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Adsorption of Ni (II) from aqueous solution by magnetic chitosan resin

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ABSTRACT

The purpose of this work is to prepare a low-cost biosorbent, Magnetic chitosan resin (MCR), and determine the ability of this biosorbent to removing Ni (II) ion from aqueous medium. The characteristics of this biosorbent such as adsorption isotherms, the influence of pH value, adsorption time and temperature were all researched. The adsorption equilibrium was achieved after about 150 min at pH = 6 and the equilibrium data were fitted better with the Langmuir isotherm equation than Freundlich mode. The maximum adsorption capacity was 14.47 mg·g⁻¹. Both kinetics and thermodynamic parameters of the adsorption process were also estimated. The thermodynamic parameters indicated an exothermic spontaneous process and the kinetics followed the second-order adsorption process. Moreover, the magnetic chitosan resin (MCR) could be regenerated through the desorption of the Ni (II) ions using 0.1 mol·L⁻¹ HCL solution and could be reused to adsorb again. Overall the results reported herein indicated that the magnetic chitosan resin (MCR) with high adsorption efficiency and magnetic property is very attractive and implies a potential of practical application for removing Ni (II) ion from aqueous medium. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Magnetic chitosan resin;
Biosorbents;
Adsorption;
Nickel (II).

INTRODUCTION

Heavy metals are potentially hazardous to human beings and environment. Various industrial processes result in the production of considerable residual water contaminated with heavy metals^[1]. Metallic nickel and nickel compounds have many industrial and commercial applications including use in stainless steels and other nickel alloys, catalysts, batteries, pigments, and ceramics^[2,3]. Nickel and nickel compounds generally cause a variety of pathologic effects like skin allergy, lung fibrosis and human carcinogen. The most important health

problems induced by nickel and nickel compounds are allergic dermatitis and increased incidence of cancers^[4]. The U. S. Environmental Protection Agency (EPA) advises an acceptable level of nickel in drinking water should below 0.1 mg/L^[5]. Therefore, Nickel removal from aqueous waste streams is currently of great concern for public health and environmental conservation. Several treatment methods have been developed to remove nickel from aqueous waste streams, such as adsorption^[6], ion exchange^[7], microfiltration and chemical precipitation^[8]. Adsorption is considered an effective and economical method among the treatment. Re-

cently utilize low-cost adsorbents has become a new focus point mainly using biopolymers, which obtained from renewable sources and adsorbed metallic ions selectively and effectively. As available biopolymers in nature, chitosan attracted much consideration because of its excellent features, such as biocompatibility, biodegradability, and anti-bacterial properties^[9,10]. Further physical and chemical modification of chitosan has been developed to improve mechanical strength, selectivity and capacity for the adsorption of metals. Magnetic chitosan resin (MCR) is a typical modification method which keeps the properties of chitosan for the adsorption of metal ions, and moreover, techniques employing magnetism are imparted to resins facilitating their trapping from the medium using a magnetic field compared to the centrifugal methods. So it has been widely used in various applications such as enzyme purification, cell separation, and waste treatment^[11,12]. In order to improve chemical strength and stability, MCR should be chemically crosslinked, because the crosslinking method may enhance the resistance of MCR against acids and chemicals. In our present work, we aim to prepare a Magnetic chitosan resin (MCR) adsorbent and determine the ability of this biosorbent to removing Ni (II) ion from aqueous medium. Batch adsorption experiments were carried out as a function of pH value, adsorption time and temperature. The adsorption isotherm and thermodynamics parameters were also investigated.

EXPERIMENTAL

Materials and instruments

Chitosan with a deacetylation percentage of approximately 85% was purchased from Zhejiang Yuhuan Biochemical Co. Ltd. (China), and purified before use by dissolving and precipitating several times, then extracting in Soxhlet apparatus in acetone for 24 h, and dried at 40 °C under vacuum. All other chemicals (glutaraldehyde, nickel nitrate) were analytical grade. Double distilled water (conductivity <0.02 S/cm) were used throughout the work. The products were characterized by FT-IR, and SEM. IR spectra were taken with KBr pellets on a Perkin-Elmer FTIR 1725 spectrometer. The surface morphology of products was studied using JSM-120 microscope (Japan). The adsorption experi-

ments were carried out at a thermostated Shaker (SHA-C) and the samples were centrifuged at 3000 rpm for 10 min, then the supernatant liquid were used to determine metal ions concentration. Atomic absorption spectrophotometer (ZEEnit700P, Jena) was used to measure Ni (II) concentration following standard methods for examination of water and wastewater^[13].

