 6.0 and 150 mg L^{-1} Cu^{2+} based-aqueous solution having pH 5.5 in a 100 mL flask. An optimum amount of Na-SGX (50 mg) was added to it and magnetically stirred for a time period of 30 min at 298 K temperature. The material of flask was allowed to settle and then filtered, and centrifuged. The absorbance of supernatant was first measured at 327.70 nm and then at 283.3 nm. In this way the effect of each metal ion was predicted in the presence of other metal. Later, the ratio of sorption capacities of binary mixture (q^{mix}) to the sorption capacity of metal ions present alone ($q°$) in the aqueous solutions was calculated to observe the effect of background ions on sorption capacities. In a case where $q^{mix}/q°$ appeared as greater than 1, then it shows increase in sorption capacities. Converse is also true.

3. Results and discussions

3.1. Synthesis of SGX and sorbent Na-SGX

Two different conjugates of GX, that is, acidic (SGX) and sodic (Na-SGX) were prepared by a succinylation reaction scheme to determine their affinity for exchange of ions (hydrogen and sodium) with Pb^{2+} and Cu^{2+} present in aqueous solutions (Fig. 1). The yield (1.45 g, 72%) and degree of succinylation (DS = 2.3) were counted on behalf of SGX. The tests regarding solubility of both the newly fabricated conjugates were also conducted in different solvents, such as deionized water, ethanol,

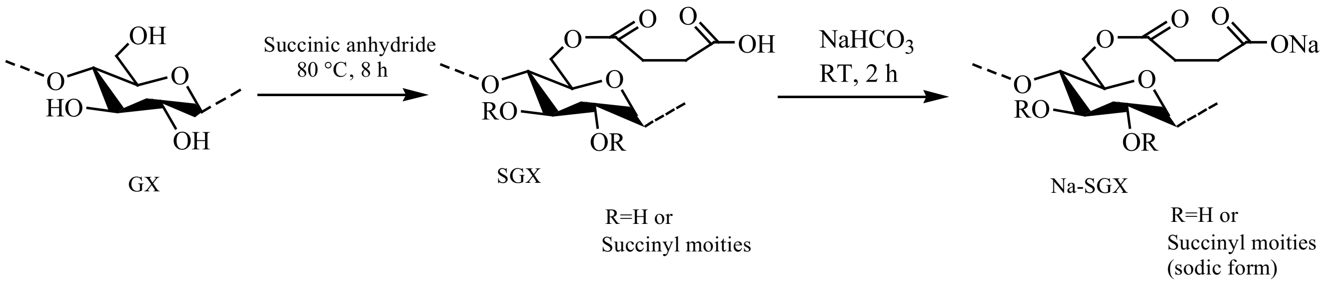

Fig. 1. Synthesis of sorbents SGX and Na-SGX taking glucose as a model monomer of GX.

methanol, *n*-hexane, acetone, etc. and found entirely insoluble. Therefore, based on this assumption SGX and Na-SGX could be descent choice for the water purification.

3.2. FTIR spectroscopic analysis

To ensure the successful grafting of succinic acid onto GX, FTIR (KBr) spectra of GX, SGX, and Na-SGX were recorded (Fig. 2) and distinct features were illustrated. A novel peak at wavenumber 1,730 cm^{-1} and 1,728 cm^{-1} due to carbonyl bond (C=O) of carboxylic acid and ester appeared in the spectra of SGX and Na-SGX, respectively confirmed the incorporation of succinate moieties on GX backbone [24]. Besides, a concomitant and prominent peak at 1,564 cm^{-1} can be seen in the spectrum of Na-SGX due to formation of ester linkage (–COO$^-$) also confirmed the conversion of SGX to Na-SGX [25]. Additionally, the presence of signals at 3,423 (–OH), 2,895 (–CH$_2$), and 1,045 (–COC–) cm^{-1} because of stretching vibrations in the spectrum of Na-SGX may identify its polymeric getup.

3.3. Determination of zero-point charge pH

5.2 is the zero-point charge pH (pH$_{ZPC}$) obtained for sorbent Na-SGX using solid addition method (Fig. 3a). This value equally suggested the presence of weak acidic character of sorbent due carboxylic acid groups. In such cases where pH < pH$_{ZPC}$, the sorbent surface is saturated with positively charged particles and retarded the sorption whereas in those cases where pH > pH$_{ZPC}$, the sorbent offered negative charge on its surface and can attract the positively charged metal ions of sorbate, hence sorption is feasible [22].

3.4. Sorption studies

3.4.1. Effect of pH

pH value of solution is an important parameter while describing the behavior of sorbent towards metal ions during sorption process. We can predict the sorbent surface charge, degree at which sorbent can ionize, and chances of

