

Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (*Daucus carota L.*) residues

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Abstract

In this study, the effect of temperature on the adsorption of Mn(II), Ni(II), Co(II) and Cu(II) from aqueous solution by modified carrot residues (MCR) was investigated. The equilibrium contact times of adsorption process for each heavy metals-MCR systems were determined. Kinetic data obtained for each heavy metal by MCR at different temperatures were applied to the Lagergren equation, and adsorption rate constants (k_{ads}) at these temperatures were determined. These rate constants related to the adsorption of heavy metal by MCR were applied to the Arrhenius equation, and activation energies (E_a) were determined. In addition, the isotherms for adsorption of each heavy metal by MCR at different temperatures were also determined. These isothermal data were applied to linear forms of isotherm equations that they fit the Langmuir adsorption isotherm, and the Langmuir constants (q_m and b) were calculated. b constants determined at different temperatures were applied to thermodynamic equations, and thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG), and entropy (ΔS) were calculated and these values show that adsorption of heavy metal on MCR was an endothermic process and process of adsorption was favoured at high temperatures.

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1. Introduction

Toxic metals accumulation from plastics manufacturing, electroplating, pigments, fertilizers, mining and metallurgical process in waste streams impose big threat on environment and many ecosystems as a result of increasing industrial activities. The problems of ecosystem are increasing with developing technology. The contamination of water by toxic heavy metals is a worldwide environmental problem. Their presence in streams and lakes has been responsible for several health problems with animals, plants, and human beings. The discharge of toxic and polluting metal ions into the environment and municipal sewers by the mining, metallurgical, electroplating, electronic, nuclear and other industries constitutes one of the major causes of ground water contamination [1]. Toxic metal compounds coming to the earth's surface not only contaminate

earth's water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's water may contain various toxic metals. One of the most important problems is the accumulation of toxic metals in food structures. As a result of accumulation, the concentrations of metals can be more than those in water and air. The contaminated food can cause poisoning in humans and animals. Although some heavy metals are necessary for growth of plants, after certain concentrations heavy metals become poisonous for both plants and heavy metal microorganisms. Another important risk concerning contamination is the accumulation of these substances in the long term. Heavy metals are held in soil as a result of adsorption, chemical reaction and ion exchange of soil. Heavy metals have an effect on the enzymes. It has been determined that various metal ions hinder various enzymes responsible for mineralization of organic compounds in the earth. Pollution by metal ions such as Cr(III), Cu(II), Co(II), Mn(II), Ni(II), Zn(II), etc., in wastewater are hazardous to the environment. Due to the associated adverse health effects, a number of stringent

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Nomenclature

A	Arrhenius constant related to adsorption system
b	Langmuir constant related to the energy of adsorption (L mg^{-1})
C	concentration of adsorbate at time t (mg L^{-1})
C_0	initial concentration of adsorbate (mg L^{-1})
C_e	equilibrium concentration of adsorbate (mg L^{-1})
E_a	activation energy of adsorption (kJ mol^{-1})
ΔG	free energy change of the sorption reactions (kJ mol^{-1})
ΔH	biosorption enthalpy (kJ mol^{-1})
$k_{1,\text{ads}}$	Lagergren rate constant of sorption (min^{-1})
$k_{2,\text{ads}}$	pseudo-second-order rate constant of sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
q	amount of adsorbate adsorbed at time t (mg g^{-1})
q_e	amount of adsorbate adsorbed at equilibrium (mg g^{-1})
q_m	Langmuir constant related to the capacity of adsorption (mg g^{-1})
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R^2	correlation coefficient
ΔS	entropy change of the sorption reaction ($\text{kJ mol}^{-1} \text{ K}^{-1}$)
t	time (min)
T	absolute temperature (K)
V	volume of adsorbate solution (L)
W	weight of adsorbent (g)

regulations have been established to limit levels of toxic metals in the environment. Toxic metal ions cause physical discomfort and sometimes life-threatening illness including irreversible damage to vital body system. Heavy metals such as Mn(II), Co(II), Ni(II), and Cu(II) using in this study are among very hazardous metals. The presence of manganese and ferrous in water can influence the development manganese bacteria on walls of pipes. The growing microorganisms cause corrosion of pipes. Manganese is also toxic to the brain. This metal is abnormally concentrated in the brain, especially in the basal ganglia, resulting in neurological disorders similar to the Parkinson's disease [2]. Cobalt as a pollutant has many toxic effects such as imparting neurotoxicological disorders, genotoxicity, carcinogenicity, cardionopathy and branchial asthma [3]. The chronic toxicity of nickel to humans and environment has been well documented. For example, high concentration of nickel causes cancer of lungs, nose and bone [4]. Copper can cause serious problems such as stomach intestinal distress, kidney damage and anemia [5]. Therefore, studies on the removal of heavy metal pollution are increasing [6]. Elements in every group of the periodic table have been found to be stimulatory to animals. Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional [7]. The removal of metal ions from dilute wastewaters has become an important and widely studied research area where a number of technolo-

gies have been developed over the years. The most important of these conventional physico-chemical methods for removing heavy metals from water include chemical reduction, electrochemical treatment, ion exchange, precipitation and evaporative recovery. These processes are not generally economical enough for wastewater treatment when the initial heavy metal concentrations are in the range of 10–100 mg L^{-1} . Precipitation methods are particularly reliable but require large setting tanks for the precipitation of voluminous alkalines sludges and a subsequent treatment is need. Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. This has encouraged research into discovering materials that are both efficient and cheap. Recently, many of researchers reviewed a wide variety of low cost sorbents for the removal of heavy metals. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. Biological wastes (microorganisms) obtained from certain industries (brewers, dairy products and pharmaceutical) may be employed as a potential alternative to remove the heavy metals from industrial solutions with remarkable economic advantages. Because the biosorption has been reported as the more rapid mechanism, it has a more significant role in the metal sorption from wastewater. The agricultural and forest industries were studied as these materials could be assumed as low-cost since they require little processing and are abundant in nature. Commonly, it concerns vegetal materials, then the term of contaminants onto biomaterials [7–10].

In our study, modified black carrot residues (MCR) were used as low-cost adsorbent because of heaving etheric, esteric carbonyl and aliphatic hydroxyl functional groups which have high potential for heavy metal adsorption. The objective of this study was to feasibility of using the MCR for the removal of Mn(II), Co(II), Ni(II), and Cu(II) which are heavy metals being carcinogenic by means of adsorption from aqueous solution as a function of temperature accompanied with constants of the adsorption isotherm, well-known kinetic and thermodynamic parameters. Batch experiments were carried out to investigate adsorption properties onto MCR of used heavy metal.