Preparation of magnetic chitosan resins (MCR) adsorbent

The Magnetic chitosan resin (MCR) was prepared according to the literature procedures^[14]. A known volume of ferric chloride ($0.5\text{ mol}\cdot\text{L}^{-1}$) and ferrous chloride ($1\text{ mol}\cdot\text{L}^{-1}$) solution were added to three necked flask purged with nitrogen consecutive stirred at room temperature for an hour. Then ammonium hydroxide (20%) solution were added into flask to adjust the pH value at 9.0-10.0. The magnetite were filtered and extensively rinsed with redistilled water then dried at 80 °C.

Chitosan powder (1.0g) was dissolved in 2.0% aqueous acetic acid (200 ml) and 5 g magnetite was added and stirred at room temperature for 2h until the mixture dispersed sufficiently. Next, the magnetic chitosan precipitation was obtained after the addition of ethanol. After dried at 80 °C, it was placed in ethanol solution in contact with 5% of glutaraldehyde for 2 h, according to the chemical crosslinking with glutaraldehyde occurs by Schiff's reaction. Next the magnetic chitosan resins were collected by magnetic separation and further washed with distilled water and ethanol in order to remove the unreacted glutaraldehyde. At last, it was dried at 80 °C and the magnetic chitosan resin (MCR) was finally prepared.

Regeneration of adsorbent

For the purpose of reducing the operating cost and minimizing waste disposal, a practical recycling method of MCR was developed. 0.2 g Ni (II) saturated MCR was immersed in a 100 ml beaker with 20 ml of $0.1\text{ mol}\cdot\text{L}^{-1}$ hydrochloric acid solution for 24 h at room temperature. After filtration, the residual was washed with distilled water until no Ni (II) was left in the effluent. The CMC was then dried under vacuum.

Adsorption experiments

The sorption experiments were studied by batch technique. 0.2g MCR were equilibrated with 50 mL of

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aqueous Ni (NO₃)₂ solution with 50mg·L⁻¹ in a 100 mL glass stoppered Erlenmeyer flask at 30±2 °C in a shaking bath. The initial pH was adjusted with 0.1 M HNO₃ or 0.1 M NaOH before adding the adsorbent. After shaking for 150 min to ensure full equilibration, the MCR were collected and the concentration of nickel (II) ions in the supernatant was estimated by monitoring with atomic absorption spectrophotometer. The adsorption capacity was calculated from the following expression:

$$Q = \frac{(C_i - C_f)V}{m} \quad (1)$$

where, Q is the adsorption capacity of the adsorbent (mg/g), C_i and C_f (mg/L) are the initial and terminal concentrations of Ni (II) respectively, m (g) is the mass of adsorbent, and V is volume of solution liters.

RESULTS AND DISCUSSION

Characterization

FT-IR spectra of CTS and MCR are exhibited in Figure 1. The characteristic CTS bands are C-H stretching around 2870 cm⁻¹ and intense bands near 3360 cm⁻¹ due to O-H and N-H stretchings. The bands corresponding to acetamide groups, remaining from chitin, due its incomplete deacetylation appear at around 1650 cm⁻¹ and 1380 cm⁻¹, attributed to C=O and C-H de-

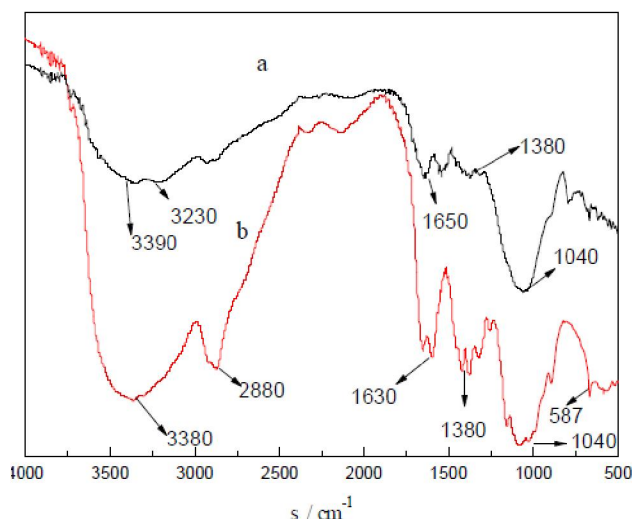


Figure 1 : FT-IR of CTS (a) and MCR (b)

formations respectively. The presence of saccharide structure is confirmed by having bands in 1200–800 cm⁻¹ region, especially 1154 cm⁻¹ and 896 cm⁻¹ assigned to β-(1, 4)-glycoside bridges. The spectra of MCR shows new absorption at 1630 cm⁻¹ and 1550 cm⁻¹ ascribed to stretching vibrations of C=N due to the reaction of imine which reveals that functional groups of Schiff bases have been present in chitosan. There is also an evidence of presenting Fe₃O₄ at 589 cm⁻¹ which attributed to Fe-O bond vibration. From the FT-IR spectra, it can be concluded that the preparation of magnetic chitosan resins is successful.