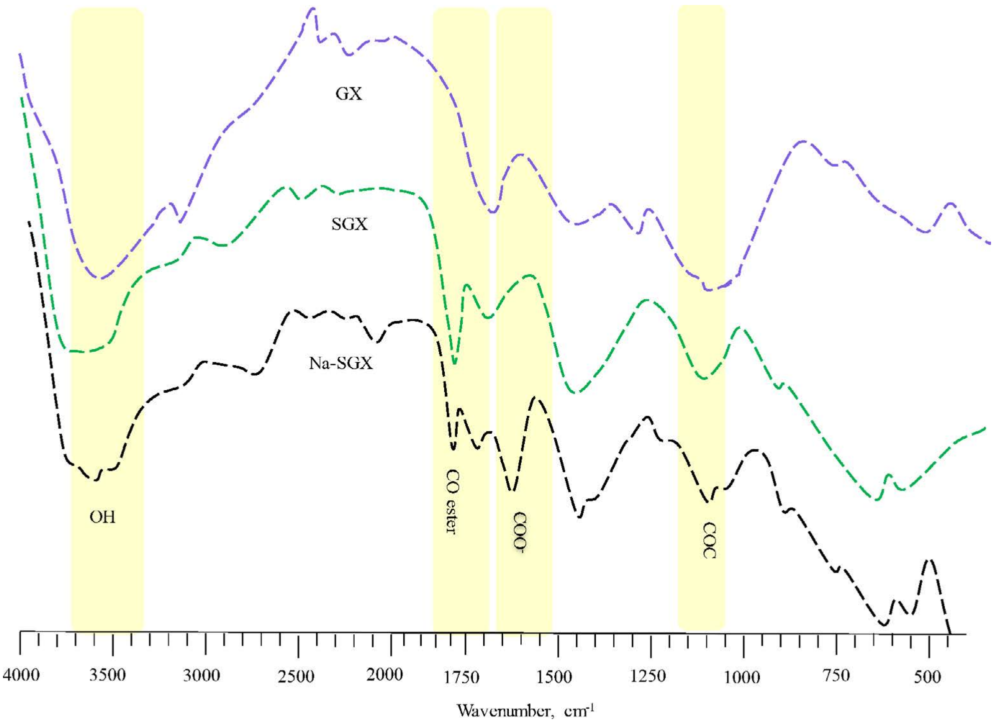

Fig. 2. Overlay FTIR (KBr) spectra of GX, SGX, and Na-SGX.

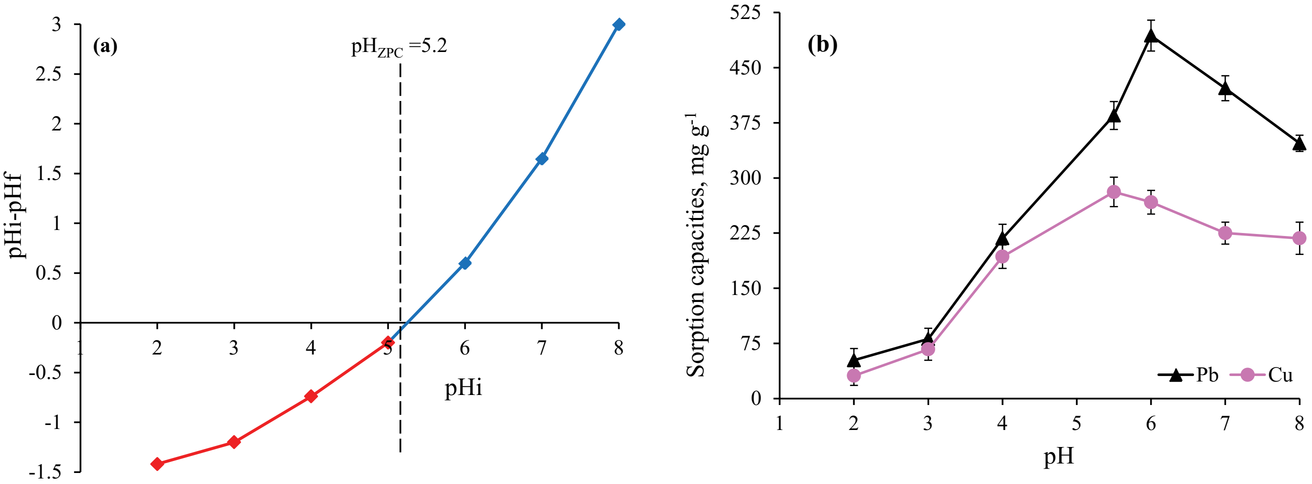

Fig. 3. Zero-point charge pH (pH$_{ZPC}$) estimation of Na-SGX (a), and effect of pH (2–8) (b) on ability of Na-SGX to remove Pb^{2+} and Cu^{2+} from aqueous solution (Optimum sorption conditions for Pb^{2+}: pH = 6, concentration = 250 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution; optimum sorption conditions for Cu^{2+}: pH = 5.5, concentration = 150 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution).

diffusion between liquid–solid (sorbent–sorbate) at interface layer by knowing the effect of pH on metal sorption from aqueous solution. Since, pH effect was elucidated within pH range 2–8 at pre-optimized sorption conditions, that is, concentration of metal ion (250 mg L^{-1} of Pb^{2+} and 150 mg L^{-1} of Cu^{2+}), sorbent dose (50 mg), and interaction time (30 min), and temperature (298 K). Graphical representation of q_e vs. pH indicated that at lower pH, that is, pH ≤ 3.0 only a small fragments of both the targeted metal ions removed by Na-SGX. However, once the solution pH > 3.0 then q_e values were lifted to higher degree and reached maximum at 6.0 and 5.5 for Pb^{2+} and Cu^{2+}, respectively. After that optimized pHs, the q_e values were lifted significantly to lower degree (Fig. 3b). Hence, pH = 6.0 for Pb^{2+} sorption and 5.5 for Cu^{2+} sorption were picked as ideal pHs to conduct other experiments in this present investigation. The possible reason behind underlying trends might be that at lower pH, the acidic contents (carboxylic acids) present in the solution were increased due to the protonation of Na-SGX to SGX. Conversely, at higher pH the chances of protonation reduces and SGX gets de-protonation to Na-SGX. Hence, possess more sites for metal uptake in sodic form rather acidic and sorbed more and more metal ions [26]. Moreover, as increase in q_e was observed at pH > pH$_{ZPC}$, this might also explain the fact that sorbent occupied negatively charge at its surface and can attract positively charged metallic species from aqueous solutions and favourable to purify water from Pb^{2+} and Cu^{2+} [12].