2. Materials and methods

2.1. Chemicals

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were the heavy metal salts used as adsorbate in this study. In addition, acetic acid, ethanol, sodium bicarbonate, sodium carbonate and sodium hydroxide were used as analytical chemicals. All the chemicals used were of analytical reagent grade.

2.2. Determination surface area

The specific surface area of MCR was determined as $1.127 \text{ m}^2 \text{ g}^{-1}$ by applying the BET method using nitrogen gas adsorption at 77 K.

2.3. Preparation of MCR

Carrot residue was used as a biosorbent for removal of using heavy metals. It contained up to 12% of the weight of the original fruit. CR was collected in Adana region of Turkey, was first dried at 80 °C, then washed with double distilled water several times to remove the adhering any dust and other water-soluble impurities. The sun dried biomass was cut into approximately 0.5 cm sized pieces. The CR was dried in an oven at 80 °C for 24 h. Then, in order to eliminate soluble components such as tannins, resins, reducing sugars and coloring agents, the resulting dried CR were heated under reflux conditions by suspending with acetic acid–ethanol solutions (1:1, w/w) for 24 h, and washed with double distilled water until a constant pH was achieved. The modified CR (MCR) was later dried at room temperature overnight, sieved through 60-mesh size, and stored in desiccators, until used for the used heavy metals sorption experiments.

2.4. IR spectra

The IR spectra of raw CR, MCR and MCR adsorbed metals used were obtained by using infrared spectrometer (IR) (Perkin-Elmer spectrophotometer). For IR studies, 5 mg of sorbent was encapsulated in 400 mg of KBr. Translucent disks were obtained by pressing the ground material with the aid of a bench press (955 kg for 10 min). The IR spectrums were then recorded.

2.5. Determination of the functional groups on MCR

The functional acidic groups on MCR were determined by using Boehm's titration method. As follows: 1 g of the MCR was dispersed in 50 ml deionized water. The suspension was mixed with 0.1N solutions of sodium bicarbonate, sodium carbonate and sodium hydroxide, and then shaken for 48 h at room temperature. This sample was then left 6 h so that particles can settle. The sample was then filtered and 10 ml filtrate was titrated with 0.1N volumetric standards HCl using a methyl red as the indicator [5,11].

2.6. Modeling of sorption kinetics

Kinetic values of adsorption were determined by analyzing adsorptive uptake of the heavy metals used from aqueous solution at different time intervals at 20, 40, and 60 °C temperatures. All the kinetical experiments were carried out at initial pH (pH: 5.25) which is determined by waiting throughout a night in distilled water of MCR. Kinetical experiments were repeated three times and the plots were drawn by calculating the average of closed each other values of the experimental data. Then, equilibrium contact times for heavy metals used were determined from graph drawing residual concentrations no adsorbed of adsorbate versus times. The kinetics of Cu(II), Ni(II), Co(II), and Mn(II) sorptions by MCR at 20, 40 and 60 °C have been modeled using the first-rate equation of Lagergren, the pseudo-second-rate equation second-order rate equation shown below as Eqs.

(1) and (2) [12,13].

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (1)$$

A straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. q_e and $k_{1,ads}$ can be determined from the intercept and slope of plot, respectively.

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{t}{q_e} \quad (2)$$

The plot t/q versus t should give a straight line and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively.

Numerical values for activation energy (E_a) of biosorption process which were determined using the Arrhenius equation (Eq. (3)) [14].

$$\ln k_{ads} = \ln A - \frac{E_a}{RT} \quad (3)$$

The plots of $\ln k_{ads}$ versus $1/T$ were found to be linear. Numerical values for activation energy (E_a) were determined from slopes of Arrhenius graphs related to biosorption process of heavy metals onto MCR.

2.7. Isotherm studies

Adsorption measurements were made by batch technique at 20, 40 and 60 °C temperatures to observe of temperature effect. Known amounts of MCR were placed in 100 ml reagent bottles containing 50 ml of Mn(II), Ni(II), Co(II) and Cu(II) solutions of known concentration prepared from the stock solutions (1 g/L) by dissolving their sulphate salts in deionized water separately and were shaken for determined equilibrium contact times concerning heavy metals used, after contacting, the contents of the flask were filtered and centrifuged to separate the sorbent from the solution. Then, the filtrates were analyzed with an atomic absorption spectrophotometer (UNICAN model 929) to determine concentrations after sorption. All the sorption experiments were carried out at pH (pH 5.25) as defined above. Sorption experiments were repeated three times and the plots were drawn by calculating the average of closed each other value of the experimental data. In this study, we take. The amount of adsorption at equilibrium, q was calculated using (Eq. (4)).

$$q = \frac{(C_0 - C)}{W} V \quad (4)$$

Isothermal data related to biosorptions of Mn(II), Ni(II), Co(II) and Cu(II) from aqueous solutions at different temperatures were analyzed using Langmuir linear isotherm equation (Eq. (5)) [15].

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (5)$$

2.8. Thermodynamics studies

Thermodynamic parameters such as ΔH , ΔG , and ΔS for using heavy metal ions adsorption by MRC were calculated

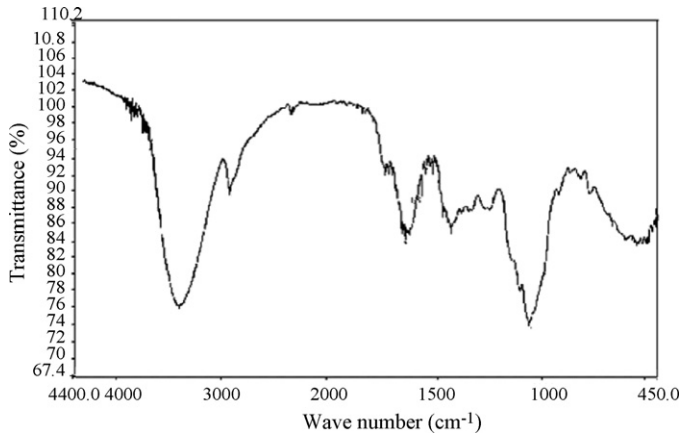


Fig. 1. Infrared spectra of raw CR.

using the following equations [16].

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = -RT \ln b \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

The ΔH is determined graphically by plotting $\ln b$ versus $1/T$ which is obtained a straight line.