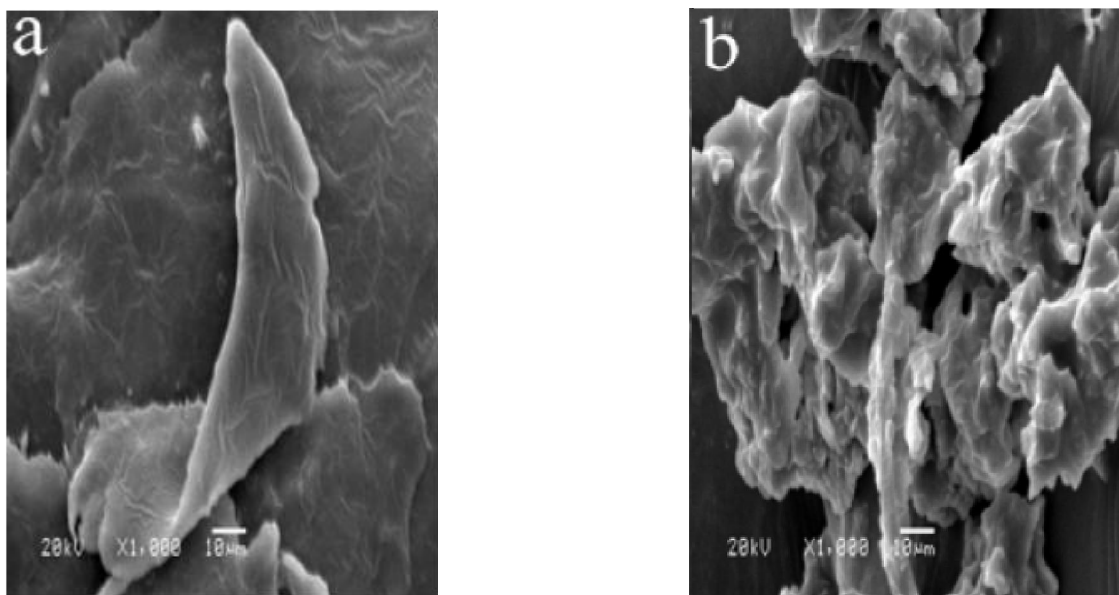


Figure 2 : SEM images of CTS (a) and MCR (b)

The surface morphology of CTS and MCR were investigated by SEM. As show in Figure 2, CTS has

flaky and smooth surface, whereas MCR shows clustered shapes and polyporous on the surface, and the

particles conglomerated closely particularly. The appearance of MCR indicates that the porous structure should be propitious to nickel ion uptake.

The characteristic of magnetism provides an easy

and efficient way to separate the MCR from aqueous solutions. It can be seen that the magnetic chitosan resins with adsorbed Ni could be easily separated by a magnetic field, resulting in clean water (Figure 3).

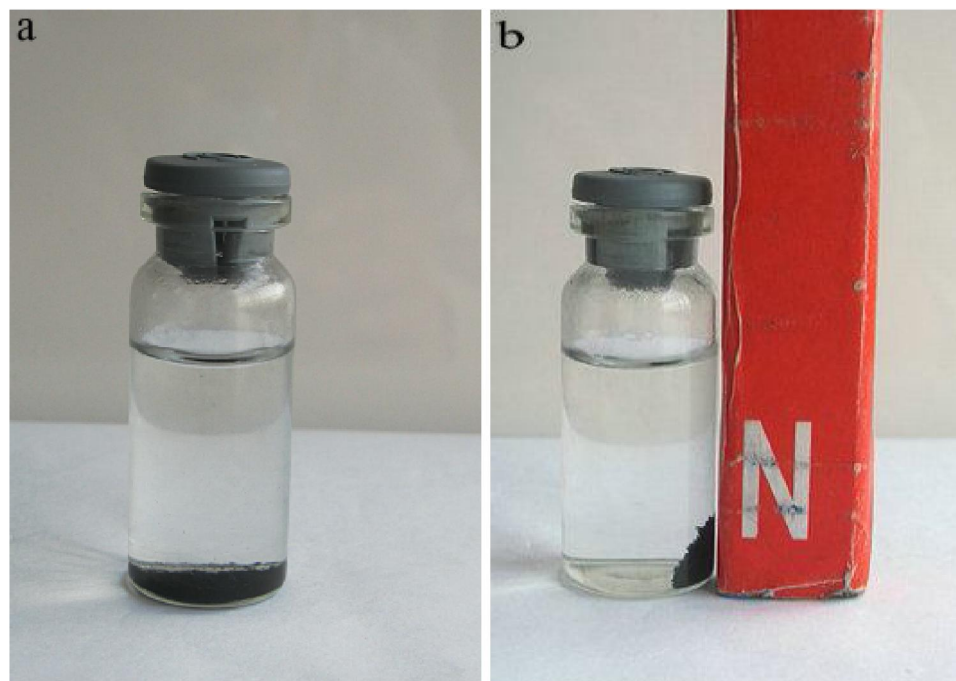


Figure 3 : MCR gathered in solution (a) and separated with magnet (b)