3.4.2. Effect of initial metal ion concentration

In this study, the dependency of Pb^{2+} and Cu^{2+} sorption by Na-SGX as a function of concentration was evaluated. The concentrations of Pb^{2+} and Cu^{2+} were varied from 50–450 mg L^{-1} and 50–350 mg L^{-1} in 100 mL solution, respectively and the data regarding concentration of metal ions sorbed by Na-SGX from aqueous solution and concentration of metal ions left behind in aqueous solution as analyte was acquired on FASS. After plotting equilibrium sorption capacity (q_e, mg g^{-1}) vs. initial metal ion concentration (C_i, mg L^{-1}) it was noted that at the start once the concentration of Pb^{2+} increased from 50 to 250 mg L^{-1} and Cu^{2+} from 50 to 150 mg L^{-1}, the q_e increases. At 250 mg L^{-1} of Pb^{2+} and 150 mg L^{-1} of Cu^{2+} the equilibrium was achieved and maximum quantity of both the targeted metal ions loaded onto Na-SGX. Later, no more prominent increase in q_e was observed as can be evidenced from Fig. 4a. The main factor controlling the loading of metal ions after equilibrium, is actually the saturation of Na-SGX surface with Pb^{2+} and Cu^{2+} ions. Therefore, at lower concentration of metal ions more activities were available for metal sorption through exchange of ions and after equilibrium these activities became shorter in number and degree of ionic exchange supressed [27]. That is why first q_e increases and then became constant in our study.

3.4.3. Effect of sorbent dosage

Surface area of sorbent plays crucial role in deciding the rate of sorption, that is, greater the surface area greater will be the amount of metal get adsorbed and vice versa. Thus, the optimization of sorbent amount is necessary to develop an ideal filter for water purification. In this investigation, we came to know that at early stage, that is, at low amount of sorbent (20–50 mg/100 mL), more and more Pb^{2+} and Cu^{2+} ions sorbed on Na-SGX and after 50 mg of sorbent dose the q_e decreases sharply (Fig. 4b). The increase in q_e was observed at beginning due greater surface area of sorbent and greater surface area provides more sites for exchange of ions in the aqueous solution. But beyond an optimum dose (50 mg), the sorption sites of Na-SGX gets occupied and hindered the sorption of more metal ions by offering small number of surface sites [28]. Hence, we observed aforesaid trend.

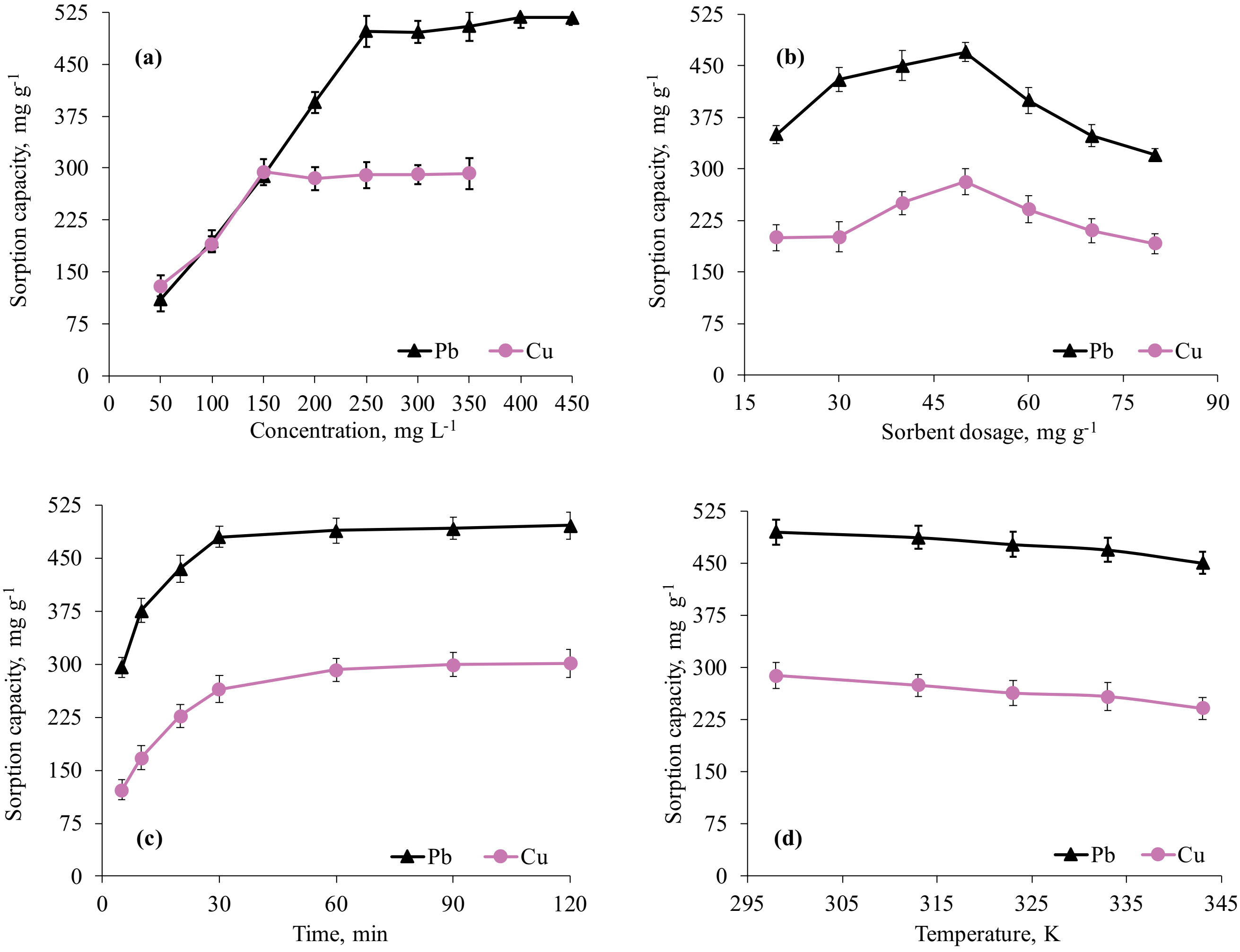

Fig. 4. Effect of initial concentration of metal ions (a), sorbent dosage (b), contact time (c), and temperature (d) on ability of Na-SGX to remove Pb^{2+} and Cu^{2+} from aqueous solution (Optimum sorption conditions for Pb^{2+}: pH = 6, concentration = 250 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution; optimum sorption conditions for Cu^{2+}: pH = 5.5, concentration = 150 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution).

