Removal of copper(II) ions from aqueous solution by modified bagasse

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ABSTRACT

Bagasse-based ion adsorbent was prepared by chemically modifying bagasse with acrylonitrile and hydroxylamine with the aim to enhance the ability of removal heavy metal ions from wastewater. The purified modified materials were characterized by Fourier transform infrared (FT-IR). Batch experiments of Cu(II) ions (Cu^{2+}) adsorption on the bagasse adsorbent were performed. Effects of the adsorbent dosage, initial pH of the solution, temperature of the Cu^{2+} solution, and initial Cu^{2+} concentration on the adsorption of Cu^{2+} were studied, respectively. Langmuir and Freundlich models were applied to describe the adsorption isotherm of Cu^{2+} by bagasse adsorbent. The results indicated that Langmuir model fitted the adsorption equilibrium data better than the Freundlich isotherm model. Two kinetic models, including pseudo-first-order and pseudo-second-order, were also used to analyze the Cu^{2+} adsorption process, and the results showed that the pseudo-second-order with correlation coefficients greater than 0.999 was more suitable than pseudo-first-order.

1. Introduction

The water pollution by toxic heavy metals through the discharge of industrial waste is a world-wide environment problem [1,2]. Metals such as copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), chromium (Cr), and zinc (Zn), which have been considered as hazardous heavy metals are commonly found in waste. These heavy metals are toxic and their presence in steams leads to accumulation in living organisms, causing health problems in human beings, plants, and animals. So the removal of these metals from wastewater is necessary. Traditional methods for the removal and recovery of heavy metals from industrial waste streams are precipitation, ion exchange, electrolysis, adsorption on activated carbon, etc. [3–5]. Most of these methods are extremely expensive or inefficient, especially for a large amount of solution at relatively low concentrations [6,7]. Adsorption is now recognized as an efficient and economic method to remove metal ions from aqueous solution [8]. The adsorbents may be of mineral, organic or biological origin. Recently, there has been an increasing emphasis on the adsorbent with low cost for the heavy metal ions removal. Biomaterials such as byproducts or the wastes from agriculture deserve particular attention [9]. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, and high reactivity resulting from the presence of repetitive functional groups in polymer chains. Moreover, it is well known that the biopolymers which are abundant, renewable and biodegradable resources, have a capacity to associate with a wide variety of molecules by physical and chemical interactions [8]. Some agriculture byproducts or wastes, such as tree fern [10], sawdust [3], rice bran [11], wheat bran [4], corncobs [12], etc., have been widely studied for heavy metals removal from aqueous solution.

Bagasse, which is a complex material containing lignin and cellulose as major constituents, is an industrial solid waste from the sugar industry. As its adsorption capacity on metal ions is poor, by introducing some functional groups with higher adsorption ability the adsorption capacity can be improved. In earlier research, bagasse has been studied as a raw material for the preparation of ion adsorbent. Different chemical modifications have been carried out to introduce different functional groups such as phosphate, sulfonate and carboxyl onto bagasse to increase its adsorption capacity [13,14]. In this work, bagasse was modified with acrylonitrile and hydroxylamine to introduce amidoxime functional groups in order to enhance its adsorption ability to heavy metal ions. And the present study was focused on the adsorption of Cu^{2+} onto the amidoximated bagasse at different conditions. The effects of the adsorbent dosage, initial pH of the solution, temperature of the solution, and initial Cu^{2+} concentration on the Cu^{2+} adsorption were investigated and discussed. The adsorption kinetics and equilibrium isotherms were also studied.

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2. Methods

2.1. Materials

Bagasse as received from the provider was milled to the particle diameter less than 80-mesh, and dried in an oven at 100 °C for a period of 24 h. Acrylonitrile (AN) was purchased from Tianjin kemiou Chemical Reagent Co., Ltd., China; hydroxylamine hydrochloride, sodium carbonate, and $CuCl_2 \cdot 2H_2O$ were supplied by Guangzhou Chemical Reagent Factory, China, Tianjin Chemical Reagent Factory, China, and Tianjin Fuchen Chemical Reagent Factory, China, respectively. All the other chemicals used were of analytical grade without further purification.

Copper solution of desired concentration were prepared from $CuCl_2 \cdot 2H_2O$, by dissolving the exact quantities of copper salts in deionized water.

2.2. Modification of bagasse

2.2.1. Preparation of cyanoethylated bagasse

2 mL water, in which 0.1 g tetramethylammonium chloride was dissolved, was atomized onto 3.0 g bagasse sample. Then the treated bagasse was dispersed in 72 mL AN, and 2 mL 36% aqueous sodium hydroxide solution was added. The mixture was reacted at 25 °C for 2 h. When the reaction was completed, the mixture was treated with isopropanol in order to dissolve and eliminate the unreacted AN [15]. Finally the product was filtered, washed with deionized water, and dried under reduced pressure at 30 °C.

2.2.2. Preparation of amidoximated bagasse

3.0 g cyanoethylated bagasse was treated with an aqueous solution of hydroxylamine hydrochloride at pH 10. The pH of the solution was adjusted by sodium carbonate. The mass ratio of hydroxylamine hydrochloride and sodium carbonate was 1:0.75. The mixture was heated to 80 °C for desired time, then the product was filtered, washed with deionized water for several times to remove the unreacted hydroxylamine hydrochloride, and finally dried at 60 °C.