Effect of pH value

To evaluate the effect of pH value on nickel (II) adsorption capacity on MCR, experiments were conducted with 50 ml of $50 \text{ mg}\cdot\text{L}^{-1}$ of metal solution containing 200 mg of adsorbent at room temperature. These results were graphically represented in Figure 4. At pH 2.0 adsorption capacity for nickel (II) is low, while a vigorous growth appeared in the range of 3.0–6.0. The results can be summarized as in lower pH value the functional free $-\text{NH}_2$ groups and $(-\text{C}=\text{N}-)$ of Schiff's base group in MCR were highly protonated to $-\text{NH}_3^+$ and $(-\text{C}=\text{N}^+)$ which increased the electrostatic repulsion on the surface sites and prevented the metal cations approaching to. With pH increasing gradually (3.0–6.0), the decrease of H^+ reduced positive charge density on the surface sites resulting in an enhancement of metal adsorption.

Effect of adsorption time

The experimental results of Ni (II) adsorption on MCR versus time are shown in Figure 5. The extent of adsorption increases with time and attained equilibrium

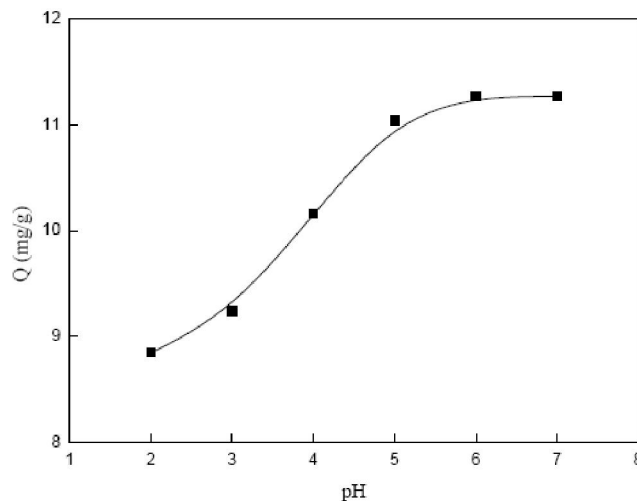


Figure 4 : Effect of initial pH value on adsorption capacity of Ni (II)

near 150 minutes. After this equilibrium period, the amount of metal adsorbed did not change remarkably with time. Many researchers have found that if the reaction rate is chemically controlled, the pseudo-second-order model^[15] will be the most appropriate model to describe the reaction^[16] The experimental data were tested by the pseudo-second-order model whose ex-

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pression is given as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (2)$$

For boundary conditions $t=0$ for $Q_t=0$ and $t=t$ for $Q_t=Q_t$ integrating Eq (2) gives below:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t (mg/g) and q_e (mg/g) are the absorbances at time t and at equilibrium respectively. The slope and intercept of plot of t/Q_t vs. t were used to calculate the pseudo-second-order rate constant k and q_e .

As illustrated in Figure 6, the pseudo-second-order model fitted well with the kinetic experimental data and the correlation coefficients were greater than 0.99. Therefore, the Ni (II) adsorption process is controlled by the chemical process.

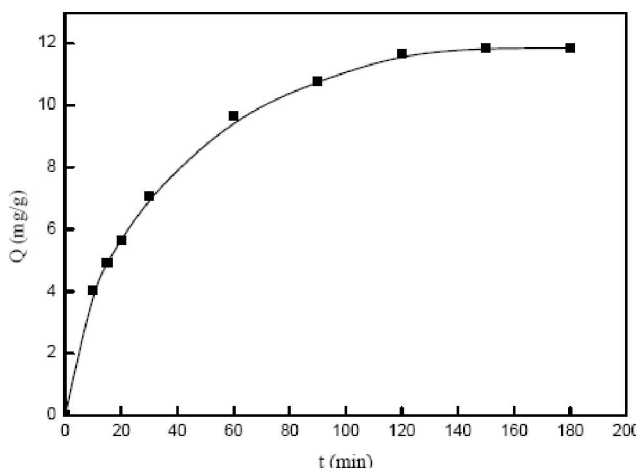


Figure 5 : Effect of adsorption time on adsorption capacity of Ni (II)