3.4.4. Effect of contact time

The exact time at which sorbent interact with metallic species of sorbate not only help to study the rate of sorption process but also favour in describing the sorption mechanism. To interpret this effect, sorption experiments were performed within time intervals of 5–120 min. Results demonstrated in Fig. 4c indicated that at the beginning the rate of sorption was rapid enough so that more than 85% of both the metal ions were removed by Na-SGX ions in 20 min only from aqueous solution because at the beginning the number of succinate group present in excess on Na-SGX surface and responsible for ionic exchange. However, sorption takes 30 min to achieve equilibrium. After that no more obvious increase in sorption was noticed and it is evidenced from nearly parallel steepness of curves to *X*-axis because with the passage of time forces of repulsion might operate between ions of Pb^{2+} and Cu^{2+} and water molecules [20]. Consequently, sorbent surface is no more available to sorb more ions of tested metals from aqueous solutions.

3.4.5. Effect of temperature

From the estimation of metal ion sorption onto sorbent as a function of temperature one can estimate the sorption thermodynamics. For this purpose, we evaluated the effect of temperature on Pb^{2+} and Cu^{2+} removal efficiency of Na-SGX from aqueous environment. Temperature range selected was 298 to 343 K. Obtained results address that by increasing temperature from 298 to 343 K, the affinity of Na-SGX to capture Pb^{2+} (45 mg g^{-1}) and Cu^{2+} (47 mg g^{-1}) decreases. The maximum uptake was appeared at 298 K, that is, 495.2 mg g^{-1} of Pb^{2+} and 288.13 mg g^{-1} of Cu^{2+} (Fig. 4d). Therefore, it can be extrapolated that the current sorption process was exothermic. The reason of this reciprocation is actually the lowering of kinetic energy at low temperature which in turn enhanced the interaction between Na-SGX and metallic species of sorbate. However, high temperature reduces these interactions by increasing kinetic energy and offer high sorption onto Na-SGX [25].

3.5. Isothermal modelling

The equilibrium sorption data obtained previously from experiments conducted to expose the influence of different concentrations of Pb^{2+} and Cu^{2+} in aqueous solutions on the aptitude of Na-SGX to capture said metal ions was further fitted to Freundlich and Langmuir sorption isotherms. This could map-up to intimate the ideal conditions for the maximum removal of Pb^{2+} and Cu^{2+}, physical or chemical nature of sorption, and feasibility of sorption by forming monolayer or multilayer. Moreover, the possible interactions between solid and liquid phases, that is, sorbent and sorbate has also been exploited from this study. Eqs. (6) and (7) present the linear form of Freundlich and Langmuir isotherms.

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{6}$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times b} \tag{7}$$

where q_e, C_e, and $Q_{\max}$ were taken as the experimental sorption capacity at equilibrium, concentration of Pb^{2+} and Cu^{2+} at equilibrium, and theoretically calculated sorption capacity from Langmuir equation, respectively. The values of all of these parameters were measured in term of mg g^{-1}. Additionally, k_F and n are dimensionless factors for Freundlich equation and b is a constant related to Langmuir isotherm having dimension mg L^{-1}.

Plot of values of $\log q_e$ and $\log C_e$ for Freundlich isotherm, and C_e/q_e and C_e for Langmuir isotherm is presented as straight line in Fig. 5a and b. On comparison, it reveals that the values of correlation coefficient (R^2) were higher for the Langmuir isotherm (>0.99) than Freundlich

