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Equilibrium studies of copper ion adsorption onto modified kernel of date (*Fructus dactylus*)

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Abstract Heavy metal pollution of water is a serious problem because of its toxic effects on the human health and living organism. Therefore, there is a need to develop technologies to remove toxic pollutants found in polluted water. There are different ways to remove the toxic metals from wastewater. Among all treatments proposed, the adsorption process is one of the most promising technologies in water pollution control. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many low-cost adsorbents, including natural materials, biosorbents and waste materials from industry and agriculture, have been proposed by several researchers. In this study, removal of copper from aqueous solution by using powdered and modified kernel of date (Fructus dactylus) with apocarbonic anhydrase enzyme has been investigated. The operating variables studied were contact time, initial solution pH, initial metal concentration, temperature and adsorbent dosage. The experimental investigation results showed that modified and powdered kernel of date (F. dactylus) has a high level of adsorption capacity for copper ions. The adsorption data were correlated with the Langmuir and Freundlich isotherm models. It was found that the

H. Celik

Langmuir and Freundlich isotherms fitted well to the data. The results revealed that copper is considerably adsorbed on modified and powdered kernel of date (F. dactylus). Consequently, it is concluded that the modified and powdered kernel of date (F. dactylus) can be successfully used for the removal of the copper ions from the aqueous solutions.

Keywords Kernel of date (Fructus dactylus) .

Apocarbonic anhydrase \cdot Heavy metal \cdot Copper removal \cdot Adsorption isotherms

Introduction

It is an accepted truth that the contamination of water by toxic heavy metals through discharge of industrial wastewater is a worldwide environmental problem. Water contamination, reported by the World Health Organization (WHO), is responsible for more than 3.5 million deaths per year worldwide, and heavy metals pollution makes the situation worse due to their immense toxicity and nonbiodegradability (Jayakumar et al. 2010; Pronczuk et al. 2011). High concentration of heavy metals in the environment can be detrimental to a variety of living species. Heavy metal ions can be accumulated through the food chain even at lower concentrations, leading to reduced mental and central nervous function, lower energy levels and damaged blood composition, lungs, kidneys, liver and other vital organs (Kalkan et al. 2012).

Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have led to an increased disposal of heavy metals into the environment. The presence of these heavy metals is an



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important concern for the environment due to their toxicity and health effects on the human and living creatures (Gupta and Ali 2004; Gupta and Rastogi 2008; Jiang et al. 2008; El-Said et al. 2010). Heavy metals are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing and others. Their removal has attracted much practical and academic interest owing to an increased concern with their environmental impact. The world industry comes across the ever-increasing need for decreasing of heavy metal ions content in water as well as industrial waste to the admissible level. For the past several years, high levels of heavy metals in drinking water and foods have been associated with several acute and chronic illnesses in humans throughout the world (Gupta et al. 2006; Aman et al. 2008; Nadaroglu et al. 2010; Gupta et al. 2011).

Due to the increased awareness of environmentalists and governments on the effects of heavy metals and attempts to protect public health, researches were increased related to the removal of heavy metals from waters and wastewaters in the development of treatment technologies (Bong et al. 2004; Karbassi et al. 2007; Shetty and Rajkumar 2009; Onundi et al. 2010; Resmi et al. 2010; Celebi et al. 2012; Nadaroglu and Kalkan 2012). Removal of toxic metal ions can be achieved by techniques such as coagulation, flocculation, precipitation, filtration, ozonation and ion exchange. However, these methods have high operating costs (Rao et al. 2008), while adsorption proved to be versatile and readily applicable (Gupta and Ali 2004). Activated charcoal can be selected as a adsorbent, but its cost is very high (Pollard et al. 1992; Aravindhan et al. 2009; Sousa et al. 2010). Therefore, cheap natural materials of renewable sources are suitable alternatives. In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, when these materials reach the end of their life time, they can be disposed of without expensive regeneration (Bailey et al. 1999; Bable and Kurniawan 2003).

Copper is a widely used industrial metal used for electrical wiring, plumbing, air-conditioning tubing and roofing. The properties of copper, which make it suitable for these applications, include high electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation, attractive appearance, ready availability and high recyclability. Additionally, copper, which is an essential nutrient to humans and other life forms, is biostatic/biocidal to certain organisms (Aksu and Isoglu 2005;



Habib et al. 2007). However, copper is known to be one of the heavy metals most toxic to living organisms, and it is one of the more widespread heavy metal contaminants of the environment. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production and the fertilizer industry, etc. Consequently, wastewater of these industries contains high levels of copper ions, and in order to avoid water pollution, treatment is needed before disposal (Ong et al. 2003; Aksu and Isoglu 2005; Mukhopadhyay et al. 2007; Nadaroglu et al. 2010).