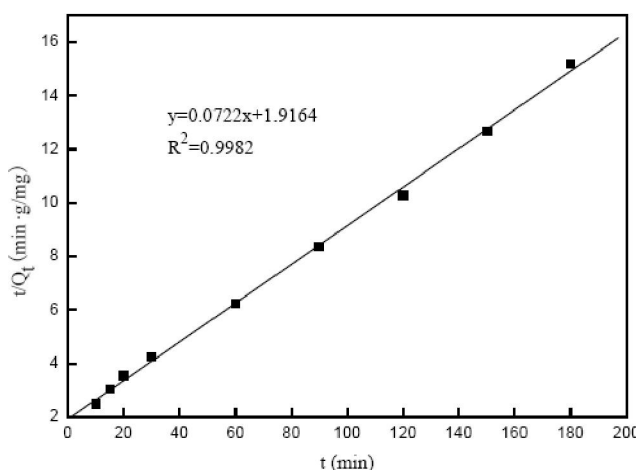


Figure 6 : Pseudo-second-order equation for the adsorption of Ni (II) on MCR

Adsorption equilibrium isotherm

Analysis of the equilibrium data is the most significant to accurately represent the adsorption isotherm. To determine the equilibrium data, the adsorption of the Ni (II) at different initial concentration (25-100 mg·L⁻¹) were studied while the weight of MCR, pH value and adsorption time being constant. Langmuir and Freundlich adsorption isotherms were often used to fit the experimental data^[17]. The Langmuir isotherms assume monolayer coverage of adsorption of each molecule onto the surface has equal sorption activation energy and no interaction between sorbed species. It has traditionally been used to quantify and contrast the performance of different biosorbents. In mathematical form, it is written as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{(Q_m b)} \quad (4)$$

where C_e is the equilibrium concentration of metal ions ((mg·L⁻¹), Q_e is the amount of metal ions adsorbed ((mg·g⁻¹), Q_m is the maximum adsorption capacity of metal ions (mg·g⁻¹), and b is the Langmuir adsorption equilibrium constant (L·mg⁻¹). Therefore, the plot of C_e/Q_e against C_e gives a straight line with a slope of $1/Q_m$ and an intercept of $1/(Q_m b)$ (Figure 7 and TABLE 1). TABLE 1 indicates that Langmuir model has perfectly application for nickel (II) sorption with a regression coefficient. The maximum sorption capacity revealed MCR can remove Ni (II) with a higher affinity compared to chitosan in its natural form and most of the modified forms reported in the literature^[18-20].

TABLE 1 : Langmuir and freundlich constants for Ni (II) biosorption on MCR

Temperature (K)	Langmuir constants			Freundlich constants		
	Q _m (mg/g)	b (L/mg)	R ²	K _f	n	R ²
303	13.93	0.4503	0.9908	9.861	12.66	0.8134
318	14.29	0.6393	0.9936	9.992	12.91	0.8270
333	14.47	1.509	0.9942	10.31	14.18	0.8712

The equilibrium adsorption data were applied to the Freundlich isotherm equation for multilayer adsorption isotherm on heterogeneous surfaces. The Freundlich isotherm is an empirical equation based on an exponential distribution of sorption sites and energies. In mathematical form, it is represented as:

$$Q_e = K_f C_e^{1/n} \tag{5}$$

$$\lg Q_e = \lg K_f + \frac{1}{n} \lg C_e \tag{6}$$

In the equations, C_e and Q_e are equilibrium Ni (II) ion concentration (mg/L) and equilibrium adsorption capacity (mg/g), respectively. Freundlich constants, K_f and n can be determined from a liner plot of $\lg Q_e$ versus $\lg C_e$, which affect the adsorption process such as adsorption capacity and intensity of adsorption, respectively. Figure 8 depicts the plots obtained by the Freundlich isotherm for the adsorbents along with their R^2 values. The Freundlich constants for the adsorption were also presented in TABLE 1. As can be seen, the experimental data did not fit well in the Freundlich isotherm equation with low correlation coefficients from 0.81 to 0.87.