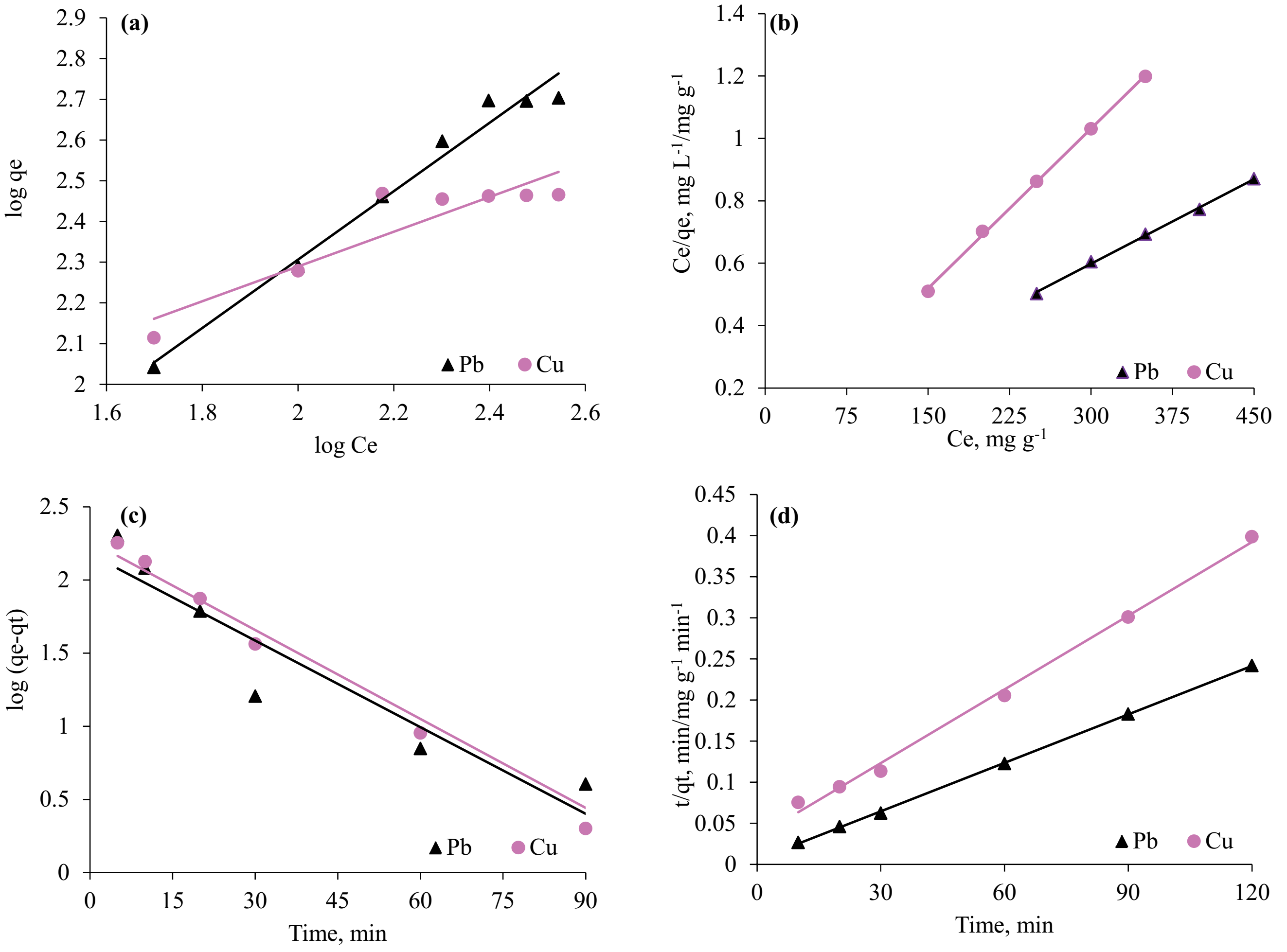

Fig. 5. Fitting of Freundlich (a), Langmuir (b), pseudo-first-order (c), and pseudo-second-order (d) models to remove Pb^{2+} and Cu^{2+} from aqueous solution by Na-SGX (Optimum sorption conditions for Pb^{2+}: pH = 6, concentration = 250 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution; optimum sorption conditions for Cu^{2+}: pH = 5.5, concentration = 150 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution).

isotherm (<0.99). It suggested that Langmuir isotherm fitted nicely to the available sorption data. Moreover, the values of n and k_F were acquired from the slope and intercept of Freundlich isotherm and $Q_{\max}$ and b were calculated from the slope and intercept of Langmuir plots, respectively. The values of n and b were fall in between 1 and 10 and provided a more fruitful approximation about the feasibility of sorption through the involvement of chemisorption in the rate determining step by forming monolayer. The calculation of $Q_{\max}$ revealed a close get-up with experimental ones which also ensured the suitability of Langmuir model to the sorption data (Table 1).

Additional information about the favourable or unfavourable adsorption of Pb^{2+} and Cu^{2+} onto Na-SGX can be acquired from a separation factor, that is, R_L whose value has been determined by using Eq. (8):

$$R_L = \frac{1}{1+bC_i} \tag{8}$$

where b denotes the Langmuir constant and measured in mg L^{-1}, and C_i is the optimum concentration of metal ions (250 mg L^{-1} for Pb(II) and 150 mg L^{-1} for Cu(II)). The R_L values falls in between 0 and 1 and suggested that the removal of Pb^{2+} and Cu^{2+} by Na-SGX is a favourable process [29] (Table 1).

Maximum adsorption of about 555 mg g^{-1} for Pb(II) and 294 mg g^{-1} for Cu(II) corresponds to stoichiometry in terms of functional groups. Calculation of which are provided as under:

- DS for a SGX substituted by succinate groups is 2.3. It means 2.3 out of three hydroxyl groups (three OH groups are supposed to be present on cellulosic material) are esterified with succinic acid. It means if molecular mass of GX is 162.14 g mol^{-1} including hydroxyl and if 2.3 OH groups are esterified with succinate group then we will replace 2.4 hydrogen with succinate. So mass of one mole of substituted SGX = 162.14 + 2.3 × 100 = 392.04 g mol^{-1} and if H of terminal OH of succinate are replaced with Na ions then = 392.14 + 2.3 × 23 = 440.15 g mol^{-1}.
- If sodium ions are replaced with Pb(II) and Cu(II) then DS will be half of the above 2.3, that is, 2.3/2 = 1.15. It means total Pb(II) and Cu(II) adsorbed are 1.15 ions per mole of sodium salt and now the mass of adsorbed or replaced Pb ions will be = 1.15 × 208 = 239.20 and replaced Cu ions will be = 1.15 × 63.5 = 73.02 (At mass of Pb = 208 amu and At. mass of Cu = 63.5 amu).
- 440.15 g mol^{-1} of sodium succinate can adsorb Pb(II) = 239.20 g mol^{-1}.

1.0 g of sodium succinate can adsorb = 239.20/440.15 = 0.5 43 g of Pb(II) = 543 mg g^{-1} (sorption capacity).

Similarly, 440.15 g mol^{-1} of sodium succinate can adsorb Cu(II) = 73.02 g mol^{-1} 1 g of sodium succinate can adsorb Cu(II) = 73.02/440.15 = 0.165 g of Cu(II) = 165 mg g^{-1} (sorption capacity).