2.3. Fourier transform infrared (FT-IR) analysis

The Fourier transform infrared (FT-IR) spectra of the modified bagasse were recorded with a FT-IR Analect RFX-65A spectrometer (American). Samples were pressed into discs with potassium bromide and analyzed in transmittance and absorbance.

2.4. Equilibrium isotherm

The equilibrium isotherm was measured by contacting 0.1 g amidoximated bagasse with a range of different initial concentrations of 40 mL Cu^{2+} solution (76–600 mg/L). The mixtures were agitated in a conical flask for 24 h, which was sufficient time to reach adsorption equilibrium at various temperatures. The experiments were carried out at pH values below the pH where metal hydroxide chemical precipitation occurs, which had been estimated as pH > 6.3 for $Cu(OH)_2(s)$ [16]. The initial pH of the solution was adjusted to 6.0 using Clark-clubs buffer solution [17] without any further adjustment during the sorption process. After stirring for 24 h, the amidoximated bagasse was separated by filtration, and the residual Cu^{2+} concentration in the aqueous solution was measured by atomic absorption spectrometer (AAS Z-5000, Japan). Amount of Cu^{2+} uptake at equilibrium, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 (mg/L) is the initial concentration of Cu^{2+}, C_e (mg/L) is the concentration of Cu^{2+} at equilibrium, V (L) is the volume of the solution, and m (g) is the weight of bagasse adsorbent.

2.5. Adsorption kinetics

The initial copper ions concentration was 76 mg/L for all experiments except for the study of the effect of the initial concentration on Cu^{2+} adsorption. For Cu^{2+} adsorption kinetics studies, 1 g amidoximated bagasse was contact with 400 mL Cu^{2+} solution in a flask stirred continuously in a water bath maintained at different temperatures (30, 40, 50 and 60 °C). The initial pH of the solution was adjusted to 6.0 without any further adjustment during the sorption process. After appropriate time intervals, samples of the mixture were withdrawn and filtered through a paper filter. The residual concentration of Cu^{2+} in the solution was also measured by atomic absorption spectrometer (AAS Z-5000, Japan).

3. Results and discussion

3.1. Physico-chemical analysis of the adsorbent

Bagasse is a plant biomass containing large number of complex organic components, namely, proteins, lipids, and carbohydrate, etc. there are –OH, –COOH functional groups in the lignocellulosic and protein moieties of biomass [18]. And after the modification of bagasse with acrylonitrile and hydroxylamine, a series of amidoxime groups were introduced into the complex polysaccharide matrix. These functional groups may affect the adsorption capacity of the adsorbent. In order to characterize the adsorbent used in this study, various physical properties and chemical analysis of the bagasse adsorbent were determined. Elemental analyses were accomplished in Analyzer 2400 CHNS/O PerkinElmer series II, USA. The surface area and porosity were determined by Accelerated Surface Area and Porosimetry System, model ASAP2010M, Micromeritics Corporation, USA. Particle size of the adsorbent was determined by Automatic particle size analyzer, model Sedigraph III 5120, Micromeritics Corporation, USA. The results are given in Table 1.

3.2. FT-IR study of modified bagasse

3.2.1. FT-IR spectra of modified bagasse

FT-IR spectra of untreated bagasse, cyanoethylated bagasse, and amidoximated bagasse are shown in Fig. 1. The broad and strong bands around 3500 cm^{-1} were due to bounded hydroxyl group (–OH). Compared with the untreated bagasse Fig. 1a, a sharp peak appeared in cyanoethylated bagasse at 2254 cm^{-1} (Fig. 1b), corresponding to the stretching of the cyano group. On the other hand, three new bands appeared at 2254, 1660, and 910 cm^{-1} in the amidoximated bagasse (Fig. 1c), which were characteristic of the –C≡N, –C=N and –N–OH groups, respectively. A reduction of the intensity of cyano absorption at 2254 cm^{-1} in Fig. 1c was observed, con-

Table 1
Physical and chemical properties of bagasse adsorbent

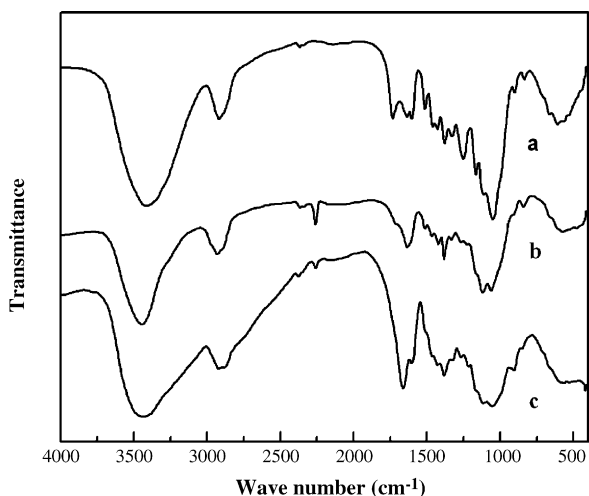| Chemical analysis		Physical analysis	
Constituents	Weight (%)	Parameter	Value
C	43.96	Surface area (m^2 g^{-1})	107.69
H	7.13	Mean size (μm)	174.63
N	13.64	Porosity	0.31

Fig. 1. FT-IR spectra of (a) untreated bagasse, (b) cyanoethylated bagasse, and (c) amidoximated bagasse.

tributed to the amidoximation of cyano group in the cyanoethylated bagasse.