3. Results and discussion

3.1. Infrared Spectrums

Figs. 1–6 show the IR spectrums related to raw CR, MCR and MCR adsorbed metals used. The O–H stretching frequency of the cellulose in MCR ligand was observed at *ca.* 3600 cm^{-1} as broader peak. Aliphatic C–H stretching band was observed at 2920 cm^{-1} . The bands at *ca.* $1636\text{--}1420 \text{ cm}^{-1}$ and *ca.* $1326\text{--}1120 \text{ cm}^{-1}$ in spectra of the CR are ascribed to olefinic C=C stretching vibrations and the C–H bending vibrations, respectively.

In the IR spectra of MCR, most of the unreacted functional groups (C=C, C–H, etc.) were like as free carrot but the stretching vibrations of the carbonyl groups were appeared in

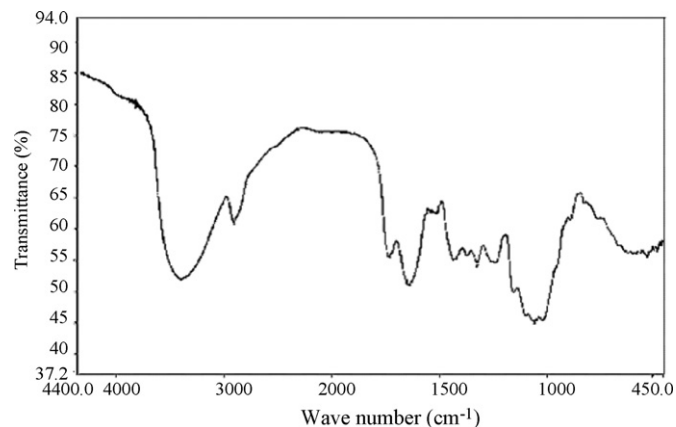


Fig. 2. Infrared spectra of raw MCR.

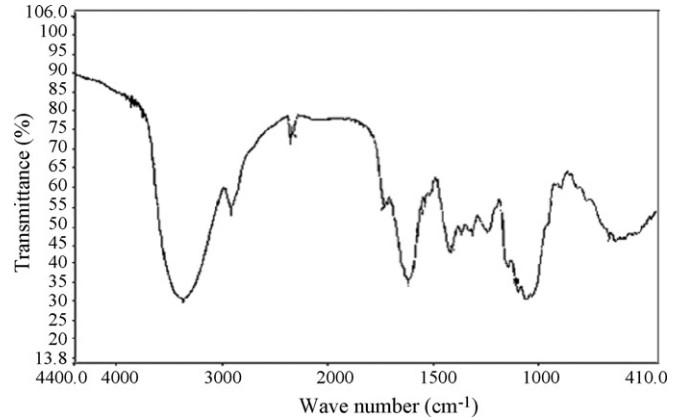


Fig. 3. Infrared spectra of MCR adsorbed Mn(II).

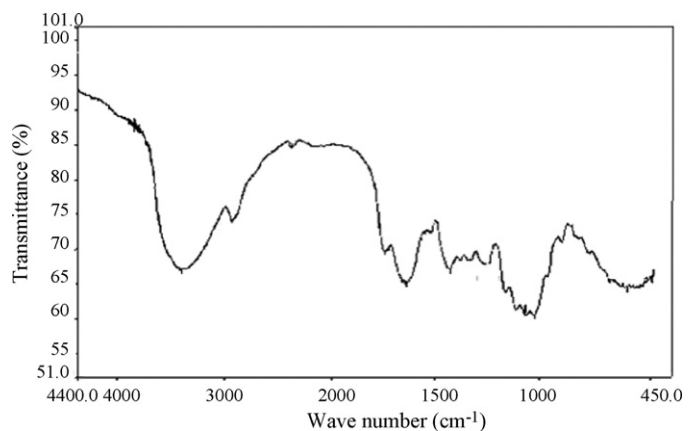


Fig. 4. Infrared spectra of MCR adsorbed Co(II).

1736 cm^{-1} . The existence of the bounding of --COOR groups is the evidence of the successful esterification or modification. On the other hand, since the acetic acid used in esterification was diluted all of the OH groups in CR were not esterified. So, O–H bond stretching vibrations peaks were observed $3600\text{--}3400 \text{ cm}^{-1}$ and bending vibration of O–H bonds appeared in 1326 and 1242 cm^{-1} .

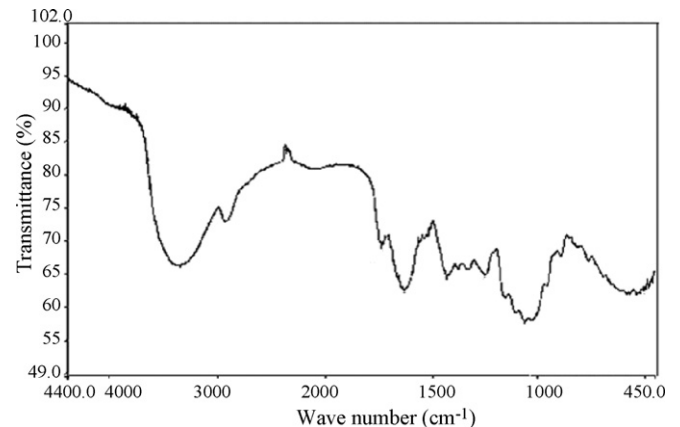


Fig. 5. Infrared spectra of MCR adsorbed Ni(II).

Table 1
The wave numbers (cm^{-1}) of functional groups obtained from IR analysis of CR and MCR

CR	MCR adsorbed				Assignment
	Cu(II)	Ni(II)	Co(II)	Mn(II)	
3600–3400	3600–3400	3600–3400	3600–3400	3600–3400	O–H (intermolecular H bounded)
2920	–	–	–	–	Aliphatic C–H
1636–1420	1593	1618	1636	1677	Aliphatic C=C
–	1736	1773	1805	1826	Carbonyl group (C=O)
1055	–	–	–	–	C–O
–	482	539	582	634	$\text{M}^{2+} \cdots \text{O}$

The most of the functional groups vibrations were shifted to high frequency region $5\text{--}10\text{ cm}^{-1}$ in MCR. Owing to formation of hydrogen bonds between carbonyl oxygen and hydroxyl groups of MCR, highly extended in the stretching vibration peak of the O–H was observed.