If all of the sodium ions are replaced with Pb(II) and Cu(II) then adsorption capacity will be 543.00 and 165.00 mg g^{-1}, respectively. Adsorption capacity value of 555 mg g^{-1} for

Table 1
Sorption data for Freundlich, Langmuir, pseudo-first-order, pseudo-second-order, ion-exchange models and thermodynamic parameters for Pb^{2+} and Cu^{2+} removal from aqueous solution by sorbent Na-SGX

Models	Parameters	Pb^{2+}	Cu^{2+}
Experimental	q_e (mg g^{-1})	497.3	294.2
Freundlich parameters	n	1.190	2.3419
	k_F	4.2247	27.2627
	R^2	0.9772	0.8392
Langmuir parameters	$Q_{\max}$ (mg g^{-1})	555.55	294.11
	b (mg L^{-1})	0.0316	0.4658
	R^2	0.9984	0.9992
	R_L	0.1115	0.01411
Pseudo-first-order	q_e (mg g^{-1})	150.1758	183.9077
	k_1 (g mg^{-1} min^{-1})	0.04537	0.04675
	R^2	0.8775	0.9838
Pseudo-second-order	q_e (mg g^{-1})	500.00	344.82
	k_2 (g mg^{-1} min^{-1})	0.00070	0.00020
	R^2	0.9998	0.9993
Ion-exchange model	s (min^{-1})	0.041	0.0518
	R^2	0.8764	0.9966
Thermodynamics	$\Delta S°$ (J mol^{-1} K^{-1})	–13.204	–9.6240
	$\Delta H°$ (kJ mol^{-1})	–11.01	–22.9549
	$\Delta G°$ (kJ mol^{-1})	–12.1750	–37.7098
	R^2	0.9854	0.9954

Pb(II) and 294 mg g^{-1} for Cu(II) might be justified by removal of Cd(II) through adsorption through physio-sorption.

3.6. Kinetics modelling

The establishment of sorption kinetics is very crucial to gained information about the mechanism as well as mode of sorption, that is, either physical or chemical. This may help in the development of an effective and eco-friendly filter for water purification. Two different kinetic models, such as pseudo-first-order and the pseudo-second-order were selected to analyse the sorption data obtained from the studies of contact time influences on Pb^{2+} and Cu^{2+} uptake by Na-SGX. General linearized forms of both of the models are given as Eqs. (9) and (10):

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{9}$$

$$\frac{t}{q_t} = \left(\frac{1}{kq_e^{\,2}} + \frac{t}{q_e}\right) \tag{10}$$

where q_e and q_t represented the sorption capacities at equilibrium and at any time t (min), while k_1 and k were rate constants for pseudo-first-order and the pseudo-second-order kinetic models, respectively. Both of these constants were measured in g mg^{-1} min^{-1}. The values of log(q_e − q_t) and t were plotted to acquired sorption data for pseudo-first-order kinetic model while the values of t/q_t and t were plotted to obtained acquire sorption data for pseudo-second-order kinetic model (Fig. 5c, d and Table 1).

Slope of the straight lines provided the values of rate constants and from intercept we have calculated the theoretical sorption capacities. A comparison between the values of R^2 and maximum sorption capacities revealed that the pseudo-second-order kinetic model was fitted nicely to the available sorption data. Moreover, the comparison between k_1 and k illustrated that $k_1 > k$. This finding also supported that the equilibrium attained sharply at lower concentration. Hence, the mode of underlying sorption study was chemisorption.

3.7. Sorption mechanism

For the evaluation of mechanism through which sorption of Pb^{2+} and Cu^{2+} occurred, experiments were also conducted using succinylated sorbent, that is, SGX. SGX removed negligible quantity of both the tested metals from aqueous solutions, that is, 13.4% Pb^{2+} and 10.12% Cu^{2+} due to unavailability of exchangeable sites. Na-SGX removed >90% of both the metals from aqueous solution due to availability of exchangeable Na$^+$ ions. Thus, Na-SGX captured Pb^{2+} and Cu^{2+} from aqueous solution and made it pollution free through the exchange of Na$^+$ ions with Pb^{2+} and Cu^{2+} ions. Also the existence of ion-exchange mechanism could be witnessed from the adjustment of sorption data to Langmuir and pseudo-second-order kinetic models because both of these models fitted-well only when sorption took place through the ion-exchange. Besides, the applicability of Boyd et al. [30] equation [Eq. (11)] to the sorption data, that is, plot between log(1–F) vs. t presented straight lines with negative slope (S = sorption constant) and high value of R^2 also evidenced about the ion-exchange mechanism (Fig. 6a, Table 1). The equation is given as under.

$$\log\left(1 - F\right) = -\frac{S}{2.303}t \tag{11}$$

$$F = \frac{q_t}{q_e} \tag{12}$$

3.8. Determination of thermodynamic parameters

Thermodynamics of Pb^{2+} and Cu^{2+} sorption onto Na-SGX were studied by measuring the values of sorption

