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Kinetics and mechanism of Cu^{2+} ions adsorption on PEGylated-citric acid-based hydrogel

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ABSTRACT

In view of the critical concern for the toxic materials accumulation in environment, new materials synthesized from biocompatible feedstock are being investigated for purification technologies. In the present study we report a new hydrogel as adsorbent for Cu^{2+} ions under the simulated conditions. Citric acid (CA) was reacted with poly(ethylene glycol) [PEG] via the lipase catalyzed reaction. The PEGylated-CA was characterized with SEM, ^{1}H–NMR and FTIR spectroscopy and evaluated as an adsorbent of Cu^{2+} ions by variation of adsorption conditions with respect to time, temperature, solution pH and ion concentration. Subsequently, the maximum retention capacity (172.3 g/mg up to five feeds) was evaluated under the optimal adsorption conditions. The material is reusable and reusability studies were carried out up to 10 feeds.

Keywords: PEGylatedCA; Water pollution; Maximum adsorption capacity; Langmuir isotherm; Pseudo–second order kinetics

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1. Introduction

Intensification of environmental pollution has severely deteriorated several ecosystems with the accumulation of pollutants, especially the heavy metal ions present in the untreated effluents from various industrial processes [1]. As a result, over 70% of the health issues especially in the developing countries are related to water contamination, with huge adverse impact on human beings. Cu^{2+} ions are common contaminants in water bodies because of their applications in many industrial fields [2]. Though Cu^{2+} ions are present as cofactors in various enzymes in human body, but their presence at higher levels leads to many hazardous effects such as lipid peroxidation or increase in the methemoglobin content which causes death [3]. Also, they pose serious problem in water used in reactors or in the industrial processes. Huge scarcity of potable water coupled with its poor quality is a serious challenge to the humankind. Water is contaminated by various effluents including heavy metals, bacteria, organic and synthetic dyes and so on. Wastewater from industries contains many toxic and carcinogenic materials including Cu^{2+} ions and these needs to be treated before the recycling of water [4]. Hence its removal from the aqueous solutions has been attempted by osmosis or UV treatment, but these are very expensive techniques [5]. Adsorption is the basic technique for the removal of heavy metal ions from water bodies and it is also cost-effective [6]. In literature there are many reports on the adsorption of Cu^{2+} ions from the aqueous solutions using biopolymers as well as synthetic polymer–based hydrogels [7–16]. There are several polymeric network used for removal of heavy metal ions from wastewater and can be interoperated by UV- spectroscopic techniques [17].

In the present study the objective was to synthesize citric acid (CA) and polyethyleneglycol (PEG) based environmentally-friendly adsorbent for Cu^{2+} ions. PEG is an important biocompatible amphiphilic synthetic polymer with repeated ethylene oxide subunits and it is approved by FDA for human oral, intravenous dermal pharmaceutical and water treatment applications [18]. PEGylation is the covalent attachment of the end ethylene oxide subunit with an active functional group of bioactive compound for an enhancement of its chain length consequently to improve or extend the properties of the substrate molecule [19]. It has been reported to enhance ion removal capacity

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of poly(acrylonitrile) membrane in ultrafiltration process [20]. CA is an inexpensive, bioactive and non-toxic material was used to anchor PEG via lipase catalyzed esterification reaction. CA has a reactive hydroxyl and three carboxyl groups and the latter act as the reactive centers where modification via PEG linkage can be affected. Modification of CA has been reported with eco-friendly and biodegradable materials and the resultant materials were investigated as adsorbents of heavy metal ions. Modification of different bio-wastes with CA has been reported to enhance their capacity for the adsorption of heavy metal ions [21–24]. In a study the microfiltration technique was used to separate the metal ions wherein PEG and polyacrylic acid (PAAc) were complexed with each other and then used for the removal of toxic heavy metals such as Ni^{2+}, Cu^{2+} and Cr^{6+} from the wastewater [25]. The new dendritic-type PEGylated CA-based hydrogel (PEGylated CA) was synthesized from CA and PEG via a greener protocol using lipase as biocatalyst at 45°C. The PEGylated-CA so synthesized was well characterized by different techniques and used as adsorbent for the removal of Cu^{2+} ions from the aqueous solutions. The adsorption kinetics and isotherm were also investigated. Modification of CA with PEG results in high adsorption capacity making the resultant PEGylated-CA a good candidate for Cu^{2+} ions adsorption.

2. Experimental

2.1.Materials

Citric Acid (Loba Chemie, Mumbai, India), polyethylene glycol (PEG_{400}) (Merck, Mumbai, India), sodium hydroxide, hydrochloric acid, *di*-sodium hydrogen orthophosphate anhydrous (Na_2HPO_4), sodium dihydrogen orthophosphate dehydrate ($NaH_2PO_4 \cdot 2H_2O$) (all from S.D. Fine Chem Ltd, Mumbai), copper sulphate, potassium chloride, lipase, reagent Cu-1, reagent Cu-2 (all from Merck, Mumbai, India, 99.9% purity), were used as received. The concentration of Cu^{2+} ions in the adsorption experiments were determined with PhotoLab 6600 UV-Vis spectrophotometer and pH values were measured with pH meter (Eutech 20).