3.2.2. Effect of reaction time on the FT-IR spectra of amidoximated bagasse

FT-IR spectra of amidoximated bagasse with different reaction time are shown in Fig. 2. It is clear that all amidoximated bagasse have two bands at 1660 and 910 cm^{-1} due to the formation of oxime group –C=N and –N–OH compared with the spectra of cyanoethylated bagasse. The reaction degree of the amidoxime group can be quantified with FT-IR scaling method [19]. The peak at 1325 cm^{-1} (assigned to bending vibration band of cellulose ring C–H in bagasse) could be used as internal reference [20]. The relative absorbance intensity of 2254, 1660 and 910 cm^{-1} were given by A_{2254}/A_{1325}, A_{1660}/A_{1325} and A_{910}/A_{1325}, respectively. Where A_{1325} is the absorbed intensity at 1325 cm^{-1}, A_{2254} is the absorbed intensity at 2254 cm^{-1}, A_{1660} and A_{910} is the absorbed intensity at 1660 and 910 cm^{-1}, respectively. The values can be calculated from FT-IR spectra using IR scaling method and are presented in Table 2. It is clear that the relative absorbance intensity of 2254 cm^{-1} decreases with the reaction time with the conversion of cyano group to oxime group. And the relative absorbance intensity of the bands 1660 and
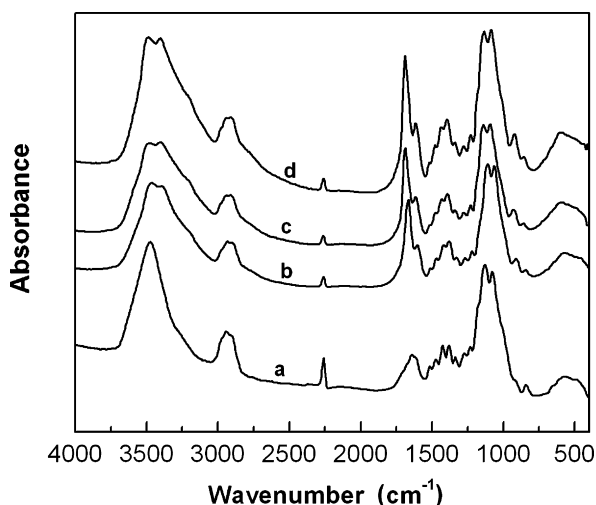
Table 2
Relative absorbance intensity of different bands of amidoximated bagasse at different reaction time

Samples	A_{2254}/A_{1325}	A_{1660}/A_{1325}	A_{910}/A_{1325}
Amidoximated bagasse ($t = 0$ min)	1.008	–	–
Amidoximated bagasse ($t = 90$ min)	0.346	1.094	0.806
Amidoximated bagasse ($t = 150$ min)	0.289	2.776	1.008
Amidoximated bagasse ($t = 180$ min)	0.269	2.862	1.173

910 cm^{-1} increase with the time due to the formation of oxime group. As In the modified process of bagasse with hydroxylamine hydrochloride, new group –NH$_2$ appeared in the bagasse adsorbent with the conversion of cyano group to amidoxime group. While its absorption band is in lower wave number than that of –OH group. So there are two bands around 3500 cm^{-1} appeared after bagasse modified with hydroxylamine hydrochloride and the intensity of the new band increased as the contact time increasing. According to the study, the bagasse adsorbents used in later adsorption experiments were all prepared with reaction time 180 min.

3.3. Effect of adsorbent dosage on the adsorption of Cu^{2+}

The effect of adsorbent dosage on the removal percentage of Cu^{2+} and Cu^{2+} uptake amount by amidoximated bagasse is shown in Fig. 3. It is clear that the percentage of Cu^{2+} removal increases with the adsorbent dosage increasing from 0.5 to 10 g/L. This may be attributed to the increase of the number of adsorption sites and surface area with the weight of adsorbent increasing. At higher dosage, all the Cu^{2+} in the solution could interact with the binding sites and thus resulting in a higher percentage of copper removal. While the amount of Cu^{2+} adsorbed on per unit weight of bagasse adsorbent decreases with the adsorbent dosage, which was in accordance with the results of Amarasinghe and Williams [21]. This is due to the split in the flux or the concentration gradient between the solute concentration in the solution and the one in the surface of the adsorbent [22]. When the adsorbent dosage is higher, there is a very fast adsorption onto the adsorbent surface, which results in a lower adsorbate concentration in the solution. However, the adsorption sites on the adsorbent surface remain unsaturated when the adsorbate concentration in the solution drops to a lower value. Thus, the amount of Cu^{2+} adsorbed onto per unit weight of adsorbent gets reduced with the adsorbent dosage increasing. The removal percentage of Cu^{2+} and the Cu^{2+} uptake amount have the opposite trend toward adsorbent dosage. When the dosage is 2.5 g/L, both
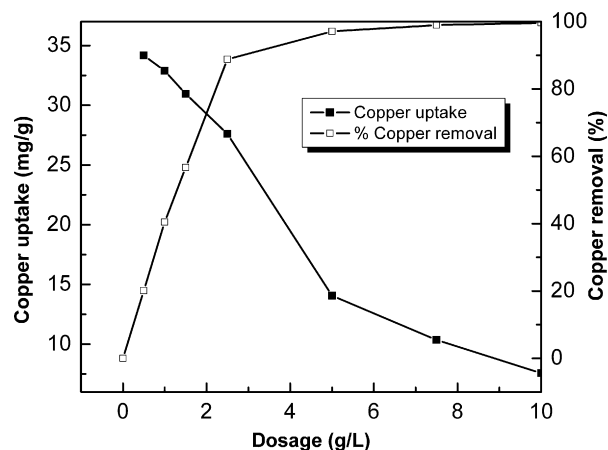

Fig. 2. FT-IR spectra of bagasse amidoximated at different reaction time: (a) 0 min, (b) 90 min, (c) 120 min, and (d) 180 min.