Carbonic anhydrase (CA), which catalyzes the reversible hydration of carbon dioxide (CO₂), was one of the first proteins for which a crystal structure was obtained (Kannan et al. 1967, Liljas et al. 1972). CA is categorized into three main classes: α , β and γ , which share no significant similarity in primary sequence or overall structure (Demir et al. 2001a), but which all rely on Zn for activity. Whereas α and χ -CA use three histidine residues to coordinate the Zn atom, β -CA uses two cysteine residues and one histidine residue (Demir et al. 2001a, b, 2007, 2009).

When the zinc is removed from active site of CA, which is covalently bound, the apocarbonic anhydrase (apoCA) obtained. ApoCA is the deactivated enzyme. The structure of apoCA can be bound metal ions in the environmental (Nadaroglu et al. 2008). It is thought that Cu^{2+} can be connected with both apoCA's active center and surface of powdered and modified kernel of date (Xu et al. 2008).

The waste materials are generally used as adsorbent for the removal of heavy metal from wastewater. Tons of palm kernels are disposed every year. It was determined that palm kernels have some medicinal effects. So, in this study, the palm kernels were selected as adsorbent. The purpose of this work was to investigate the possibility of the kernel of date (*Fructus dactylus*) modified with apoCA as an adsorbent for removal of copper ions from aqueous solution. The experimental studies were carried out in 2012, at laboratories of Erzurum Vocational School of Ataturk University, Erzurum, Turkey.

Materials and methods

Adsorbent

The kernels of date (F. dactylus) were collected from local markets. Then, these kernels were ground to obtain granular absorbent material by using ring grinder. The powdered kernels were washed with distilled water to remove fines and dirt following the procedure of Nadaroglu et al. 2010. The suspension was wet-sieved through a 200-mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed

five times with distilled water following the sequence of mixing, settling and decanting. The last suspension was filtered, and the residual solid was then dried at 65 °C, ground in a mortar and sieved through a 200-mesh sieve. The product was used in the study as an adsorbent.

Adsorbent characterization

The pH values were determined with a pH meter (Thermo scientific Orion 5 star plus multi-function). The scanning electron microscope (SEM) was used to examine the surface of the adsorbent. Images of native and metal adsorbents were magnified 5,000 times by JEOL JSM-6400 SEM. The same instrument was also used for the energy-dispersive X-ray (EDX) spectra analysis to know the elemental composition of the powdered kernel of date (F. dactylus) (Unabia and Zaide 2002). In addition, the Fourier transform infrared spectroscopy (FT-IR) analyses were carried out to identify functional groups and molecular structures in the raw and copper-binding kernel of date. The FT-IR spectra were recorded on the on Perkin-a Perkin-Elmer GX2000 FT-IR spectrometer. The spectrum of the adsorbent was measured within the range of 4,000 to 650 cm^{-1} wave number (Barsberg et al. 2011).

Preparation of apoCA from bovine erythrocytes

Bovine blood was easily obtained from slaughter houses in Erzurum, Turkey. Bovine carbonic anhydrase (BCA) was purified by a Sepharose-4B-L tyrosine sulfanilamide affinity chromatography from bovine erythrocytes (Arslan et al. 1996). Balanced gel with only buffer solution was used again and again. This also extremely reduced the cost. For obtaining CA, carbonic anhydrase was dialyzed against 0.075 M dipicolinic acid. By using this method, almost 100 % pure apoenzyme was obtained. Five milliliters of the apoenzyme reagent can be prepared by using 100 mg of carbonic anhydrase (Nadaroglu et al. 2008). ApoCA was concentrated by using membrane filter, and this concentrated enzyme was used at a dose of 50 mg apoCA/g kernel of dates.

Adsorbent preparation

One gram of this powdered kernel of date sample was shaken with 50 mg apoCA/g kernel of date 10 mL solution for approximately 1 h, and then, the separated particles were stored. Enzyme-modified kernel of date (E-MKD) was used in the study.