2.2. Synthesis of adsorbent

Citric acid-based adsorbent was modified by PEGylation process. In this method the esterification reaction between citric acid (CA) and PEG (1: 3 molar ratio by weight) at 45°C for 8 h in Chemical Reactor (Miniblock™, Germany) was carried out. Lipase (1% by weight of total reaction mixture) was used as catalyst for the esterification reaction. The synthesized ester was named as polyethylene glycolcitrate (PEGylated-CA). The latter was washed thoroughly (4 times) to remove any unreacted materials. PEGylated-CA was separated out by washing it with acetone and afterward dried in hot air oven at 40°C. After purification, it was refluxed by thermal treatment at 70°C in the deionized water to remove unreacted reaction components. The washing and drying cycles were repeated until a constant weight was obtained.

2.3. Characterization of hydrogel

Characterization of the synthesized adsorbent was carried out by Fourier transform infrared FTIR spectroscopy (Nicollet 5700), ^1H nuclear magnetic resonance spectroscopy NMR (Bruker Advance II 400 MHz spectrophotometer) and scanning electron micrograph (Joel Stereoscan-150).

2.4. Adsorption studies of Cu^{2+} ions

PEGylated-CA (0.02 g) was immersed in 50 ppm (10.0 mL) solution of Cu^{2+} ions that was prepared in the deionized water and placed in a water bath (accuracy ± 0.01°C) at 20°C. The adsorption capacity was studied as a function of time from 5 to 180 min. The determination of Cu^{2+} ions was carried by the specific cupric test reagents and determined photometrically with PhotoLab® 6600 spectrophotometer at 540 nm. PEGylated-CA showed maximum uptake for Cu^{2+} ions within 120 min and thereafter it attained equilibrium. Therefore, the effect of temperature (20–40°C), Cu^{2+} ions concentration (5–150 ppm) and pH (2.0–9.0) was studied for 120 min. The maximum retention capacity (MRC) was determined by repeated treatments of the adsorbent with Cu^{2+} ions (concentration 100 ppm) at the optimum conditions obtained. To evaluate the reusability of the adsorbent, the Cu^{2+}-loaded adsorbent was treated with 0.1 *N* HCl for 30 min to leach out the adsorbed ions and the regenerated adsorbent was reused in the successive feeds. The adsorption results were evaluated by using the following expressions:

$$\text{Adsorption capacity}\left(q\right)\left(\frac{mg}{g}\right) = \left(C_o - C_t\right) * \frac{V}{m} \tag{1}$$

where q is the amount of Cu^{2+} ions adsorbed onto the unit dry mass of the PEGylated CA(mg/g), C_o and C_t are the concentrations of ions in the feed solutions and in the aqueous phase after treatment for time t, respectively (mg L^{-1}), V is the volume of the aqueous phase (L) and m is the weight of dry polymer (g).

3. Results and discussion

3.1. Characterization studies

Scheme for the synthesis of PEGylated CA is presented in Fig. 1.

Confirmation of CA esterification by the incorporation of PEG resulting in network structure was obtained from the FTIR spectroscopy (Fig. 2). Such structure is visualized to have dendritic structure with three arms as all the three carboxylic groups present on CA were converted to ester groups. However, the second group of the PEG may get attached to the other CA molecule. FTIR spectrum of the synthesized ester PEGylated-CA has characteristic ester peaks at 1735.3 cm^{-1} due to (–C=O stretching in ester group) and at 1104.1 cm^{-1} (–C–O–C stretching) of ester and it also has adsorption band at 2929 cm^{-1}. PEGC absorbs at 2987 cm^{-1}, 2925.3 cm^{-1}, 1104.1 cm^{-1} due to –CH and –C–O–C– stretching. FTIR spectrum of PEGylated-CA and its Cu^{2+}-loaded sample has bands at 1731.2 cm^{-1} (–C=O stretching in ester group), 1104.1 cm^{-1} (C–O–C stretching) and 836.3

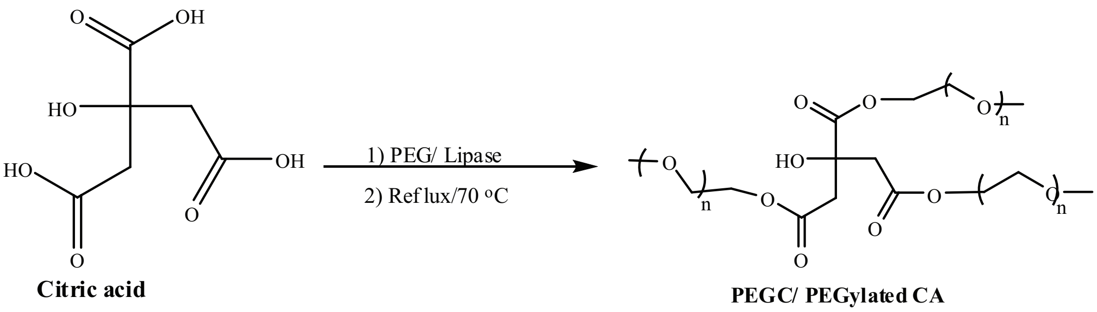

Fig. 1. Scheme for synthesis of PEGylated-CA.