Fig. 3. Effect of adsorbent dosage on the removal of Cu(II) ions and Cu(II) ions uptake by modified bagasse: concentration, 76 mg/L; temperature, 30 °C; initial pH, 6.0; contact time, 24 h.

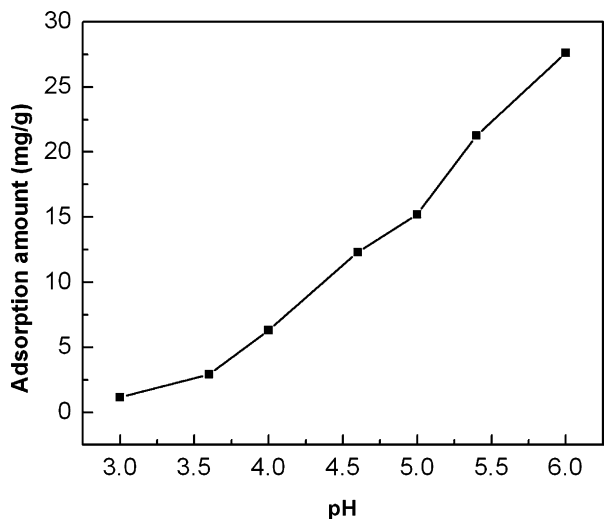**Fig. 4.** Effect of initial pH on the adsorption of Cu^{2+} by amidoximated bagasse: concentration, 76 mg/L; temperature, 30 °C; adsorbent dose, 2.5 g/L; contact time, 24 h.
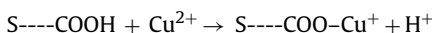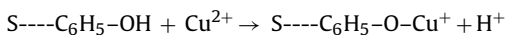
the adsorption amount and removal percentage of Cu^{2+} reach relative high values. So the following studies were performed with adsorbent dosage 2.5 g/L.

### 3.4. Effect of initial pH on the adsorption of Cu^{2+}

Many researchers have verified that the pH of the medium has significant influence on the adsorption capacity of the biosorbents [23,24]. The effect of pH on the adsorption capacity of Cu^{2+} by bagasse adsorbent was evaluated within the pH range of 3.0–6.0 (Fig. 4). The highest adsorption amount of Cu^{2+} with bagasse adsorbent was obtained at pH 6.0. The acidity of the medium can affect the metal ions uptake amount of the bagasse adsorbent because hydrogen ions in the solution could compete with Cu^{2+} for active sites on the adsorbents surface. The possible sites on bagasse adsorbent for specific adsorption include –OH and –COOH functional groups [25]. These functional groups are dissociated at various pH values and consequently take part in surface exchange of Cu^{2+}.

$$-OH \rightleftharpoons -O^- + H^+$$

$$-COOH \rightleftharpoons -COO^- + H^+$$
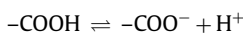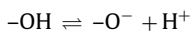
The surfaces of the adsorbent are expected to be negatively charged which facilitate the adsorption of the positively charged Cu^{2+}. The increase of the pH value favors the surface of the bagasse adsorbent become negative and the adsorption capacity of Cu^{2+} increases.

$$S\text{----}C_6H_5\text{--}OH + Cu^{2+} \rightarrow S\text{----}C_6H_5\text{--}O\text{--}Cu^+ + H^+$$

$$S\text{----}COOH + Cu^{2+} \rightarrow S\text{----}COO\text{--}Cu^+ + H^+$$

where S donates the adsorbent surface, however, the sites responsible for the adsorption process are not exclusively due to the –COOH and –C_6H_5–OH groups, other sites introduced by modification on the bagasse adsorbent also contribute to the adsorption through the surface complexation with Cu^{2+} [26,27].
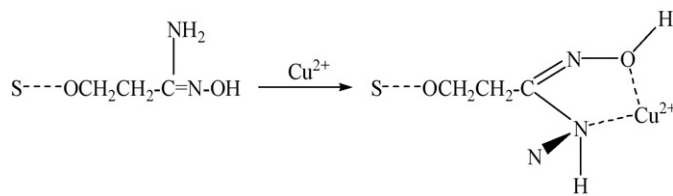
3.5. Adsorption isotherms

The adsorption isotherm provides a relationship between the concentration of metal ions in solution and the amount of metal ions adsorbed onto the adsorbent when both phases are at equilibrium [28]. Several equilibrium models have been developed to describe adsorption isotherm relationships [29]. The Langumuir [30] and Freundlich [31] equations are the world-widely used models because of their simplicity. The adsorption isotherms for Cu^{2+} on amidoximated bagasse at different temperatures are shown in Fig. 5. The adsorption data has been analyzed with the two adsorption models.