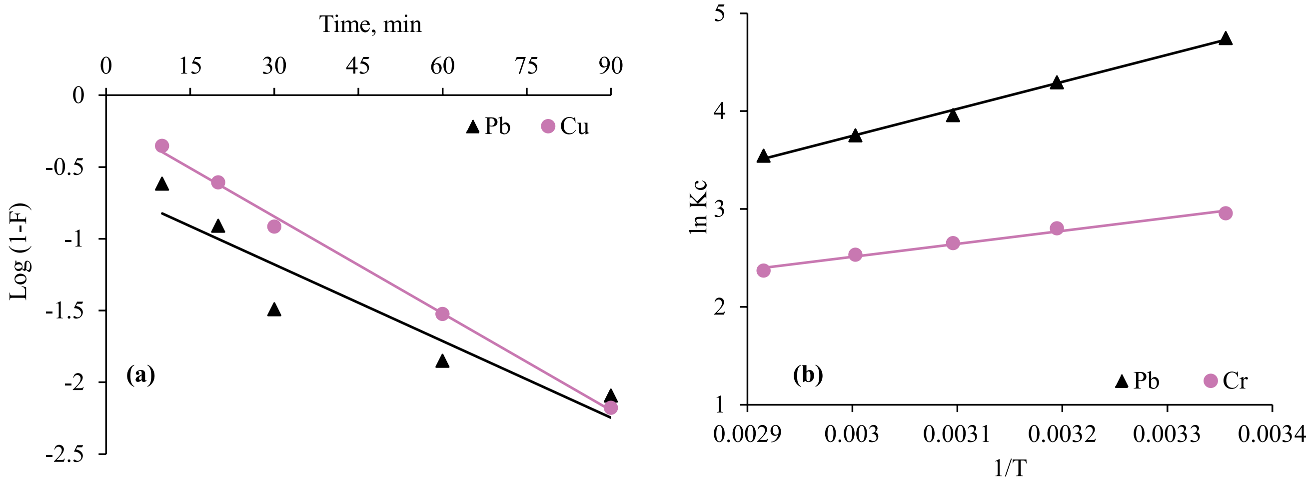

Fig. 6. Ion-exchange mechanism (a), effect of temperature (b) on ability of Na-SGX to remove Pb^{2+} and Cu^{2+} from aqueous solution (Optimum sorption conditions for Pb^{2+}: pH = 6, concentration = 250 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution; optimum sorption conditions for Cu^{2+}: pH = 5.5, concentration = 150 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature=298 K in 100 mL aqueous solution).

parameters, such as standard free energy, entropy, and enthalpy changes, that is, $\Delta G°$, $\Delta S°$, $\Delta H°$, respectively by applying Vant's Hoff isotherms [Eqs. (13)–(15)] to the temperature dependent sorption data.

$$K_C = \frac{C_{\text{ads}}}{C_e} \quad (13)$$

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (14)$$

$$\Delta G° = -RT\ln K_C \quad (15)$$

where C_{ads} and C_e denoted the uptake-concentration of tested metals by Na-SGX and remaining concentration in the aqueous solutions. Both of these concentrations were elucidated in mg L^{-1}. Additionally, T, R, and K_C represented the absolute temperature, ideal gas constant, and equilibrium constant, respectively.

A plot of lnK_C against $1/T$ (K^{-1}) for Pb^{2+} and Cu^{2+} sorption is shown in Fig. 6b and the relevant thermodynamics data is presented in Table 1. The slope of obtained straight lines was used to calculate the values of $\Delta H°$ whereas intercept was used to determine the values of $\Delta G°$. The values of sorption factors $\Delta S°$ was estimated using Eq. (14). The negative values of all of these parameters were obtained and indicated the spontaneous and

Table 2
Pb^{2+} and Cu^{2+} sorption capacities by Na-SGX for single metal system and binary system

Metal ion	System	q_e (mg g^{-1})	$q^{\text{mix}}/q°$
Pb^{2+}	Pb(II) alone	555.3	
Cu^{2+}	Cu(II) alone	322.2	
Pb^{2+}	Cu(II) + Pb(II)	426.2	0.767
Cu^{2+}	Cu(II) + Pb(II)	56.1	0.174