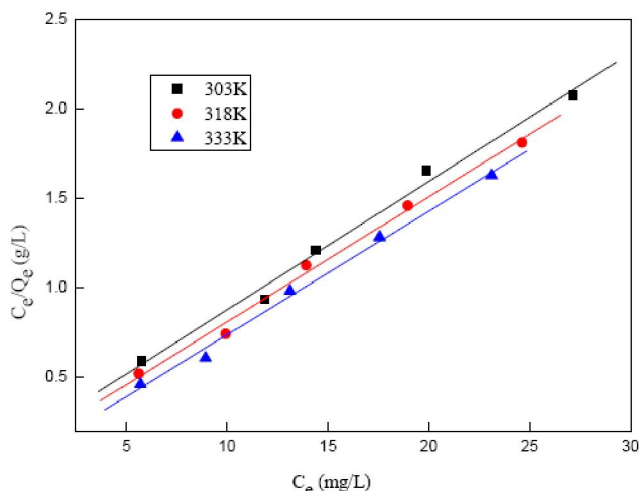


Figure 7 : Langmuir isotherms for Ni (II) the adsorption of nickel (II) on MCR

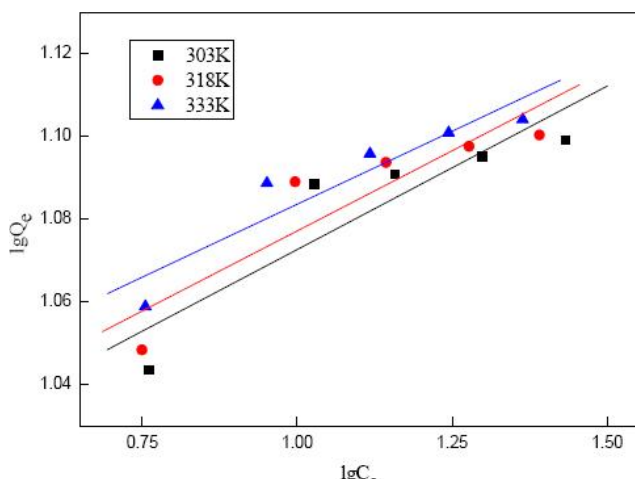


Figure 8 : Freundlich isotherms for the adsorption of nickel (II) on MCR

Thermodynamic parameters of adsorption

In order to explain the effect of temperature on the adsorption thermodynamic parameters, the adsorption behavior of Ni (II) on the adsorbent at different temperatures were also investigated (Figure 9). The results showed that as the temperature increased, the value of Q increased, which implied that the adsorption process was endothermic.

The thermodynamic equilibrium constant (K) for each system was obtained by calculating the apparent equilibrium constant K'_c at different initial concentration of Ni (II) and extrapolating the same to zero.

$$K'_c = \frac{C_a}{C_e} \tag{7}$$

where C_a is the concentration of Ni (II) on the adsorbent at equilibrium in mg/L and C_e is the equilibrium concentration of Ni (II) in solution in $\text{mg}\cdot\text{L}^{-1}$. The adsorption parameters thermodynamic standard enthalpy (ΔH^\ominus), standard entropy (ΔS^\ominus), and standard Gibbs free energy (ΔG^\ominus) can be calculated by the thermodynamic equation^[21]:

$$\lg K = \frac{\Delta S^\ominus}{2.303R} - \frac{\Delta H^\ominus}{2.303RT} \tag{8}$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \tag{9}$$

In the Eq (8), R is the gas constant, 8.314×10^{-3} (kJ/mol·K), T is absolute temperature, K is equilibrium constant at the temperature T , respectively. When $\lg K$ is plotted against $1/T$, a straight line with slope $\Delta H^\ominus/2.303RT$, and intercept $\Delta S^\ominus/2.303R$ were obtained (Figure 10). The values of ΔH^\ominus and ΔS^\ominus were also obtained from the slope and intercept of the Van't Hoff plots of $\ln K$ versus $1/T$ (Figure 10). The thermodynamic parameters for the adsorption process are given in TABLE 2. It can be observed that the positive value of ΔH^\ominus indicates the adsorption is endothermic and higher temperature makes the adsorption easier. In addition, this also indicates that adsorption of Ni (II) on MCR is rather chemical process. If it was only physisorption process, the enthalpy of the system would be exothermic^[22]. The positive value of ΔS^\ominus indicates that there is an increase in the randomness at the solid/solution interface during the adsorption process^[23]. The negative value of ΔG^\ominus decreases with the increase of temperature indicating that the spontaneous nature of adsorp-

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tion of Ni (II) are inversely proportional to the temperature, and the adsorption is more favorable at high temperatures.

Desorption and reuse of MCR

The adsorption/desorption cycles were investigated in a batch reactor and the adsorbent was recycled to adsorb Ni (II) from 50 ml of solution with an initial concentration of 50 mg·L⁻¹ under the same adsorption con-

TABLE 2 : Thermodynamic parameters for for Ni (II) biosorption on MCR

Temperature (K)	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	(J·mol ⁻¹ ·K ⁻¹)
303	-3.506		
318	-3.848	3.421	22.86
333	-4.191		

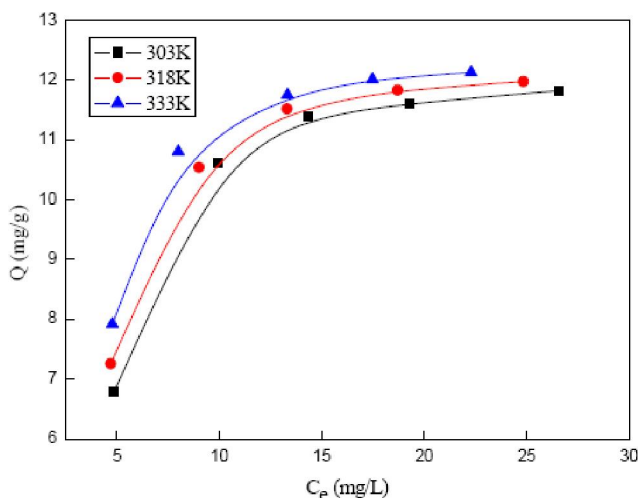


Figure 9 : Equilibrium isotherms for the adsorption of nickel (II) on MCR at different temperature