3.5.1. Langmuir isotherm

Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of adsorbent. The basic assumption of Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent [32]. The Langmuir adsorption isotherm is given as

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{2}$$

where C_e (mg/L) is the equilibrium concentration of adsorbate in solution, q_e (mg/g) is the adsorption amount of adsorbent at equilibrium. K_L (L/mg) is the equilibrium adsorption constant which is related to the affinity of the binding sites and q_m (mg/g) is the maximum adsorption amount of metal ions. They can be determined from a linear form of Eq. (2) (by plotting the C_e/q_e versus C_e), represented by

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

The Langmuir constants K_L and q_m have been calculated with the Eq. (3) and are presented in Table 3. The values of regression coefficient R^2 are higher than 0.99. The high coefficient suggests that
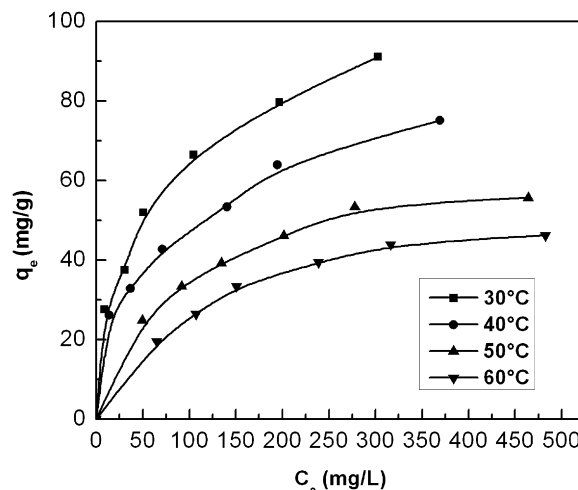

Fig. 5. Equilibrium isotherms of Cu^{2+} adsorption by amidoximated bagasse at different temperatures: contact time, 24 h; initial pH, 6.0; adsorbent dosage, 2.5 g/L.

Table 3

Adsorption isotherm parameters of Cu^{2+} adsorbed by amidoximated bagasse at different temperatures: contact time, 24 h; initial pH, 6.0; adsorbent dosage, 2.5 g/L

Parameters	Temperature (°C)			
	30	40	50	60
Langmuir isotherm				
q_m (mg/g)	101.01	83.963	67.024	59.277
K_L (L/mg)	22.9×10^{-3}	17.35×10^{-3}	11.33×10^{-3}	7.99×10^{-3}
R^2	0.9937	0.9906	0.9981	0.9977
Freundlich isotherm				
K_F (mg/g)	12.714	10.455	6.011	3.336
n	2.880	2.996	2.654	2.264
R^2	0.9925	0.9946	0.9822	0.9753

the Cu^{2+} adsorbed by amidoximated bagasse form monolayer coverage on the surface of the adsorbent. The maximum adsorption capacity q_m is found to decrease from 101.01 to 59.28 mg/g with an increase of the solution temperatures from 30 to 60 °C. The sorption constant K_L also decreases from 22.9×10^{-3} to 7.99×10^{-3} L/mg as temperature increasing from 30 to 60 °C. The decrease of q_m and K_L with temperature indicates that the Cu^{2+} are more easily adsorbed by amidoximated bagasse at lower temperature. It indicates that the adsorption process of Cu^{2+} on the amidoximated bagasse is an exothermic process.

Based on the Langmuir isotherm, the maximum adsorption capacity q_m of Cu^{2+} adsorbed by amidoximated bagasse is 101.01 mg/g at 30 °C. Table 4 shows several other materials reported in literature for the removal of Cu^{2+} from aqueous solution although this direct comparison is difficult due to the varying experimental conditions used in these studies. However, an examination of the sorption value with that given in the literature can provide basic information to evaluate the possibility of using the bagasse adsorbent for the removal of Cu^{2+}. From Table 4, it is evident that the bagasse adsorbent prepared in this paper has demonstrated outstanding removal capabilities for Cu^{2+} and was competitive against other adsorbents. Differences of Cu^{2+} uptake are due to the properties of each adsorbent material structure, functional groups and surface area.

The type of the Langmuir isotherm can be predicted whether the adsorption is favorable or unfavorable in term of equilibrium parameter or dimensionless constant separation factor R_L, which is defined by the following equation, according to Hall et al. [41]:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{4}$$

where C_0 (mg/L) is the initial concentration of Cu^{2+} and K_L is the Langmuir constant as described above. The separation factor R_L indicates the shape of the isotherm, whether the adsorption is favorable or not, according to the following criteria [42,43].

Table 4

Comparison of maximum capacities of Cu^{2+} on some adsorbents

Adsorbent material	q_m (mg/g)	References
Ion-exchange resin	146	[33]
Bagasse	101.01	This work
Dried flower leaves	89.37	[34]
Peanut hull carbon	65.57	[35]
Corncob	62.87	[36]
Wheat bran	51.5	[4]
Natural clay	44.84	[37]
Soybean hulls	38.7	[38]
Rice bran	33.58	[11]
Kaolinite	10.79	[39]
Zeolite	8.9	[40]

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L versus Cu^{2+} initial concentration at various temperatures are shown in Fig. 6. The values are found to be less than 1 and greater than 0 for all experiments carried out at different concentrations and temperatures, which indicates that the adsorption of Cu^{2+} on amidoximated bagasse is favorable. And the lower temperature and higher concentration is more favorable to the adsorption.