Adsorption study

For studying metal adsorption, 1 g of E-MKD was taken as adsorbent and it was then suspended in 50 mL of 1 mg/mL CuCl₂ at pH between 2 and 6 and contacted batchwise in a thermostatic ($t = 25 \pm 0.1$ °C) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases. This reaction was carried out at pH between 2 and 6 for 1 h. The suspension was centrifuged at 3,000 rpm for 10 min, and the supernatant was filtered through a 0.45um-pore, cellulosic membrane filter to make possible the measurement of the heavy metal concentration in the filtrate. After centrifuging, absorbance of solution was measured at 450 nm using spectrophotometer (PG Instrument T80, USA) for determining the amount of decreasing copper ion concentration. The copper ion concentration was determined by spectrophotometric method using 1amino-2-hydroxy-4-naphthalenesulfonic acid (Seifullina and Skorokhod, 1991). The amount of adsorption capacity of adsorbent (q_e in mg/mL) was calculated using Eq. (1).

$$q_{\rm e} = \frac{(C_{\rm o} - C_{\rm e}) * V}{m} \tag{1}$$

where $C_{\rm o}$ and $C_{\rm e}$ are the initial and equilibrium concentrations of copper in solution (mg/L); *V* is the volume of solution (L); and *m* is the mass of adsorbent (g). The metal removal percentage (*R* %) was calculated using Eq. (2).

$$R(\%) = \frac{(C_{\rm o} - C_{\rm t}) * 100}{C_{\rm o}}$$
(2)

Equilibrium studies

Adsorption isotherms, or known as equilibrium data, are the fundamental requirements for the design of adsorption systems. The Langmuir and Freundlich isotherms are most frequent in the literature describing the nonlinear equilibrium. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationships (Zawani et al. 2009; Jiang et al. 2008). The Freundlich (Freundlich and Hatfield 1926) and Langmuir (Langmuir 1918) equations are the worldwide used models because of their simplicity (Nadaroglu and Kalkan 2012).

The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane (Kumar et al. 2010). The Langmuir isotherm is given as:



 Table 1 Results of EDX spectrum

Elements	Native adsorbent		Copper ion loaded adsorbent		
	Weight (%)	Atom (%)	Weight (%)	Atom (%)	
Mg	0.84	1.25	0.68	1.05	
Al	2.04	2.74	1.67	2.30	
Si	21.92	28.28	20.76	27.46	
Κ	0.79	0.73	0.55	0.52	
Ca	73.45	66.38	68.86	63.82	
Fe	0.96	0.62	0.81	0.54	
Cu	0.39	0.23	5.78	3.38	

$$q_{\rm e} = \frac{q_{\rm max} * b * C_{\rm e}}{1 + b * C_{\rm e}} \tag{3}$$

where q_{max} (mg/g) and *b* (L/mg) are Langmuir constants, which are indicators of the maximum adsorption capacity and the affinity of the binding sites, respectively. They can be determined from a linear form of Eq. (2) (by plotting the C_e/q_e versus C_e), calculated with the following equation:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{b * q_{\rm max}} + \frac{C_{\rm e}}{q_{\rm max}}.$$
(4)

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved (Kumar et al. 2010). It is described by the following equation:

$$q_{\rm max} = K_{\rm F} C_{\rm e}^{1/n} \tag{5}$$

where $K_{\rm F}$ and *n* are the Freundlich constants related to the sorption capacity of the adsorbent (mg/g) and the energy of adsorption, respectively. They can be calculated in the following linear form:

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{6}$$

Results and discussion

Characterization of adsorbent

The EDX measurements were recorded for qualitative analysis of the elemental composition of the native and E-MKD adsorbents. The EDX spectra of native adsorbent and copper-ion-loaded adsorbent were obtained, and all data are shown in the Table 1. From the EDX spectra, the copper ions were sorbed onto the adsorbent. The EDX analysis provided direct evidence for the adsorption of copper onto adsorbent. It is shown from EDX spectra that after copper adsorption, copper ion concentration increased in the copper-loaded adsorbent E-MKD (Table 1).