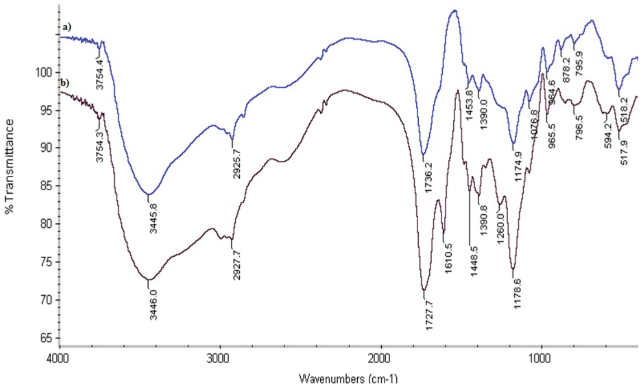

Fig. 2. FTIR spectra of a) PEGylated-CA, b) Cu-loaded PEGylated-CA.

cm^{-1} (–C–C– in-plane bending). Some extra peaks in the spectrum at 1390.0 cm^{-1}) and at 1453.8 cm^{-1} are characteristic asymmetrical COO$^-$ band and symmetrical COO$^-$ bond band which may be due to the unreacted citric acid present on the surface of PEGylated-CA. On Cu^{2+} ions adsorption, changes in the intensity and band position of the important peaks signify adsorption on the polymeric surface. The additional peaks in the range of 550–500 cm^{-1} in the Cu^{2+} ions-loaded PEGylated-CA correspond to the bridged complex of copper which has peaks at 550 and 500 cm^{-1} corresponding to the asymmetrical Cu–O and Cu–OH vibrations, respectively [26].

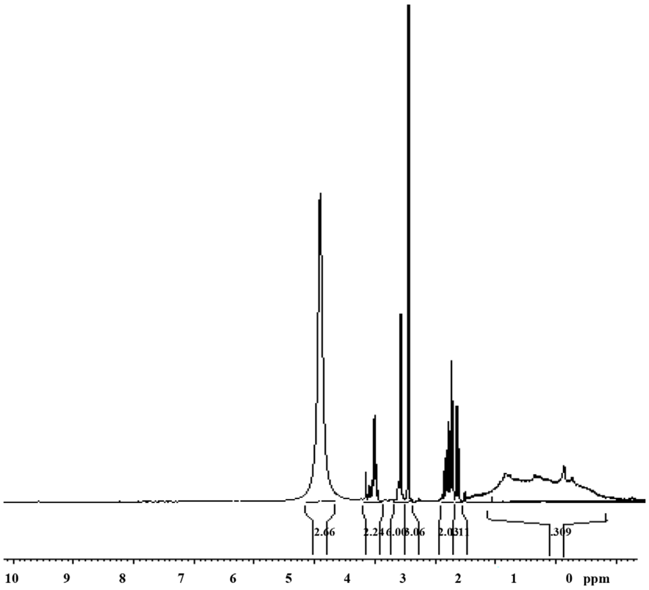

Fig. 3. ^{1}H-NMR Spectra of PEGylated-CA.

Presence of the ester group was also confirmed from the ^{1}H NMR spectrum of PEGylated-CA. The CA has 6 protons, 3 –CO_2H, 2 –CH_2 and 1 –OH, out of which two signals are expected to be in the range 2.6 ppm and 2.0 due to the – CH_2 and 1 –OH proton. Similarly, PEG has four protons per monomeric unit on the main chain, –CH_2CH_2–, and one each on two end hydroxyl groups on each polymer chain. Out of the later one or both may react. In view of the aforesaid, the resultant modified CA is expected to have one signal due to the –OH proton from both the component and other singlet from the –CH_2 of CA and other two as triplet from the PEG main chain. The PEGylated-CA has one signal at 2.7 ppm (singlet due to –CH_2–C=O of the CA) and two triplets 3.5 to 5 ppm (triplet due to –CH_2–O–CH_2–O– from PEG) (Fig. 3). A broad signal is present between 1–2 ppm due to the unreacted –OH group of CA and end –OH groups of PEG. This signal appears broad and diffused due to the dipolar interactions of these groups between the nearby components of the main chain. No signal due to the absorption by the carboxylic group proton is present in the spectrum, hence reaction was complete utilization of the all these groups but the extra signals due to the unreacted carboxylic groups may be out of the ppm range recorded.

SEM images of the Cu^{2+}-loaded PEGylated-CA is presented in Fig. 4a. These images signify that hydrogel have dense surface which may be due to the different types of inter-chain interactions of the PEG chains on each CA unit. Such morphology is indicative of an active platform for the Cu^{2+} ions adsorption on the surface. A dense layer was observed after the adsorption of Cu^{2+} ions on PEGylated-CA surface as shown in Fig. 4b. Thus, the adsorption of metal ions on the surface of the polymer enhances its intensity.