3.5.2. Freundlich isotherm

The Freundlich isotherm is based on assumption that adsorption is on a heterogeneous surface and exponential distribution of sites and their energies [44], which can be expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively [45]. They can be calculated in the following linear form:

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

The values of K_F and n at different temperatures obtained from the intercept and slope of the plots of $\log q_e$ against $\log C_e$ are also presented in Table 3. The values of K_F decrease from 12.71 to 3.34 mg/g with the temperature of the solution increasing from 30 to 60 °C. As the K_F is a measurement of adsorption capacity, the decrease of the value again confirms that the adsorption process of Cu^{2+} on the amidoximated bagasse is an exothermic process. All the values of n are between 2 and 3. According to McKay et al. [46] the values of n in the range of 2–10 represent good adsorption. From the results obtained, it is clear that the adsorption of this study is very good.

Fig. 7 shows graphical comparison of the experimental value with the calculated value from the equilibrium isotherm for Cu^{2+} adsorption by bagasse adsorbent. It is obvious that the adsorption capacities calculated from Langmuir isotherm are much closer to the experimental values of q_e than that of Freundlich isotherm. From Table 3, it also appears that Langmuir isotherm fitted the experimental results over the experimental range with a higher
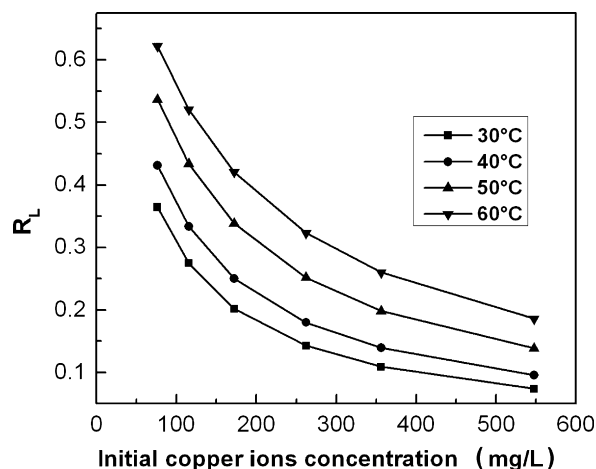

Fig. 6. Separation factor for Cu^{2+} adsorption by amidoximated bagasse at various temperatures: contact time, 24 h; initial pH, 6.0; adsorbent dosage, 2.5 g/L.
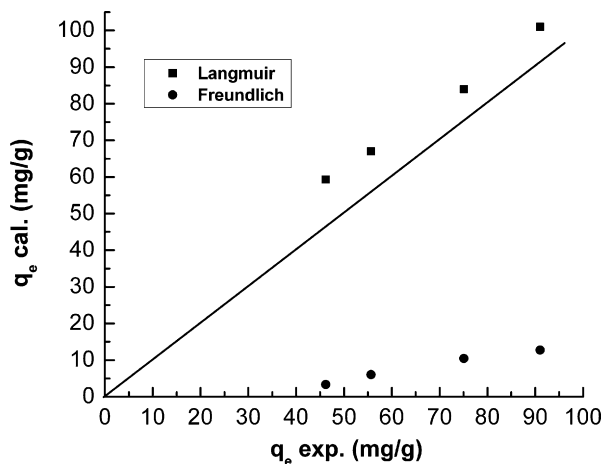
Fig. 7. Comparison of Langmuir and Freundlich models with experiment for Cu^{2+} adsorption by amidoximated bagasse.

coefficient of correlation than that of Freundlich isotherm. These results indicated that the adsorption of Cu^{2+} onto bagasse adsorbent follows better the Langmuir isotherm.

3.6. Adsorption kinetics

Adsorption kinetics describes the relationship of solute uptake rate of the adsorption and the adsorption time. For further application, the elucidation of the kinetic parameters and sorption characteristics of the adsorbent material is necessary. The primary issue to be addressed is contact time, temperature and initial Cu^{2+} concentration of the adsorption process.

3.6.1. Effect of contact time and temperature

The influence of time and temperature on the rate of Cu^{2+} uptake is shown in Fig. 8. The results of amidoximated bagasse sorption show an initial rapid adsorption rate followed by a slow one, which is consistent with the observation of Saygideger et al. [47]. It can be attributed to the fact that at the initial stage the adsorption sites are more, and the metal ions can interact easily with the sites, so a higher adsorption rate is obtained. Besides, the driving force for adsorption is the concentration gradient between the bulk solution and the solid–liquid interface, and the concentration gradient is
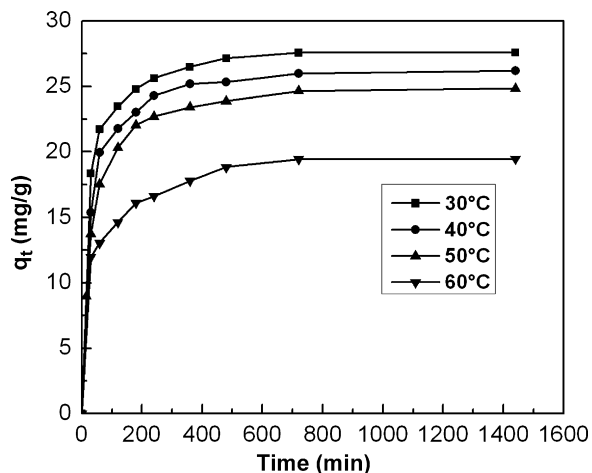

Fig. 8. Effect of contact time on the adsorption of Cu^{2+} by amidoximated bagasse at various temperatures: concentration, 76 mg/L; initial pH, 6.0; adsorbent dosage, 2.5 g/L.

higher in the initial period, which results in a higher adsorption rate. The slow adsorption rate in later stage is due to slower diffusion of solute into the interior of the adsorbent [48]. It is also found that the adsorption amount of Cu^{2+} on per unit weight of amidoximated bagasse decreases with the temperature increasing, which further confirms the adsorption of Cu^{2+} onto amidoximated bagasse was an exothermic process [49]. The decreasing adsorption capacity of amidoximated bagasse with the rising temperature may result from the weakening adsorptive forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase [50].