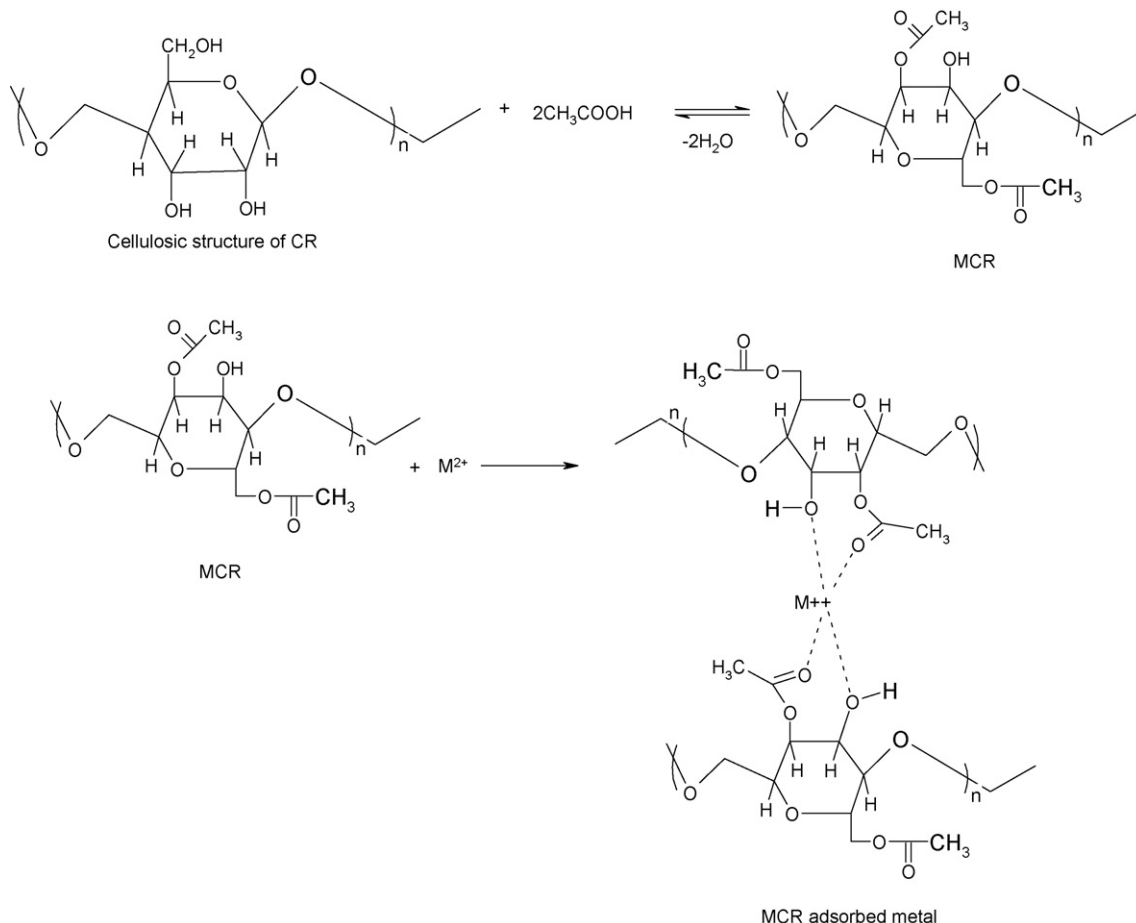
Various metal cations were adsorbed by modified carrot. IR spectrums of each metal cations were recorded separately. While the radius of metal cations (Table 1) and the wave number of $\text{M}^{2+} \cdots \text{O}$ stretching vibrations increase as parallel, decrease in amount of adsorbed of using heavy metals were observed (e.g. $\text{Co}^{2+}\text{--O}$ is 582 cm^{-1} and $\text{Ni}^{2+}\text{--O}$ is 539 cm^{-1}). The IR spectrum results of all functional groups are shown in Table 1.

3.2. Functional groups on MCR

The functional acidic groups on MCR were determined using Boehm's titration method [5,11]. The numbers of acidic sites of various types were under the assumption that sodium bicarbonate can neutralize carboxyl groups; sodium carbonate can neutralize carboxyl, lactones and lactols groups, and sodium hydroxide can neutralize carboxyl, lactones, lactols and phenols groups. Table 2 lists base neutralization capacities of MCR.

3.3. Kinetic modeling

Fig. 7 displays the kinetic curves related to adsorption of Cu(II), Ni(II), Co(II), and Mn(II) on MRC at 20, 40 and 60 °C.



Scheme 1. Binding of heavy metals onto MCR.