PEGylated-CA behaves as hydrogel as it can retain good amount of water under different conditions. Such water holding capacity of the PEGylated-CA emanates from the physical cross linking of the three chains of PEG per CA molecule those dangle being long, having molecular weight of 400, and consequently assemble and interact with each other by polar interactions to form a physical cross linked network. The swelling behavior of PEGylated-CA was investigated from pH 2.0 to 9.0. Water uptake

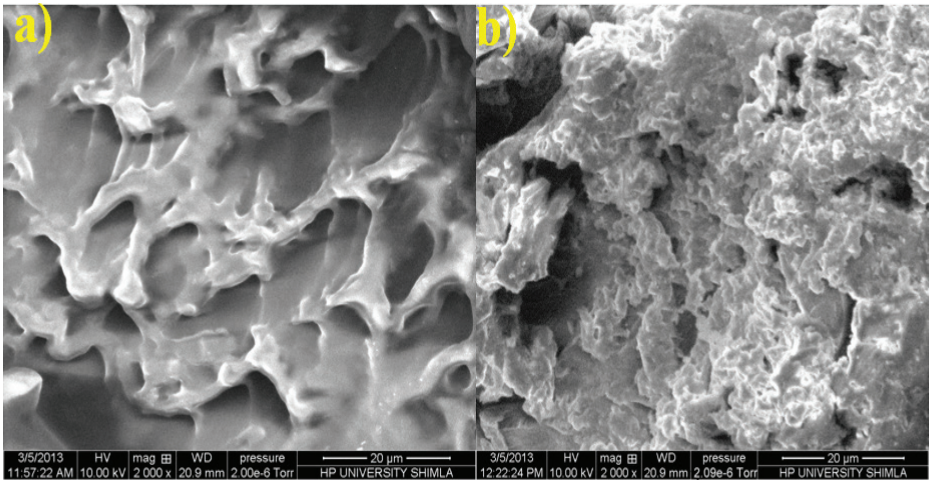

Fig. 4. SEM images of a) PEGylated-CA, b) Cu-loaded PEGylated-CA.

increased with pH as the maximum water uptake of 550% was observed at pH 7.0, at 35°C and 120 min and minimum water uptake was observed at higher acidic pH upto 200% (Fig. 5). That signifies that the hydrogel structure opens up on interactions with water and also that portrays well for the partitioning of Cu^{2+} ions from the solution. The pH-dependent swelling of hydrogels is well reported in literature. They shrink, hence absorb low amount of water, under the medium of low pH [27] , but absorb large amount of water at the higher pH.

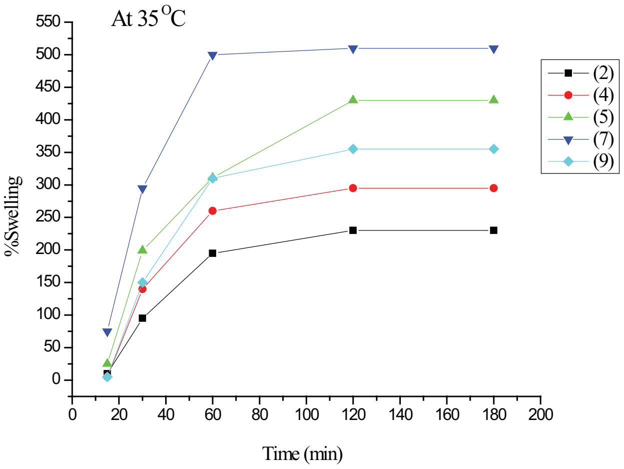

Fig. 5. Swelling studies of PEGylated-CA at : temperature (35°C), time (20–200 min) and pH (2.0–9.0).

3.2. Adsorption studies of Cu^{2+} ions

Hydrogel, per molecule of CA, has one hydroxyl, three ester and many ether groups those act as active sites for the metal ion uptake. Adsorption depends on many factors such as temperature, pH, concentration of pollutants, contact time, particle size, temperature, and nature of the adsorbate and adsorbent. The key part of an adsorption process is the adsorbents, as it can bind or capture heavy metal ions from the aqueous solutions. Initially the adsorption of Cu^{2+} ions (50 ppm) was studied for 2 h at 35°C and 5.0 pH with 0.02 g of PEGylated-CA. The adsorption capacity of PEGylated CA increased with an increase in the contact time before attaining equilibrium as all the active sites of the PEGylated-CA were occupied by the ions (Fig. 6a). The temperature variation resulted in an increase in the adsorption capacity (q) from 20°C to 35°C, thereafter decrease in q values with further increase in temperature showed that with an increase in the temperature the PEGylated-CA structure opened up to adsorb Cu^{2+} ions. Further increase in temperature, however, reduced adsorption capacity due to the enhancement of thermal mobility of the ions and consequent reduced ionic interactions (Fig. 6b).