The FT-IR can provide very useful information about functional group. The technique can be used to analyze organic materials and some of inorganic materials. The FT-IR technique is used to measure the absorption of various infrared radiations from the target material and to form an IR spectrum that can be used to identify functional groups and molecular structure in the sample. The functional groups and surface properties of the adsorbent after adsorption by FT-IR spectra are illustrated in the Fig. 1a, b. The spectra indicated the presence of alcohols, phenols or carboxylic acids. They showed a broad, intensely sharp, -OH-stretching absorption from 3,444 to 3,330 cm⁻¹, although the bands were dominated by the -OH stretch due to bonded water. The presence of asymmetric and symmetric C-H vibrations at the 2,922 and 2,853 cm⁻¹ indicated the presence of aliphatic structures. The peaks at the 1,744 and from 1,609 to 1,605 cm^{-1} were caused by the olefinic C=C and C=O vibrations in the aromatic structures. The subsequent peaks at the 1,517, 1,436 and 1,375 cm^{-1} were caused by the C-H-stretching band of the aromatic structures. Similarly, the peaks seen at the 1,240 and from 1,147 to 1,031 cm^{-1} and at the continuation of spectra between 900 and 700 cm⁻¹ were caused by C-O, C-C or C-OH vibrations of aromatic structures and C-H bonds of aromatic structures, respectively.

The SEM enables the direct observation of the surface microstructures of different adsorbents. Images of native and E-MKD adsorbents were magnified 5,000 times by SEM. The SEM photographs showed that the progressive changes occurred in the surface of native adsorbent (Fig. 2a) after its surface was loaded by copper ions (Fig. 2b). The SEM of exhausted adsorbent clearly indicates the presence of new, shiny, bulky particles and layer over the surface of metal-loaded adsorbent, which are absent in the native adsorbent before metal loading (Kalkan et al. 2012).

Effect of pH on adsorption

The pH of the aqueous solution is an important operational parameter in the adsorption process because it





Fig. 1 FT-IR spectrum of adsorbent (a) and adsorbent loaded with copper ions (b)

affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Kaonga et al. 2010; Ghazy and Ragab 2007; Kara 2005; Onundi et al. 2010). In order to find optimal pH value for the sorption process, the removal of copper ions in the pH range 2–6 was investigated and the data are illustrated in the Fig. 3. It shows the effect of pH variation in adsorption of copper ions on the modified kernel of date particle surface. It was shown that the



Fig. 2 SEM images of native adsorbent $\left(a\right)$ and copper-loaded adsorbent $\left(b\right)$



Fig. 3 Effect of pH on the adsorption of copper

adsorption amount of copper increases with increasing pH, and maximum adsorption of copper ions was obtained at pH 6.0. The uptake of copper increased from 81.2 to



Fig. 4 Effect of adsorbent dosage on the adsorption of copper

225.23 μ g/g when the pH of solution was increased from 2 to 5. This is due to changes in surface loading, which are mostly influenced by the electrostatic force of attraction between copper and the surface of the adsorbent. The acidity of the medium can affect the metal ions' uptake amount of the kernel of date adsorbent because hydrogen ions in the solution could compete with copper ions for active sites on the surface of the adsorbent (Zvinowanda et al. 2009).

From the results, it was shown that the pH of the solution played a very important role in the metal uptake. The metal-binding sites on the adsorbent surface as well as metal chemistry in solution were influenced by pH of the solution. It is to be expected that with increase in pH values, more and more ligands having negative charges would be exposed, which results in increase in attraction of positively charged metal ions (Sekher et al. 1988). In addition, at higher pH, the lower binding is attributed to reduced solubility of the metal and its precipitation (Zhou and Kiff 1991). Improved metal removal with a higher pH is related to a decrease in competition at the binding surfaces between protons (H⁺) and positively charged metal ions and to the decrease in positive charge of the binding surface, which results in a lower repulsion of the adsorbing metal ion.

Effect of adsorbent dosage

The dosage study is an important parameter in the adsorption studies because it determines the capacity of an adsorbent or a given initial concentration of metal in solution (Shetty and Rajkumar 2009). In this study, the effect of adsorbent dosage was studied by varying the sorbent amounts from 500 to 10×10^3 ppm. The effect of



Fig. 5 Effect of temperature on the adsorption of copper

adsorbent dosage on the removal of copper is presented in Fig. 4. The significant increase in uptake was observed when the dosage was increased from 0 to 10 mg/mL. This indicated that adsorption increased with increasing E-MKD dosage up to a certain value and then became almost constant (Dakiky et al. 2002; Rao et al. 2008).

The increase in adsorption with increase in adsorbent dosage is attributed to the availability of larger surface area and more adsorption sites. At high adsorbent concentrations (237.5 mg copper ion), the adsorbent surface becomes saturated with the metal ions, and the residual metal ion concentration was in the solution. It is plausible to suggest that with higher dosage of adsorbent, there would be greater availability of exchangeable sites for metal ions as noted by Nadaroglu et al. 2010. Moreover, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from metals (Pons and Fuste 1993).