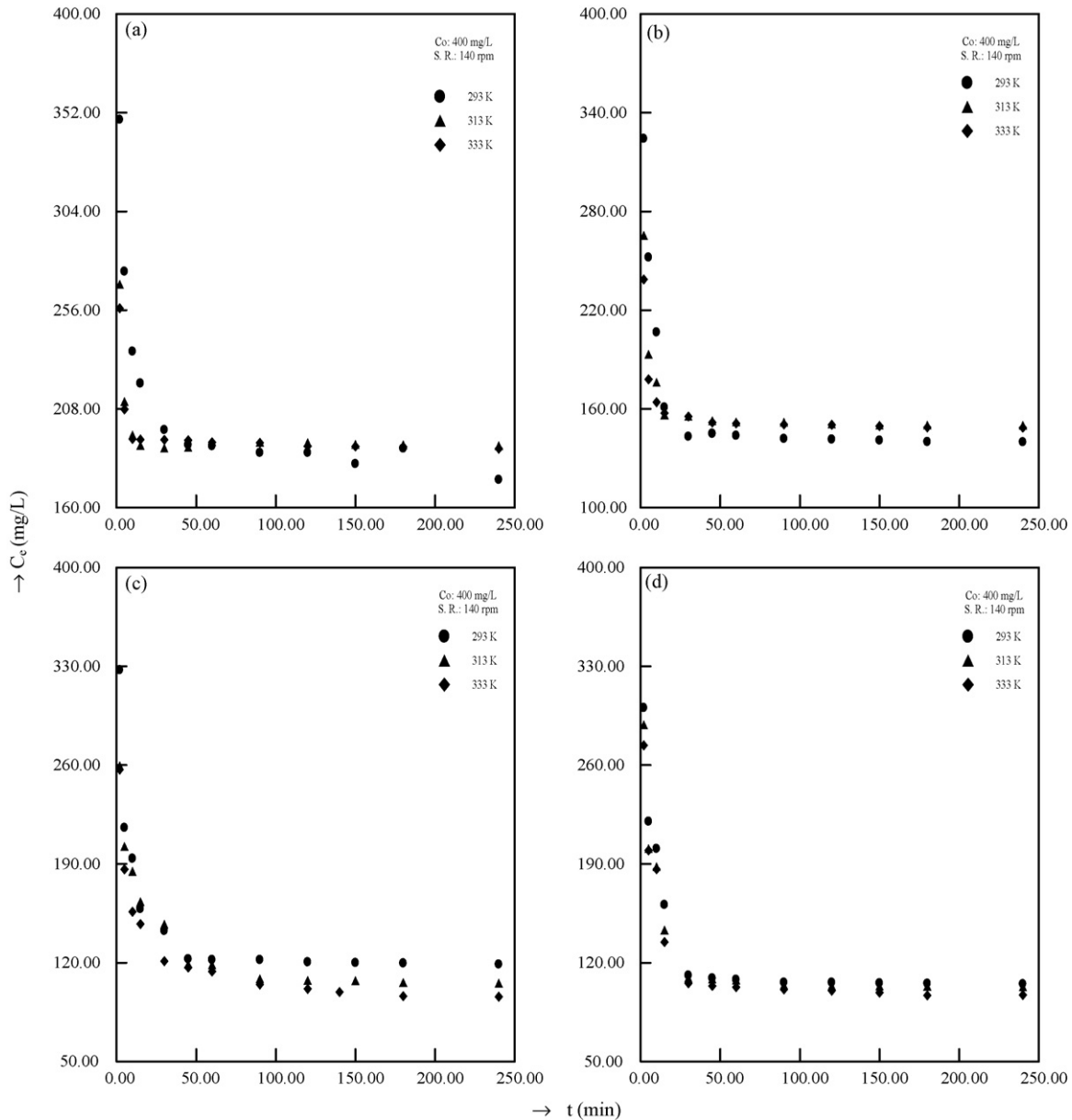


Fig. 7. The effect of temperature on adsorptions of some heavy metals by MCR from aqueous solutions: (a) Mn(II), (b) Co(II), (c) Ni(II), and (d) Cu(II).

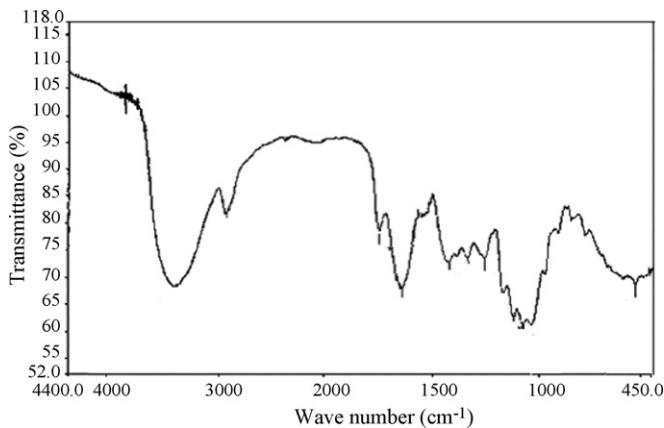


Fig. 6. Infrared spectra of MCR adsorbed Cu(II).

Equilibrium contact times from kinetic curves of all heavy metals used were determined as 60, 30, and 15 min at 20, 40 and 60 °C, respectively. For evaluating the adsorption kinetics of Cu(II), Ni(II), Co(II), and Mn(II) the pseudo-first and pseudo-second order kinetic models (Eqs. (1) and (2)) were used to fit the experimental kinetic data at 20, 40 and 60 °C. The different values of constants from the slopes and intercepts of linear plots of $\log(q_e - q)$ versus t and t/q versus t (figures not shown

Table 2
Base neutralization capacities of MCR

Base uptake	Meg H ⁺ /g MCR
NaHCO ₃	0.00296
Na ₂ CO ₃	0.01108
NaOH	0.01383

Table 3

Comparison of the first- and second-order rate constants and calculated and experimental q_e values obtained from adsorption of Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solutions onto MCR at different temperatures

Metal ions	$q_{e,exp}$ (mg g ⁻¹)	First-order kinetic model			Second-order kinetic model		
		$k_{1,ads} \times 10^3$ (min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	$k_{2,ads} \times 10^4$ (g mg ⁻¹ min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2
Mn(II)							
293	3.861	4.7	3.900	0.9939	6.2	4.918	0.9803
313	4.898	8.2	4.909	0.9908	10.1	6.016	0.9206
333	5.003	10.3	5.056	0.9918	14.0	7.112	0.9805
Co(II)							
293	5.343	5.7	5.442	0.9905	9.5	6.603	0.9872
313	5.734	8.6	5.822	0.9899	12.3	7.313	0.9711
333	6.296	10.5	6.309	0.9976	14.9	8.645	0.9805
Ni(II)							
293	5.738	6.5	5.876	0.9895	12.6	8.052	0.9744
313	5.989	8.7	6.113	0.9957	15.3	9.547	0.9699
333	6.497	11.5	6.518	0.9985	17.1	10.442	0.9703
Cu(II)							
293	8.908	7.0	9.117	0.9914	17.9	10.112	0.9756
313	9.183	9.1	9.212	0.9912	19.3	11.106	0.9706
333	11.916	12.3	12.045	0.9989	22.9	14.906	0.9767

here) and their correlation coefficients are summarized in the Table 3. It was observed that the q_e values estimated by second-order kinetic model differ substantially from those measured experimentally, suggesting that the adsorption not a second-order reaction. The correlation coefficients for the first-order kinetic model are nearly equal to 1 and the theoretical values of q_e also agree very well with the experimental values (Table 3). This suggests that the sorptions of Cu(II), Ni(II), Co(II), and Mn(II) ions follow the first-order kinetic model. The rate constants of biosorption were higher at higher temperature. Values of adsorption rate constants show that heavy metals are easily and rapidly adsorbed by MCR according to following order: Cu(II) > Ni(II) > Co(II) > Mn(II). This order was confirmed by equilibrium contact times determined from their kinetic curves. This result most probably arises from the differences between the hydrolysis constants, ionic radius, electrode potential and solubility of these heavy metal ions (Table 4) [17,18]. Namely, MOH^+ in the first step is formed and the adsorption event is completed through prompt interaction of heavy metal ions with their outer sheet of carbonyl groups on MCR (Scheme 1).