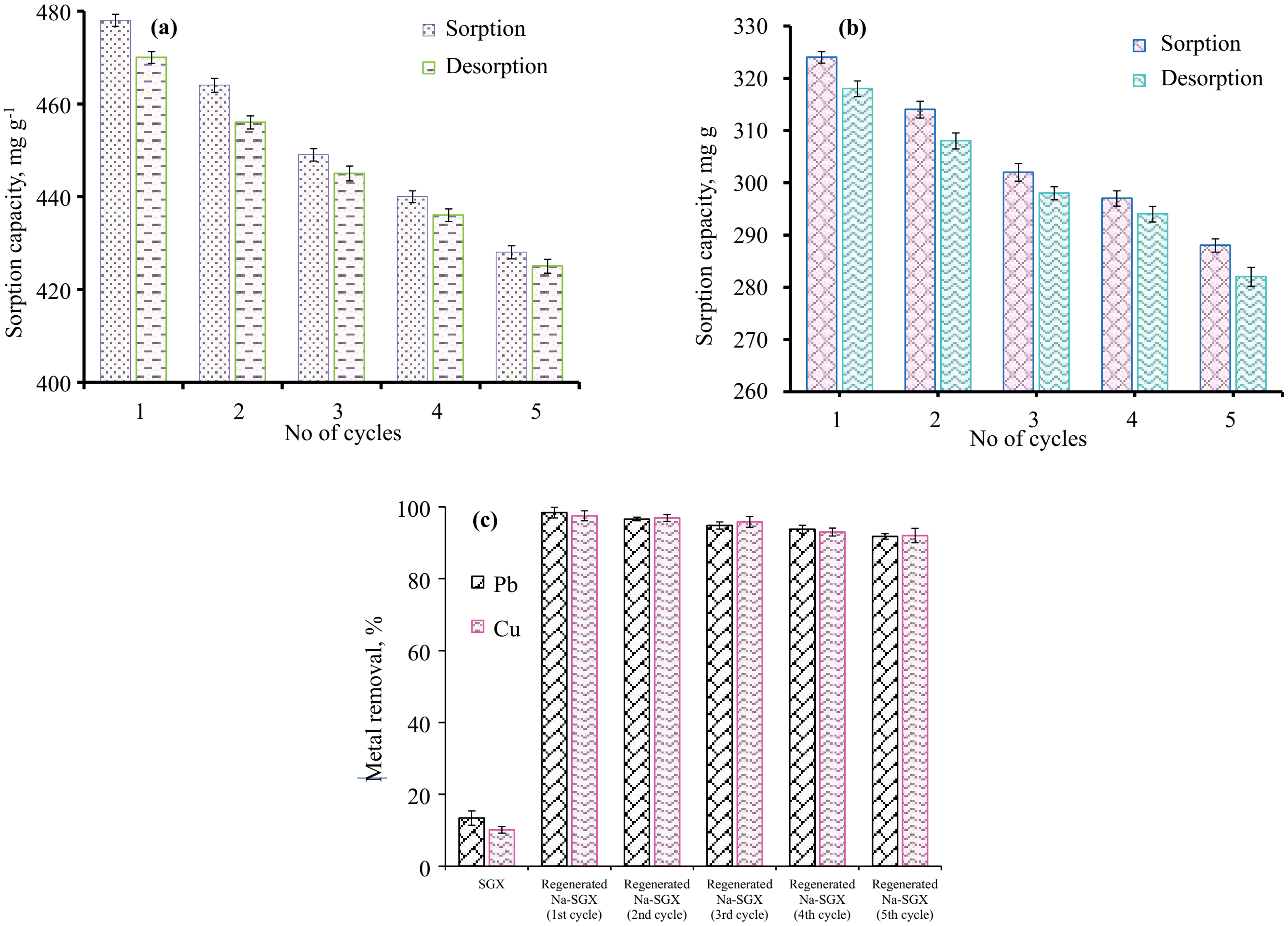

Fig. 7. Plot of sorption/desorption studies of Pb^{2+} (a), Cu^{2+} (b), and metal removal percentage (c) by the sorbents SGX and Na-SGX (Optimum sorption conditions for Pb^{2+}: pH = 6, concentration = 250 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution; optimum sorption conditions for Cu^{2+}: pH = 5.5, concentration = 150 mg L^{-1}, sorbent dose = 50 mg, contact time = 30 min and temperature = 298 K in 100 mL aqueous solution).

Table 3
Comparison of sorption capacities Na-SGX to uptake Pb^{2+} and Cu^{2+} from aqueous solution with other eco-friendly biosorbents

Sorbent (treatment)	Target metal ions	Q_{max}^{a} (mg g^{-1})	References
Poly(vinyl alcohol)/chitosan	Pb^{2+} and Cu^{2+}	238 and 166	[32]
Cellulosic okra fibers (Acrylonitrile/methacrylic acid)	Pb^{2+} and Cu^{2+}	268.32 and 76.82	[33]
Sugarcane bagasse (chemically modified with 1,3-diisopropylcarbodiimide, triethylenetetramine)	Pb^{2+} and Cu^{2+}	313 and 133	[34]
Mercerized cellulose	Pb^{2+} and Cu^{2+}	500.0 and 182.2	[27]
Magnesium phyllosilicate modified with 2-aminophenyl disulfide	Pb^{2+} and Cu^{2+}	294.22 and 208.44	[35]
Biochar	Pb^{2+} and Cu^{2+}	247.10 and 75.9	[36]
Magnetic Fe_3O_4-mesoporous MS	Pb^{2+} and Cu^{2+}	223.2 and 53.5	[37]
MS nanotubes	Pb^{2+}	424	[38]
Hierarchical MS hollow nanofibers assembled by nanosheets	Pb^{2+}	158	[39]
Succinylated GX	Pb^{2+} and Cu^{2+}	555.55 and 294.11	This study

*Q_{max} = Maximum sorption capacity determined from Langmuir model

exothermic mechanism of Pb^{2+} and Cu^{2+} sorption onto Na-SGX (Table 1).

3.9. Sorption/desorption tests

Tests regarding sorption/desorption and sorbent regeneration were conducted to monitor the profile of Na-SGX over numbers of repeated cycles (n = 5). This study is imperative as by this we can probe the ideality of Na-SGX for water purification over number of repetitions. After loading of Pb^{2+} and Cu^{2+} onto Na-SGX, Na-SGX was dried and restored to treat with a freshly prepared saturated solution of brine (100 mL). Obtained results were recorded in graphics and indicated that Na-SGX is superficially regenerated with a negligible decrease in sorption capacities, that is, nearly 50.0 mg g^{-1} in a case of Pb^{2+} and 35.0 mg g^{-1} in a case of Cu^{2+} (Fig. 7a and b). Moreover, it was predicted that after five repeated cycles only a 9.8% decrease in sorption capacity acquired for Pb^{2+} uptake and 5.7% for Cu^{2+} uptake. This will also provide a basis for the re-usability of Na-SGX (Fig. 7c).

3.10. Competitive metal sorption from binary system by Na-SGX

Some systems, such as galvanic waste water and electroplating effluent are based on multi-metal ions system. Therefore, to simulate these systems, a system containing Pb^{2+} + Cu^{2+} was designed and potential of Na-SGX was evaluated to encapsulate heavy metal ions. Obtained results are shown in Table 2. It was observed that binary metal ion system offered less sorption capacity as compared to single metal ion system due to unavailability of competitive sites in a case of single metal ion system. Moreover, the trend of sorption capacities was noted to be Pb^{2+} > Cu^{2+} in both the single as well as binary metal ion system which might be because of difference of ionic radii, charge density, and redox potentials. Furthermore, the ratio between the values of q^{mix} and $q°$ was determined and appeared as less than one which also evidenced about decrease in sorption capacities because of presence of metal ions of opposite system in a binary matrix [31].

3.11. Comparison with other similar and eco-friendly sorbents

After comparing the Pb^{2+} and Cu^{2+} removal efficiency of Na-SGX with other chemically modified and un-modified biosorbents, we came to know that our devolved novel biosorbent occupy a distinct position (Table 3).

4. Conclusions

A pristine sorbent Na-SGX was successfully designed via succinylation and appeared as an ideal filter for the removal of Pb^{2+} and Cu^{2+} from single and binary metal ion aqueous system. The equilibrium sorption studies revealed that Langmuir isothermal model fitted well to the sorption data with highest sorption capacity in order of Pb^{2+} > Cu^{2+}. The uptake-kinetics reached within 30 min of sorption process and described better by pseudo-second-order kinetic equation, hence suggested that sorption followed ion-exchange mechanism. The negative values of thermodynamic attributes ($\Delta G°$, $\Delta S°$, and $\Delta H°$) showed the exothermic and spontaneous mode of sorption. Finally, the regenerable nature, and the superior position over other chemically modified and un-modified sorbents explained that Na-SGX is highly efficient candidate for water purification.

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