Effect of pH on the Cu^{2+} ions adsorption was studied for 2 h at 35°C. The adsorption of Cu^{2+} ions under the acidic medium increased with an increase in pH and it attained maximum adsorption capacity value at pH 5.0. It decreased with subsequent increase in pH which implies that the adsorption behavior of Cu^{2+} ions is pH dependent. In the strong acidic pH (2–4) media, complexation with ions is low because of the protonation of the adsorbent from the medium and hence the observed reduction in the adsorption capacity (Fig. 6c). When pH of the medium is less acidic metal ion retention increased on the ester and ethoxy groups which favor polymer–metal ions interactions. Under the basic and neutral pH medium the active sites become inaccessible for adsorption because the negatively charged functional groups around PEGylated-CA undergo substitution, hence the adsorption capacity decreased because vacant sites are not available for adsorption. The adsorption of Cu^{2+} ions at different initial concentrations (10–150 ppm) was studied for 2 h at 35°C and pH 5.0. The linear increase in adsorption was observed up to pH 5.0 [28] and then decrease in the adsorption at pH 7.0 has been reported in literature [11]. The lower pH renders the polymer matrix to shrivel while it opens up at the higher pH making more sites available for the adsorbent-Cu^{2+} ions interactions. An increase in pH results in the opening up of the hydrogel matrix with a result in the

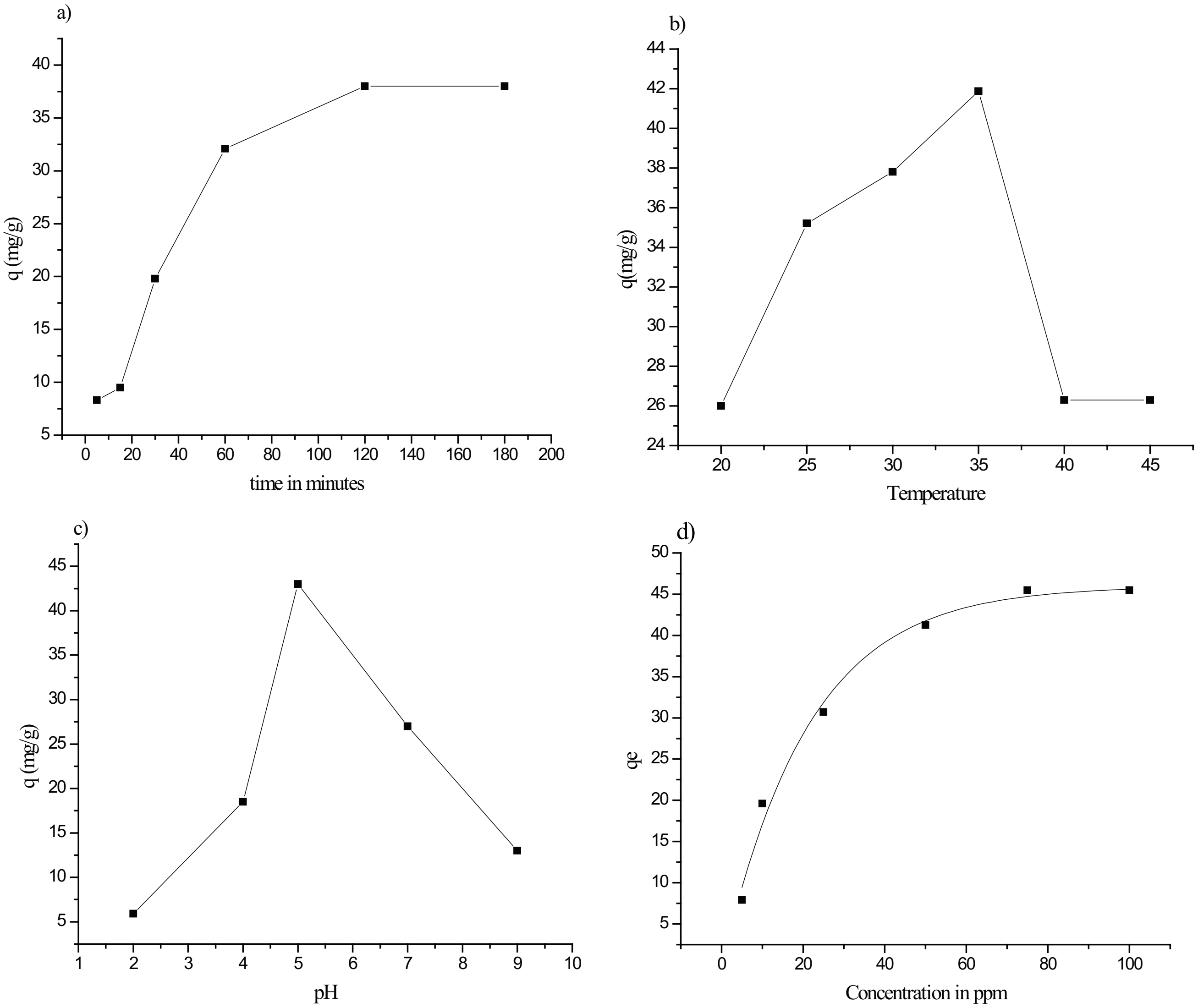

Fig. 6. Adsorption capacity of PEGylated-CA for Cu^{2+} as a function of (a) time (120 min) (b) temperature (35°C) (c) pH (5.0) and (d) concentration (100 ppm).

higher partitioning of the ions to the active sites on the hydrogel phase those are otherwise inaccessible at the lower pH due to the shriveling of the hydrogel network structure [29].