According to Pearson's hard acid-hard base theory, hard acid reacts to hard base. The hardness order of acidities of the metal ions used is Mn(II) > Co(II) > Ni(II) > Cu(II). OH^- is also a hard base [6,19]. According to Pearson's and the greatness order

Table 4

Hydrolysis constant (pK_h), ionic radius, solubility product (K_{sp}), and electrode potential related to used heavy metals [6,17,18,33]

	Metal ions			
	Mn(II)	Co(II)	Ni(II)	Cu(II)
pK_h	10.70	9.60	9.40	7.53
Ionic radius (Å)	0.80	0.74	0.72	0.70
Electrode potential (V)	-1.18	-0.28	-0.25	0.34
K_{sp} of $M(OH)_2$	2×10^{-13}	2.5×10^{-16}	1.6×10^{-16}	1.6×10^{-19}

Table 5

Activation energies for adsorption of Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solutions onto MCR

	Metal ions			
	Mn(II)	Co(II)	Ni(II)	Cu(II)
E_a (kJ mol ⁻¹)	9.81	9.91	10.02	10.58
R^2	0.9962	0.9967	0.9996	0.9946

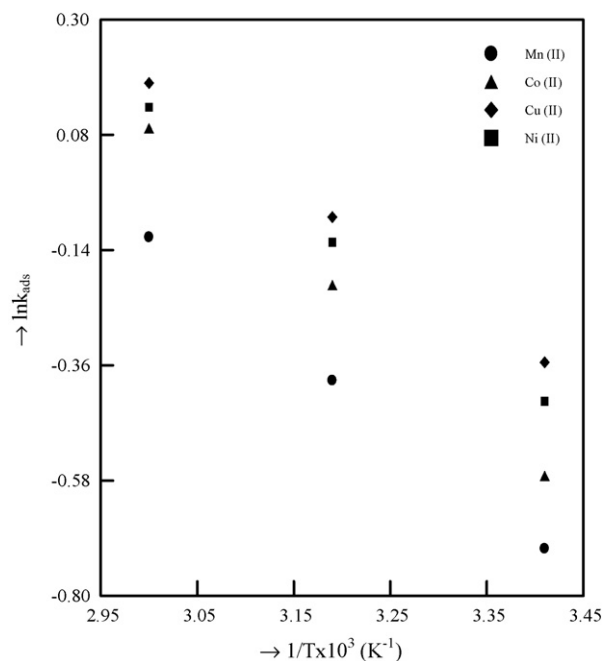


Fig. 8. $\ln k_{ads}$ versus $1/T$ for the adsorption of (a) Mn(II), (b) Co(II), (c) Ni(II), and (d) Cu(II) by MCR from aqueous solutions.

above, Mn(II) reacts more with OH^- . Mn(II) is the most hydrolysed heavy metal ion of the ions above. The hydrolysed part of Mn(II) reacts with OH^- in a short time and $\text{Mn}(\text{OH})_2$ is formed. Because there is no Mn(II) or much less Mn(II) in the medium, Mn(II) does not react or reacts a small amount with negative groups on the surface of MRC. Accordingly, the amount of adsorbed Mn(II) is very small, and because of Cu(II) has lower affinity to solvent, it is more and rapidly adsorbed on MRC. In the other words, looking into pK_h and K_{sp} values of Mn(II) and Cu(II) given in Table 4, Mn(II)'s values are greater than Cu(II)'s values. From this point of view, Mn(II) has higher affinity to solvent than Cu(II) and lower affinity to MCR surface than Cu(II). So, Mn(II) ions are adsorbed less on MCR surface and Cu(II) ions are adsorbed more on MCR surface.

It can be seen that heavy metal ions are being adsorbed when ionic radius decrease.

The ionic radius of the heavy metals used change in the order of $\text{Mn}(\text{II}) > \text{Co}(\text{II}) > \text{Ni}(\text{II}) > \text{Cu}(\text{II})$ (Table 4). Cu(II) is the most adsorbed because of its smaller ionic radius (takes easily in the pores of the MRC). This is compatible with our experimental results.

The Irving-Williams series, that is, the order of complex stabilities of heavy metal ions used as adsorbates is given $\text{Mn}(\text{II}) < \text{Co}(\text{II}) < \text{Ni}(\text{II}) < \text{Cu}(\text{II})$ [14]. According to this order, Mn(II) must be the least adsorbed and Cu(II) must be the most adsorbed, because the heavy metal whose complex to be adsorbed more. Our experimental results are consistent with this.