The adsorption kinetics data of Cu^{2+} onto amidoximated bagasse can be analyzed by pseudo-first-order Lagergren equation [51,52] and pseudo-second-order model [53]. The pseudo-first-order equation is expressed as the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where q_t and q_e (mg/g) is the amount of metal ions adsorbed on per unit weight of adsorbent at time t and equilibrium, respectively; and k_1 (min^{-1}) is the pseudo-first-order rate constant of the sorption process. The model is based on the assumption that the adsorption rate is proportional to the number of free sites. By applying the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ and integrating, Eq. (7) can be represented in linear form in the following equation:

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \tag{8}$$

Linear plots of $\log(q_e - q_t)$ versus t can be plotted to evaluate this kinetic model and to determine rate constant and q_e from the slop and intercept, respectively.

The pseudo-second-order model is based on the assumption that adsorption rate is related to the square of the number of unoccupied sites:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 is the rate constant of the pseudo-second-order (g mg^{-1} min^{-1}). Integrating Eq. (9) from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ yields the linearized version of this model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

The parameters q_e and k_2 can be calculated from the slope and the intercept of the plot t/q_t versus t. The initial sorption rate h_0 can be obtained as q_t/t approaches zero:

$$h_0 = k_2 q_e^2 \tag{11}$$

The results obtained for adsorption of Cu^{2+} onto amidoximated bagasse at different temperatures and contact time were analyzed with Eq. (8) and Eq. (10). The kinetic parameters calculated are shown in Table 5. All plots show higher correlation coefficients R^2 and better conformity with the pseudo-second-order model than pseudo-first-order model. The plots of t/q_t versus t for the linear pseudo-second-order model are shown in Fig. 9. The values of correlation coefficients R^2 for the pseudo-second-order kinetic model are greater than 0.999 at any temperature. And the calculated values of q_e estimated from the pseudo-second-order kinetic model in this study is much closer to the experimental values of q_e than that of pseudo-first-order model. So the sorption of Cu^{2+} by amidoximated bagasse in this study was better fitted to the pseudo-second-order model. The pseudo-second-order rate constant k_2 and initial adsorption rate h_0 decrease with the temperature, which confirms the exothermic nature of the adsorption process.

Table 5
Kinetic constants of Cu^{2+} adsorbed onto amidoximated bagasse at different temperatures: initial concentrations, 76 mg/L; initial pH, 6.0; adsorbent dose, 2.5 g/L

Parameters	Temperature (°C)			
	30	40	50	60
$q_{e\,exp}$ (mg g^{-1})	27.605	26.177	24.834	19.471
Pseudo-first-order				
k_1 (min^{-1})	7.876×10^{-3}	5.548×10^{-3}	5.804×10^{-3}	6.932×10^{-3}
q_{e1} (mg g^{-1})	12.204	9.072	11.223	12.879
R^2	0.9834	0.9865	0.9818	0.9260
Pseudo-second-order				
k_2 (g mg^{-1} min^{-1})	1.849×10^{-3}	1.625×10^{-3}	1.451×10^{-3}	1.378×10^{-3}
q_{e2} (mg g^{-1})	28.035	26.638	25.342	20.016
h_0 (mg g^{-1} min^{-1})	1.453	1.153	0.932	0.552
R^2	0.9999	0.9999	0.9999	0.9997

$q_{e\,exp}$: the experimental value of q_e; q_{e1} and q_{e2}: calculated values of q_e from pseudo-first-order and pseudo-second-order equation, respectively.

3.6.2. Effect of initial Cu^{2+} concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase. Batch of experiments were also performed to study the effect of the initial Cu^{2+} concentration on its adsorption kinetics in solution by amidoximated bagasse. The results are shown in Fig. 10. The adsorption curves obtained are single smooth and continuous, which suggests the formation of adsorbate monolayer on the surface of the adsorbent [54,55]. It is observed that the extent of adsorption increased rapidly in the initial stages and then the increase became slow in the later stage until reaching to equilibrium. And it also shows that the increases in initial Cu^{2+} concentration leads to an increase in the adsorption capacity of Cu^{2+} by amidoximated bagasse. It is attributed to the fact that the driving force, which depends on the concentration gradient, increases with the initial Cu^{2+} concentration. And the adsorption sites of the adsorbent in the solution with higher Cu^{2+} concentration are more easily to reach adsorption saturation. The plots of t/q_t versus t according to Eq. (10) at various initial Cu^{2+} concentrations are shown in Fig. 11. The rate constant k_2, the equilibrium sorption capacity q_e and the initial sorption rate h_0 at different concentrations can be calculated from Fig. 11, which are presented in Table 6. The equilibrium adsorption amount increases with the increasing of the initial Cu^{2+} concentration, which is due to the fact that resistance of metal ions uptake decreases as the mass transfer driving force increases with the increasing concentration.
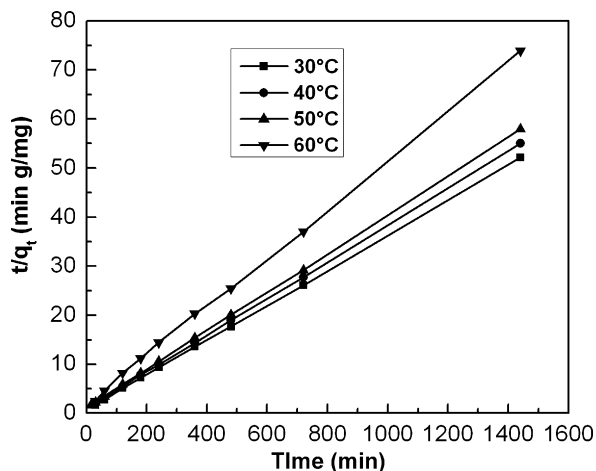