Percentage uptake (P_u) was observed to increase from 32.8% to 83.8% when Cu^{2+} ions concentration was varied from 1.0 to 50.0 ppm at 35°C and pH 5.0. The adsorption capacity values (q_e) increased upto 45.5 mg/g over the range of Cu^{2+} ions studied upto 100 ppm and thereafter afterward equilibrium was attained as shown in Fig. 6d. The adsorption of Cu^{2+} ions became constant at higher concentration as maximum adsorption was at 100 ppm because of saturation of the adsorbent active sites. From the forgone discussion it follows that optimum conditions for Cu^{2+} uptake were obtained as 120 min, 35°C, pH 5.0 and 100 ppm of Cu^{2+} ions and at these conditions maximum retention capacity (MRC) of the adsorbent was evaluated.

High MRC of 172.3 mg/g was obtained when studied repeatedly upto five feeds for 120 min, at 35°C, pH 5.0 and 100 ppm of Cu^{2+} ions in every single feed (Fig. 7). The reusability of the adsorbent was studied after the Cu^{2+}-loaded adsorbent was treated with 0.1 *N* HCl upto 10 feeds to remove the adsorbed ions. The results obtained from the present study show that the adsorbent is reusable. Regenerated adsorbent showed comparative uptake with MRC (Fig. 7).

3.3. Adsorption mechanism of Cu^{2+} ions

Adsorption is a surface phenomenon and the adsorption isotherm can determine the mechanism of adsorption. To investigate the adsorption mechanism, Langmuir and Freundlich isotherms were applied as a function of adsorption capacity q_e to the obtained experimental values. The Langmuir model assumed a monomolecular layer formation between adsorbate and adsorbent [30]. The Langmuir model is represented as:

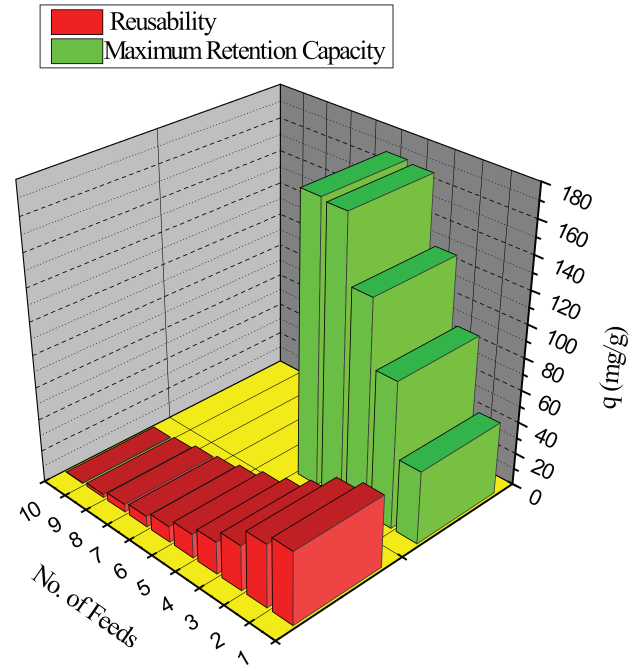

Fig. 7. Graphs of MRC and reusability graph at 2 h, 35°C and pH 5.0.

$$\frac{1}{q_e} = \frac{1}{q_{mon}} + \frac{1}{K_L q_{mon}} \frac{1}{C_e} \tag{2}$$

Where K_L the Langmuir constant, is related to the energy of adsorption (L/mg) and it reveals strength of the adsorbed ion-adsorbent binding and q_{mon} is the maximum adsorption of Cu^{2+} ions corresponding to the complete monolayer coverage on the surface. C_e is the equilibrium concentration after time 2 h. The linear plot of C_e/q_e versus C_e shows good fit of the adsorption capacity with the Langmuir adsorption isotherm model. The high correlation coefficient (r^2) value (0.999) shows that the experimental data fits reasonably well in the linearized form of the Langmuir isotherm for the PEGylated-CA [Table 1 and Fig. 8a]. The q_{mon}(80.06 mg/g) and K_L (0.00219) values were, respectively, calculated from the intercept and slope of the linear plots. A dimensionless constant of Langmuir isotherm, separation factor or equilibrium parameter, R_L, can be expressed as:

$$R_L = 1/\left(1 + K_L C_o\right) \tag{3}$$

where K_L (L mg^{-1}) is the Langmuir constant, defined earlier, and C_0 (mg L^{-1}) is the initial concentration. The calculated value of the dimensionless factor R_L (0.3134) is included in Table 1. R_L value > 1 zero and < than 1 indicates that the PEGylated-CA is favorable platform for the adsorption of Cu^{2+} ions. The adsorption process can be well described by the Langmuir model, which is monolayer adsorption onto the adsorbent surface.

The Freundlich isotherm assumes that a non-ideal adsorption process on the heterogeneous surfaces and the adsorption capacity are related to the concentration of ions at equilibrium [31].