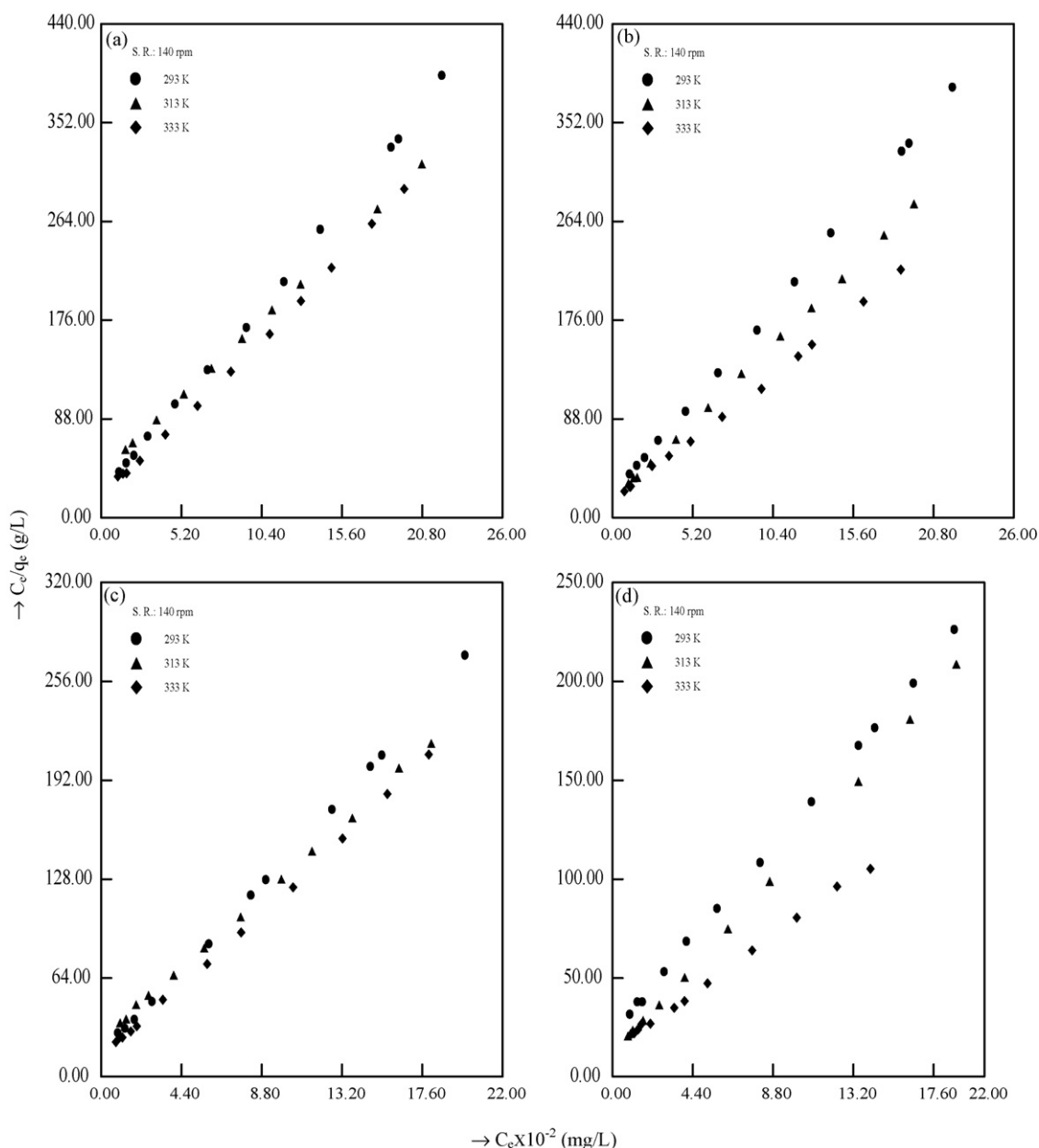


Fig. 10. Langmuir linear isotherm plots related to the adsorptions of (a) Mn(II), (b) Co(II), (c) Ni(II), and (d) Cu(II) by MCR from aqueous solutions.

Because of the MCR surface may also be negatively charged, providing adsorption sites for metal ions which is order of their electrode potential: $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)}$. The greatness order above, Cu(II) complexes more and rapidly with unshared electron pairs of oxygen of carbonyl groups of MCR. Our experimental results are consistent with this.

Table 5 show numerical values for activation energy (E_a) of biosorption process which were determined using the Arrhenius equation [14]. Since the biosorption rates of the metal ions examined increased with temperature (Table 3), the slopes of Arrhenius plots give negative values and the activation energy normally found to be positive. From the slopes of linearized Arrhenius plots obtained by using kinetic data, activation energies E_a values were determined (Fig. 8) (Table 5), and appropriate adsorption mechanism with respect to the magnitude of activation energy of biosorption has been proposed for each metal-MCR system. The correlation coefficients are greater than $R^2 = 0.9946$. For biological systems reported activation energies in literature [16,20,21]. The magnitude of activation energy may give an idea about the type of sorption. Two main types of adsorption may occur physical and chemical adsorption. In physical adsorption, equilibrium between the adsorbent surface and the adsorbate is usually rapidly attained and easily reversible, because the energy requirements are small (usually no more than $4.184 \text{ kJ mol}^{-1}$), since the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption. In chemisorption the adsorbed molecules are held on the surface by valence forces so the activation energy for chemical adsorption is of same magnitude as the heat of chemical reaction. Two kind of chemisorption are encountered, activated and non-activated. Activated chemical adsorption means that the rate varies with temperature according to the finite activation energy (between 8.4 and 83.7 kJ mol^{-1}) in the Arrhenius equation. In some systems chemisorption occurs rapidly, suggesting the activation energy is near zero. This is termed non-activated chemisorption. In the other words, the values of activation energy in the present study indicate a chemical sorption process involving weak interactions between sorbent and sorbates. The relatively low E_a values suggest that the adsorptions have a low potential energy barrier (Table 5).

3.4. Adsorption isotherms

Figs. 9 and 10 show the adsorption isotherms and Langmuir linear isotherms of Cu(II) , Ni(II) , Co(II) , and Mn(II) from aqueous solutions onto MCR at 20 , 40 and 60°C , respectively. Langmuir constant b , related to the free energy of adsorption, indicates the affinity of adsorbent for the binding the adsorbate. The plot of C_e/q_e against C_e gives a straight line (Fig. 10) at each temperature showing the applicability of Langmuir isotherm. From the reciprocal values of the slope and intercept of the Langmuir linear adsorption isotherms (Fig. 6), q_m and b were found, respectively (Table 6). The correlation coefficients are greater than $R^2 = 0.9811$. From the values of q_m and b at different temperatures obtained as a result of this investigation, the order of the sorption capacity: $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)}$.

As seen Table 6, the increase in both q_m and b increase by increasing the temperature from 20 to 60°C showing the process to be endothermic. The increasing of b values with temperature indicates that there is a chemical interaction between MRC and using heavy metals. Table 7 shows a comparison of q_{max} values related to different sorbents obtained by other researchers [22–42]. These maximum sorption capacities are also considerably higher or lower than those of some other sorbent materials reported in literatures (see Table 7). But, we do not find such a comparison logically because the removal of metals depending on varying experimental conditions and the structure, functional groups and porosity of adsorbent.

3.5. Adsorption thermodynamics

The values of ΔH are determined graphically by plotting $\ln b$ versus $1/T$ which gives a straight line (Fig. 11), and the values of ΔG and ΔS from Eq. (7) and (8) computed numerically, respectively, and are presented in Table 8. Positive values of ΔH suggest the endothermic nature of the adsorptions of heavy metals used on MCR. One possible explanation of endothermicity of the enthalpy of adsorption is the well-known fact that heavy metal ions used are well solvated in water. In order for these ions to adsorb, they are some extent denuded of their hydration sheath. This dehydration process of ions requires energy. We assume that this energy of dehydration exceeds the exothermicity of the ions attaching to the surface. The implicit assumption here is that after adsorption the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of enthalpy of adsorption by a

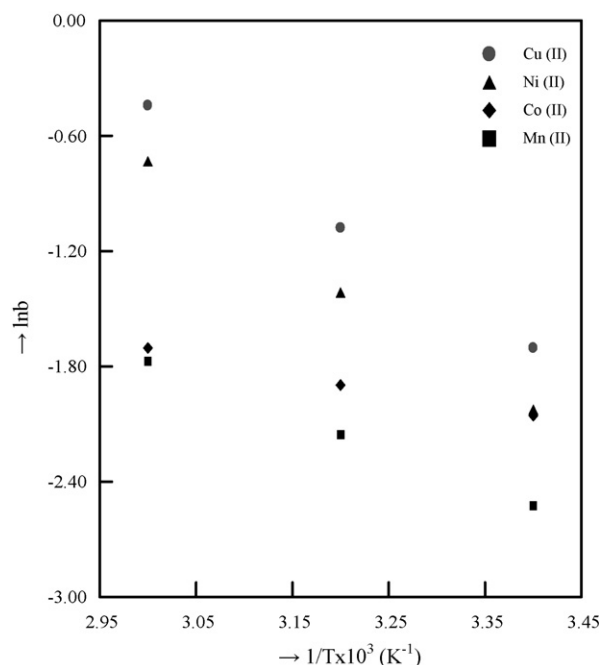


Fig. 11. Variation of $\ln b$ with reciprocal of temperature.