Effect of temperature

Temperature is known to have a profound effect on various chemical processes. Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate (Ahmaruzzaman and Sharma 2005). Figure 5 shows the effect of temperature on the adsorption of copper. The effect of temperature influencing the adsorption has been studied in the range of 10-80 °C. It is observed that the degree of adsorption increases with increasing temperature and maximum adsorption of copper ions is obtained at 40 °C, which is the temperature of the solution. The results show that the sorption capacity increased from 70.23 to 192.96 µg/g with the increase in



Fig. 6 Effect of contact time on the adsorption of copper

temperature from 10 to 80 °C. This increase in adsorption capacity is due to the chemical interaction between adsorbate and adsorbent and creation of active surface centers or by an enhanced rate of intraparticle diffusion of copper ions into the pores of the adsorbent at higher temperatures (McKay et al. 1980; Kalavathy and Miranda 2010). An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These results show the enhancement in the sorptive capacity of the adsorbent. The temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters (Das et al. 2006).

Effect of contact time

The rate at which adsorption takes place is of most importance when designing batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The relationship of percentage of metal removal by adsorbent with contact time is plotted and presented in Fig. 6. It can be observed that the removal of copper increases with time in the first 60 min of contact time. Basically, the removal of copper is rapid at this time, but it gradually decreases with time until it reaches equilibrium. This indicates that the concentration of copper in the solution decreased rapidly within 60 min and the removal was virtually completed within 120 min of contact time. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the E-MKD particle surface at the beginning. This is probably





Fig. 7 Variation in copper concentration with kernel of date on the polluted river water and CuCl_2

due to larger surface area of the E-MKD particle being available at beginning for the adsorption of copper ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Zaki and Farag 2010).

Adsorption first followed a linear rising, and then stationary state was observed following the rapid decrease in copper ions removal. The initial faster rate of metal transition may be explained by the large, uncovered available surface area of the kernel of dates and its composite. The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes insuring efficiency and economy (Kaonga et al. 2010).

The copper concentration of polluted river water and CuCl₂ solutions treated with kernel of date indicates that kernel of date enhances adsorption capacity. Without the addition of the kernel of date, the leachate copper concentration is approximately 3.263 and 1.59 µg/mL for polluted river water and CuCl₂ solutions, respectively. The addition of kernel of date strongly inhibits the leaching of copper in the polluted river water and CuCl₂ solutions. When the kernel of date is added to the copper-contaminated aqueous solutions, the copper concentration in the leachate drastically reduces, whereas the adsorption capacity increases. The copper concentration of the leachates treated by kernel of date decreases from 1.396 to 0.168 µg/mL and from 3.263 and 1.59 µg/mL for the polluted river water and CuCl₂ solutions, respectively (Fig. 7). The increase in the adsorption capacity of aqueous solutions treated by E-MKD is attributed to the pH values

Adsorption isotherm	Value			
Langmuir constants				
$q_{\rm max} \ ({\rm mg/g})$	40.0012			
<i>b</i> (L/mg)	0.7880			
R^2	0.9258			
Freundlich constants				
K _F	0.00042			
n	0.2900			
R^2	0.9309			

Table 2 Values of the Langmuir and Freundlich adsorption isotherms

and active components of kernel of date. (Nadaroglu et al. 2010).

Equilibrium adsorption isotherms

The Langmuir and Freundlich isotherm models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase. The Langmuir adsorption isotherm model represents one of the first theoretical treatments of nonlinear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules.

The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The q_{max} (mg/g) and b (L/mg) parameters are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of q_{max} and b (Table 2) were calculated from the slope and intercept of the Langmuir plot of C_{e} versus $C_{\text{e}}/q_{\text{e}}$ from graph, and the empirical constants q_{max} and b were found to be 40 mg/g and 7.88, respectively.

The $K_{\rm F}$ and *n* are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). $K_{\rm F}$ and *n* values (Table 2) were calculated from the intercept and slope of the plot. In the literature, it is pointed out that the parameters $K_{\rm F}$ and *n* affect the adsorption isotherm. The larger the $K_{\rm F}$ and *n* values, the higher the adsorption capacity. The magnitude of exponent *n* gives an indication of the favorability of the adsorption. The *n* value is 0.29 L/mg (Table 2), and it is a good



 Table 3
 Thermodynamic parameters for the copper adsorption onto

 E-MKD adsorbent
 E-MKD

	$\Delta H_{\rm ads}^{\rm o}$ (kJ/ mol)	ΔS_{ads}^{o} (J/ mol)	$\Delta G_{\rm ads}^{\rm o}$ (kJ/mol)		
			298 K	303 K	313 K
Kernel of date	-27.91	-76.256	-5.19	-4.81	-4.04

adsorption characteristic (Treybal 1980). Based on the correlation coefficient values, it has been deduced that Freundlich model better fitted to the experimental data (Table 2). The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of copper ions.