Table 1
Langmuir and Freundlich constants for adsorption of Cu^{2+} ions by PEGylated-CA

Langmuir				Freundlich		
r^2	K_L in g^{-1}	q_{mon} (mg g^{-1})	R_L	r^2	n	K_F (L/mg)
0.998	0.00219	80.06	0.3134	0.960	1.63	3.732

The linearized form of isotherm was used to calculate adsorption data by the following equation:

$$logq_e = logK_F + \left(1/n\right)logC_e \tag{4}$$

where q_e is the equilibrium adsorption capacity (mg/g) and C_e is the equilibrium concentration (mg/L). K_F (3.732) and n (1.63) are the Freundlich constants which are related to adsorption capacity and intensity. In this case value of $n > 1$ (1.63) confirmed the spontaneous adsorption, but Freundlich constant show non-linear match with the experimental data and has low correlation coefficient (r^2) which is 0.960.

In present study, the experimental values better matches the q_e values obtained from the Langmuir model rather than the Freundlich model. Hence, it is Langmuir isotherm that better describes the adsorption of Cu^{2+} ions, which signifies monolayer formation and it is obvious for these types of adsorbents which have functional groups such as –OCOR as the adsorption sites.

3.4. Kinetic Studies of Cu^{2+} ions

Kinetic modeling tells about the adsorption rate as well as the characteristic of possible reaction mechanism. These studies describe the solute uptake rate and predict the rate at which the pollutant is removed from the waste water. To study the adsorption kinetics three models were applied. Pseudo-first order kinetic model is based on the adsorption capacity of adsorbent and is generally expressed as [32]:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{5}$$

where q_e and q_t are amounts of Cu^{2+} ions adsorbed per g of adsorbent (mg g^{-1}) at equilibrium and at time t (min), respectively. K_1 is the pseudo-first order rate constant for the adsorption process (min^{-1}). Plot of ln $(q_e - q_t)$ vs. t gives a straight line for the first order adsorption kinetics and K_1 can be calculated from the slope of that line. In the present study r^2 has low value and does not match well with the experimental data.

Pseudo-second order kinetic model is based on the adsorption capacity of the expressed as [33]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where K_2 (1.2 × 10^{-5}) (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order adsorption. The pseudo-second order rate constant K_2 is determined from the experimental data by plotting t/q_t vs. t.

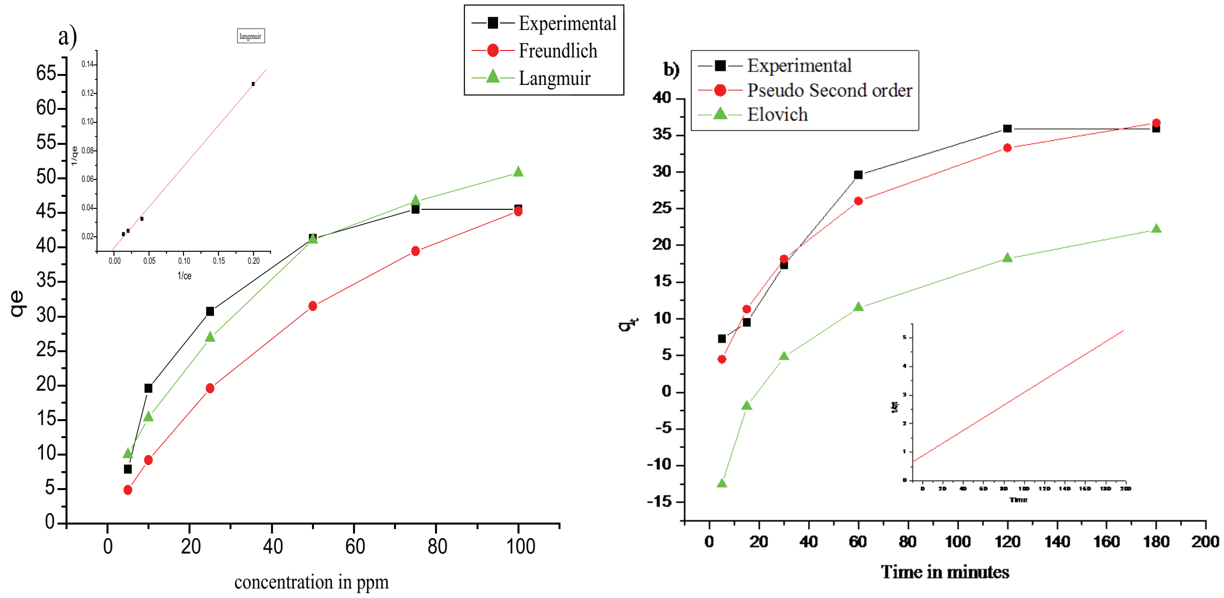

Fig. 8. (a) Langmuir isotherm, Freundlich isotherm and experimental plot for adsorption on PEGylated-CA [Inset: Langmuir isotherm] (b) Pseudo-second order kinetics, Elovich and experimental plot for Cu^{2+} ions adsorption on PEGylated-CA [Inset: Pseudo-second order kinetics].