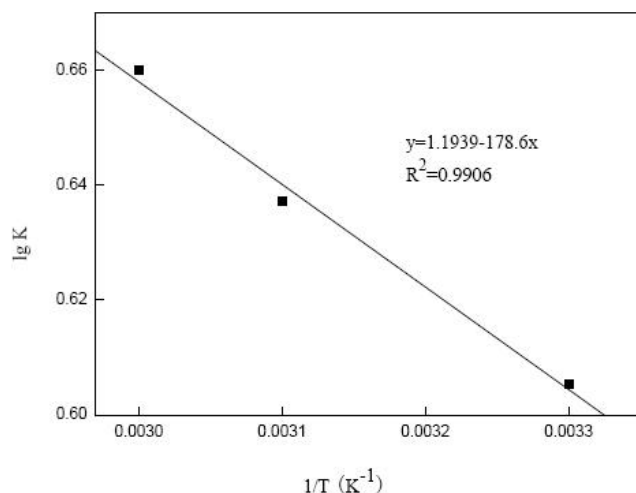


Figure 10 : Van't Hoff plot for the adsorption of nickel (II) on MCR

ditions. The recycling was repeated 5 times as shown in Figure 11. Through the Figure, we calculated the uptake amount of Ni (II) on the CMC (TABLE 3), and the results indicated there was a decrease of 11.6% from the first to second cycle, but from this cycle onward the amount remained practically constant. Therefore, we considered that the loaded CMC can be recycled for Ni (II) adsorption when regenerated with 0.1 mol·L⁻¹ hydrochloric acid solution. The mechanism of regeneration may be that in the first four cycles, both electrostatic and complex at ion reactions occur between the hydrochloric acid solution and metal ions^[24].

CONCLUSIONS

In this study, a low-cost biosorbent, Magnetic chitosan resin (MCR) was prepared by cheap and envi-

TABLE 3 : Uptake amount of Ni (II) on the CMC

Recycle times	0	1	2	3	4	5
uptake amount of Ni (II) (%)	92.66	81.08	80.40	79.92	78.49	78.25

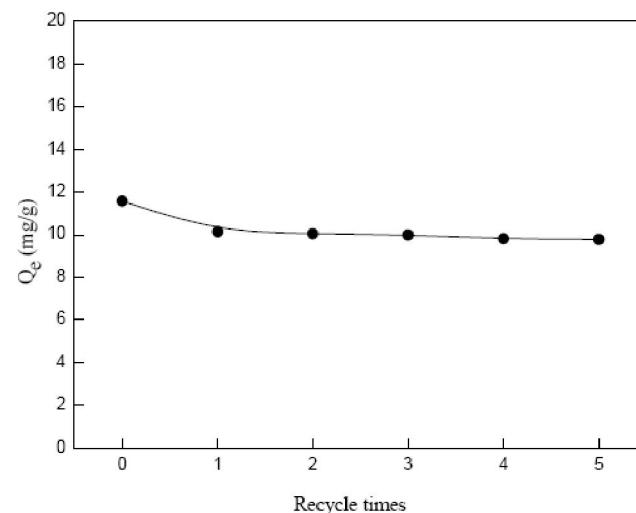


Figure 11 : Adsorption and desorption cycles of nickel (II) on MCR

ronmentally friendly chitosan and iron salts. The biosorbent could remove nickel (II) ions from aqueous solution efficiently via the chemical adsorption process which can be described by pseudo-second rate model. The Langmuir adsorption model and Freundlich equation were used for the mathematical description of the adsorption, and the results showed that the Langmuir isotherm was better compared with the Freundlich isotherm. And the adsorption thermodynamic parameters demonstrated the

adsorption process was endothermic. Further, the biosorbent could be regenerated with 0.1 mol·L⁻¹ hydrochloric acid solution and reused effectively. Thus, this biosorbent is very attractive and implies a potential of practical application as low-cost and effective absorbent for remove nickel (II) ions from aqueous solution.