Adsorption kinetics

Thermodynamic aspect of the adsorption process is important in examining the applicability of the transaction. To examine the thermodynamic aspects of absorption process is important for the applicability of process. In this adsorption study, the entropy was decreased for becoming a more regular occurrence with the accumulation of Cu on to E-MKD (Nollet et al. 2003; Dakiky et al. 2002). It is a well-established fact that the adsorption of copper ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface, and two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibrium (Kumar et al. 2010).

The sorption capacity of E-MKD adsorbent increased with increase in the temperature of the system from 293 to 303 K. Thermodynamic parameters such as change in free energy (ΔGo) kJ/mol, enthalpy (ΔH_o) kJ/mol and entropy (ΔS_o) J/Kmol were determined using the following equations (Chakravarty et al. 2008):

$$K_{\rm L} = \frac{C_{\rm s}}{C_{\rm e}} \tag{7}$$

 $\Delta G^{\rm o} = -RT \ln K_{\rm L} \tag{8}$

$$\ln K_{\rm L} = \left(\frac{\Delta S^{\rm o}}{R}\right) - \left(\frac{\Delta H}{RT}\right) \tag{9}$$

where K_L is the equilibrium constant, C_s is the solid phase concentration at equilibrium (mg/L), C_e is the liquid phase

concentration at equilibrium (mg/L), *T* is the temperature in Kelvin and *R* is the gas constant. From the temperature variation from 293 to 313 K on the sorption, ΔH° and Δ_{S}° were obtained from graph. The ΔH_{ads}° and ΔS_{ads}° values obtained from the slope and intercept of Van't Hoff plots are presented in Table 3. Gibbs free energy (ΔG) was calculated as:

$$\Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S \tag{10}$$

The values of thermodynamic parameters for the sorption of copper on E-MKD adsorbent are given in Table 3. The Gibbs free energy change (ΔG^{o}) was calculated to be -5.19, -4.81 and -4.04 kJ/mol on kernel of date for copper adsorption at 298, 303 and 313 K, respectively. Negative ΔG values indicated the feasibility of the process and spontaneous nature of the adsorption and were obtained for copper at each of the temperatures studied. The ΔG° values decreased with an increase in temperature. indicating an increased trend in the degree of spontaneity and feasibility of copper adsorption. The ΔH° parameter was found to be -27.91 kJ/mol for copper adsorption on kernel of date. The negative values of ΔH° further confirmed the exothermic nature of adsorption process. Hence, the adsorption of copper on kernel of date was chemical in nature.

The ΔS° parameter was found to be -76.26 (kJ/mol K) for copper adsorption on E-MKD. The negative value of ΔS° corresponds to a decrease in degree of freedom of the adsorbed species. During the adsorption process, the coordinated water molecules were displaced by metal cations, resulting in increased randomness in the adsorbent–adsorbate system (Baraka et al. 2007; Li et al. 2011).

Conclusion

In this study, powdered and modified kernel of date with apoCA was converted into an adsorbent, and the suitability of the E-MKD for adsorption of copper from the polluted river water and $CuCl_2$ solutions was investigated by adsorption experiments. The maximum copper removal by adsorbent was at pH 6.0. The removal of copper increases with increasing time in the first 60 min, and thereafter, the removal is not significant. It is observed that the degree of adsorption increases with increasing temperature, and maximum adsorption of copper ions is obtained at 40 °C, which is the temperature of the solution. The adsorbent



concentration increases when the number of adsorbent particles surrounding the metal ions increases. The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of copper ions. Based on the correlation coefficient values, it has been deduced that the Freundlich model better fitted to the experimental data. The investigation showed that kernel of date is a very valuable material for removal of copper ions from the aqueous solutions. Thus, it could favor chemical immobilization and could reduce the solubility of the wastewater. In addition, the use of kernel of date as natural waste material for the removal of the copper ions from the aqueous solutions can potentially reduce the remediation costs.

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