Fig. 10. Plot of Cu^{2+} adsorption amount by amidoximated bagasse at various initial concentrations: temperature, 30 °C; initial pH, 6.0; adsorbent dosage, 2.5 g/L.

Fig. 11. Pseudo-second-order sorption kinetics of Cu^{2+} by amidoximated bagasse at different initial concentrations: temperature, 30 °C; initial pH, 6.0; adsorbent dosage, 2.5 g/L.

Fig. 9. Pseudo-second-order sorption kinetics of Cu^{2+} onto amidoximated bagasse at various temperatures: concentration, 76 mg/L; initial pH, 6.0; adsorbent dosage, 2.5 g/L.
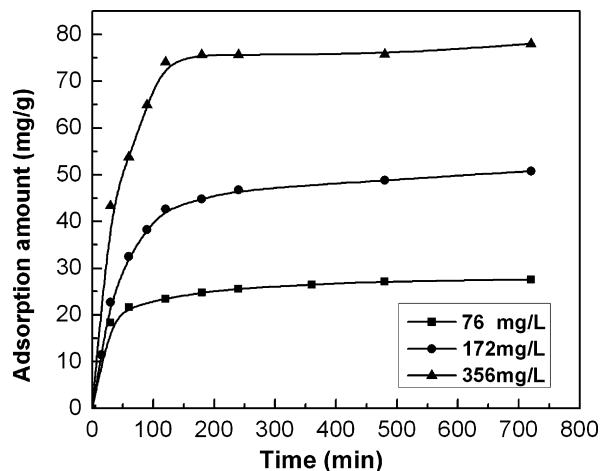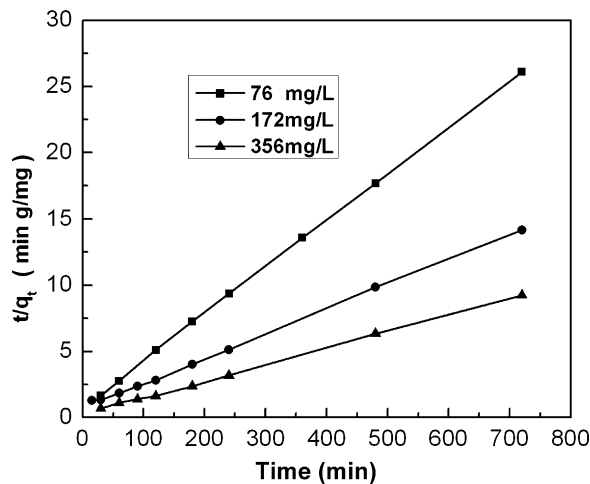
Table 6
Pseudo-second-order rate constant of Cu^{2+} adsorbed onto amidoximated bagasse at different concentrations: temperature, 30 °C; initial pH, 6.0; adsorbent dose, 2.5 g/L

Parameters	76 mg L^{-1}	172 mg L^{-1}	356 mg L^{-1}
k_2 (g mg^{-1} min^{-1})	18.49×10^{-4}	4.703×10^{-4}	6.135×10^{-4}
q_e (mg g^{-1})	28.035	53.562	80
h_0 (mg g^{-1} min^{-1})	1.453	1.349	4.118
R^2	0.9999	0.9995	0.9995

4. Conclusion

The results of the study reveal that bagasse can be converted into an adsorbent with good adsorption capacity by modifying it with acrylonitrile and hydroxylamine. The amidoximated bagasse was used to study the removal of Cu^{2+} from aqueous solution, and the adsorption capacity increased with the pH value of the solution and the initial Cu^{2+} concentration, but decreased with the adsorbent dosage.

The studies of adsorption isotherms suggested that Langmuir isotherm generated the better agreement with the experiment data of Cu^{2+} adsorbed by bagasse adsorbent than Freundlich isotherm with correlation coefficients greater than 0.99 for the adsorption systems. The value of the maximum adsorption capacity q_m calculated from Langmuir model were also closer to the experimental values of q_e than that of Frenudlich model, which decreased from 101.01 to 59.28 mg/g when the solution temperature increased from 30 to 60 °C. The decrease of the maximum adsorption capacity with temperature indicated the adsorption process of Cu^{2+} onto the amidoximated bagasse was exothermic.

A pseudo-second-order model was more suitable than a pseudo-first-order model with correlation coefficients greater than 0.999. The pseudo-second-order rate constant and initial adsorption rate decreased with the temperature increasing, which confirmed the exothermic nature of the adsorption process.

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