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REFERENCES

- [1] Y.Vijaya, S.R.M.Popuri, V.M.Boddu, A.Krishnaiah; Modified chitosan and calcium alginate biopolymersorbents for removal of nickel (II) through adsorption, *Carbohydr.Polym.*, **72**, 261 (2008).
- [2] J.W.Wang, Y.M.Kuo; Preparation and adsorption properties of chitosan-poly (acrylic acid) nanoparticles for removal of Ni (II) ions, *J.Appl.Polym.Sci.*, **107**, 2333 (2008).
- [3] K.Kadirvelu, K.Thamaraiselvi, C.Namasivayam; Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from coirpith., *Purif.Techno.*, **24**, 497 (2001).
- [4] A.Andersen, S.R.Berge, A.Engeland, T.Norseth; Exposure to nickel compounds and smoking in relation to incidence of lung and nasal cancer among nickel refinery workers, *Occup.Enviro.Med.*, **53**, 708 (1996).
- [5] Office of Water U.S. Environmental Protection Agency., Edition of the Drinking Water Standards and Health Advisories, Washington, D.C., (2006).
- [6] A.Thevannan, R.Mungroo, C.H.Niu; Biosorption of Nickel with Barley Straw, *Bioresour.Techno.*, **101**, 76 (2010).
- [7] C.Aydiner, M.Bayramoglu, B.Keskinder, O.Ince; Behavior of Inorganic Nanoparticles in Silver polymerlectrolytes and Their Effects on Silver Ion Activity for Facilitated Olefin Transport., *Ind.Eng. Chem.Res.*, **48**, 131 (2009).
- [8] T.Fukuta, H.Matsuda, F.Seto, K.Yagishita; Sulfuration treatment of electroplating wastewater for selective recovery of copper, zinc and nickel resource, *Global Nest.J.*, **8**, 131 (2006).
- [9] N.V.Majeti, R.Kumar; A review of chitin and chitosan applications, *React.Funct.Polym.*, **46**, 1 (2000).
- [10] S.R.Popuri, Y.Vijaya, V.M.Boddu; Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads, *Bioresour.Techno.*, **100**, 194 (2009).
- [11] H.Peniche, A.Osorio, N.Acosta, A.Campa; Preparation and characterization of superparamagnetic chitosan microspheres, Application as a support for the immobilization of tyrosinase, *J.Appl.Polym.Sci.*, **98**, 651 (2005).
- [12] L.M.Zhou, J.Y.Jieyun Jin, Z.R.Liu., X.Z.Liang, C.Shang; Adsorption of acid dyes from aqueous solutions by the ethylenediamine-modified magnetic chitosan nanoparticles, *J.Hazard.Mater.*, **185**, 1045 (2011).
- [13] M.E.P.; Water quality-Determination of nickel-Flame atomic absorption spectrophotometric method, GB 11912-89 (1990).
- [14] M.T.Klepka, N.Nedelko, J.M.Greeneche, et al.; Local Atomic Structure and Magnetic Ordering of Iron in Fe Chitosan Complexes, *Bio.Macro*, **9**, 1586 (2008).
- [15] Y.S.Ho, G.Mckay; Process Saf., Kinetic models for the sorption of dye from aqueous solution by wood, *Environ.Prot.*, **76(B2)**, 183 (1998).
- [16] D.Karadag, M.Turan, E.Akgul, S.Tok, A.Faki; The biosorption data for removal of Reactive Black 5 were readily modeled using the Langmuir adsorption isotherm, *J.Chem.Eng.Data*, **52**, 1615 (2007).
- [17] A.H.Chen, C.Y.Yang, C.Y.Chen, M.R.Liu; The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu (II), Zn (II), Ni (II) and Pb (II) ions in aqueous medium, *J.Hazard.Mater*, **163**, 1068 (2009).
- [18] C.Huang, Y.C.Chung, R.L.Ming; Adsorption of Cu (II) and Ni (II) by pelletized biopolymer, *J.Hazard.Mater.*, **45**, 265 (1996).
- [19] M.S.Rana, M.A.lim, S.Safiullah, M.M.Mamun, M.S.Azam, M.A.Goni, H.M.Kamal, M.M.Rana; Removal of Heavy Metal from Contaminated Water by Biopolymer Crab Shell Chitosan, *Appl.Sci.*, **9**, 2762 (2009).
- [20] S.Tan, Y.Wang, C.Peng, Y.Tang; Synthesis and adsorption properties for metal ions of crosslinked chitosan acetate crown ethers, *Appl.Polym.Sci.*, **71**, 2069 (1999).
- [21] S.I.Lyubchik, A.I.Lyubchik, O.L.Galushko, et al.;

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Kinetics and thermodynamics of the Cr (II) adsorption on the activated carbon from co-mingled wastes, *Colloids and Surfaces A, Physicochem. Eng. Aspects*, **42**, 151 (2004).

[22] M.Ajmal, A.H.Khan, S.Ahmad, A.Ahmad; Role of sawdust in the removal of copper (II) from industrial Wastes, *Water Res.*, **32**, 3085 (1998).

[23] M.J.Iqbal, M.N.Ashiq; Removal and recovery of nickel (II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana* characterization studies, *J.Hazard.Mater.*, **121**, 243 (2007).

[24] N.Sankararamakrishnan, A.Dixit, L.Iyengar, R.Sanghi; Removal of hexavalent Chromium using a novel cross linked xanthated chitosan, *Bioresour. Technol.*, **97**, 2377 (2006).