Table 2
Pseudo first order constants, Pseudo second order constants and Elovich constants for adsorption Cu^{2+} ions by PEGylated CA

Pseudo first order kinetic model			Pseudo second order kinetic model			Elovich equation		
r^2	K_1 (min^{-1})	q_e (mg/g)	r^2	K_2 (g/mg min)	q_e (mg/g)	r^2	α (mg/g min)	β (g/mg)
0.988	7.6×10^{-2}	42.59	0.993	1.2×10^{-5}	45.10	0.911	0.52882	0.1032

The kinetics studies were also studied using the Elovich equation which is expressed as below [34]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (7)$$

where α is the initial sorption rate constant (0.52882 mg/g min) and the parameter β is the extent of surface coverage and activation energy for adsorption (0.1032 g/mg). A graph of the Elovich equation between q_t and ln t over the range of contact time was plotted to calculate correlation coefficient. The adsorption capacity values obtained from different kinetic models were matched with the experimental values and were found to have good match [35]. The equilibrium adsorption capacity (q_e) was obtained from the intercept and slope of the graph of t/q_t vs. t. The calculated q_e values are in good agreement with the experimental data as shown in Table 2 (Fig. 8b). Also, higher r^2 value is a strong indicator of the fact that the model fits to describe the kinetics of Cu^{2+} ions adsorption in the present case. Therefore, present results and the adsorption process followed the pseudo-second order kinetics, which justifies significant contribution of the chemical adsorption mechanism. The rate of adsorption depends upon both on the nature of the polymeric and active functional groups.

3.5. Thermodynamic studies

A thermodynamic study is an important parameter to determine the feasibility/spontaneity of the adsorption process. The Gibbs free energy change, negative $\Delta G°$, indicates whether chemical reaction is feasible or not. The equilibrium constant K_c is given by the relation:

$$K_C = \frac{C_e}{C_o} \quad (8)$$

where C_e and C_o (both in mg L^{-1}) are the equilibrium concentration, initial concentration for Cu^{2+} ions. $\Delta G°$, $\Delta H°$ and $\Delta S°$ are related to the adsorption equilibrium constant K_c can be calculated from the following equation:

$$\Delta G° = -\mathrm{RT} \ln K_C \quad (9)$$

where $\Delta G°$ is the standard free energy change (J/mol), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

$$\ln K_C = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{T} \quad (10)$$

A plot of ln K_c vs. 1/T gives values of $\Delta H°$ and $\Delta S°$ from the slope and intercept. A plot of ln K_c vs. $1/T$ for the calculation of $\Delta G°$, $\Delta H°$ and $\Delta S°$ (not presented). The results show that adsorption process was endothermic in nature as $\Delta H°$ obtained was positive. Since adsorbent have active functional groups which can easily diffuse the Cu^{2+} ions. Thus, with an increase in temperature the Cu^{2+} ions become more accessible to the adsorbent. The values of thermodynamic parameters are presented in Table 3.

The negative values of ($-\Delta G°$) free energy of adsorption indicate the spontaneity of the process at all temperature confirms that adsorption is spontaneous [35]. The maximum adsorption capacity of other adsorbents were studied and tabulated in Table 4 for the sake of comparison.

Table 3
Thermodynamic parameters for adsorption process

Temperature (K)	$\Delta G°$ (J/mol)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol K)
293	–15187.9	18659.4	11.84
298	–15478.9		
303	–15769.9		
308	–16060.9		
313	–16351.9		

4. Conclusions

The aim of the present study was to synthesize a new PEGylated-citric acid based adsorbent via the lipase-catalyzed reaction. The adsorbent is constituted of biocompatible components and the synthetic process used is green, hence there was neither any toxic material/s generated at the synthetic stage nor will its decomposition, after use, generate any. The adsorbent mainly has ester or ethoxy groups on the polymer chains as the active functional groups those act as the active sites in the adsorption process. It has been found to be a very effective adsorbent for Cu^{2+} ions. The optimum adsorption capacity was observed after 2 h at 35°C and pH 5.0. The adsorbent is reusable and exhibited a very high maximum retention capacity upto 172.3 mg g^{-1} after 10 feed cycles. All the experimental data show better match with Langmuir isotherm and followed pseudo-second order kinetics. The adsorbent is a good candidate for the removal of Cu^{2+} ions from the industrial or natural waste water.

Table 4
The maximum adsorption capacity of other adsorbents for the sake of comparison

S.No.	Adsorbent	pH	Concentration of adsorbate Cu^{2+} (mg/L)	Contact time (h)	Maximum adsorption capacity (mg/g)	Ref.
1.	Gelatin-based hydrogel	4.0	10	2	14.9	[12]
2.	Starch-based functional hydrogel	7.0	50	2	128.26	[11]
3.	Fish scales of oreochromis niloticus (Mojarra Tilapia)	5.0	25	1	58	[36]
4.	Calcium hydroxide activated watermelon	5.0	10	1	31.25	[37]
5.	Chitosan/polyethylene oxide (PEO) nano fibres	5.5	100	3.3	94.75	[38]
6.	Wasted black tea powder	4.4	25	16 min	43.14	[39]
7.	Poly(*N*-isopropylacrylamide-co-acrylic acid) hydrogel	4.4	25	1.0	67.25	[40]
8.	Hazelnut shell activated with carbon	6.0	25	33 min	58.27	[41]
9.	PEGylated-CA	5.0	100	1	172.8	Present work

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