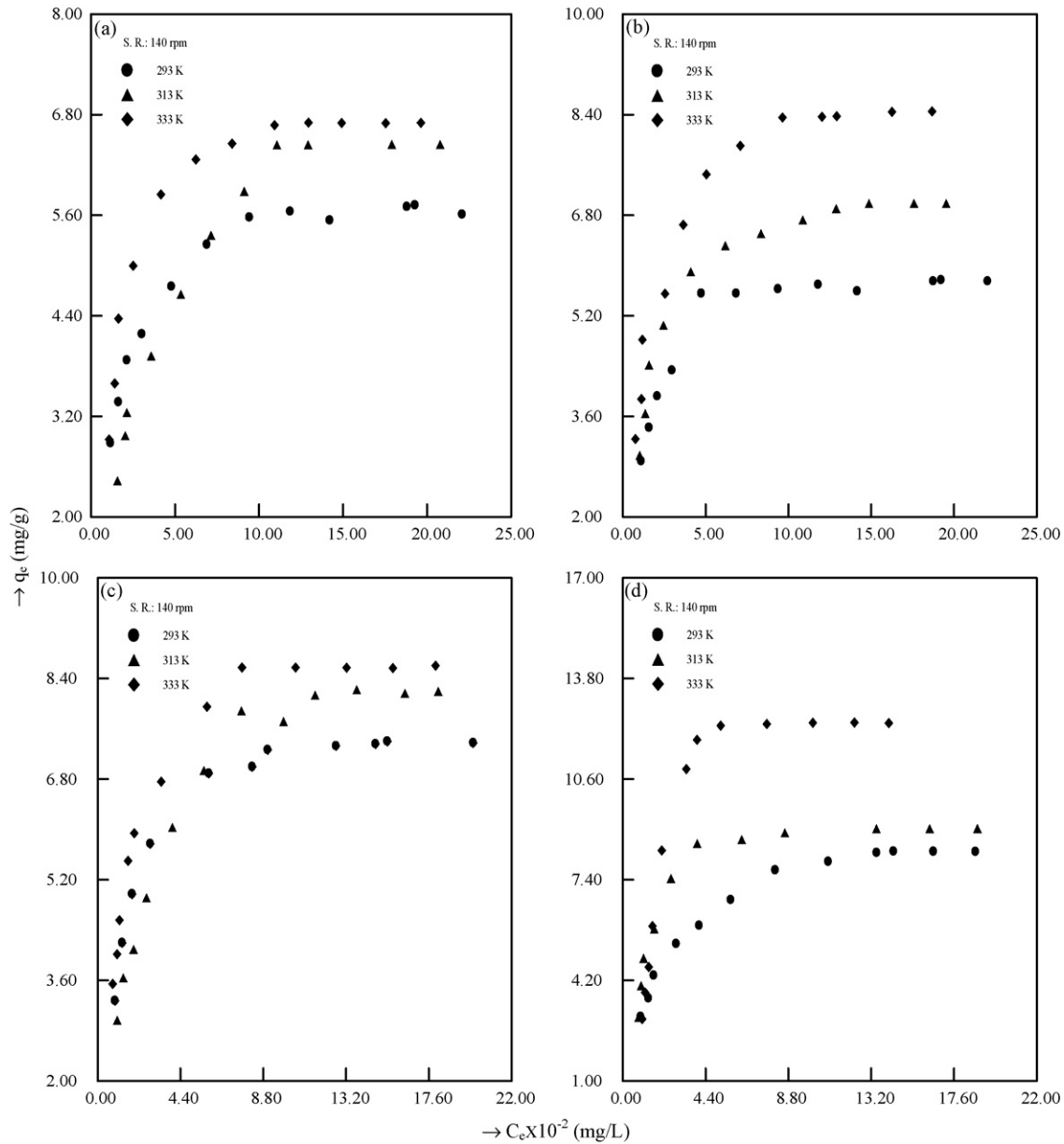


Fig. 9. Effect of temperature on the adsorption isotherms of (a) Mn(II), (b) Co(II), (c) Ni(II), and (d) Cu(II) by MCR from aqueous solutions.

considerable extent. The values of ΔG are very small and positive, and decrease with increasing of temperature. This indicates that better adsorption is obtained at higher temperature. At higher temperature, ions are readily desolvated and hence their adsorptions become more favorable at higher tempera-

tures. The positive values of ΔS show the increased randomness at the solid/solution interface during the adsorption process. Positive entropy of adsorption also reflects the affinity of adsorbent for heavy metals used. The adsorbed water molecules, which are displaced by the adsorbate species, gain more trans-

Table 6

Langmuir constants for adsorption of Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solutions onto MCR at different temperatures

Metal ions												
Mn(II)			Co(II)			Ni(II)			Cu(II)			
q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	
293 K	3.871	0.080	0.9811	5.350	0.128	0.9952	5.745	0.132	0.9985	8.745	0.182	0.9970
313 K	4.910	0.127	0.9875	5.746	0.150	0.9968	6.031	0.243	0.9955	9.081	0.340	0.9956
333 K	5.170	0.168	0.9968	6.309	0.182	0.9960	6.511	0.481	0.9982	12.390	0.643	0.9904

Table 7
Sorption capacities of Mn(II), Co(II), Ni(II) and Cu(II) ions from the selected literatures by various sorbents

Sorbent	q_e (mg g ⁻¹)				Reference
	Mn(II)	Co(II)	Ni(II)	Cu(II)	
Leaves of saltbush	–	–	–	67.945	[22]
Rice bran	–	–	39.760	–	[23]
<i>Tectona grandis</i> L. F.					
Leaves powder	–	–	–	15.430	[24]
Botrytis cinrea fungal	–	–	–	9.230	[25]
Groundnut shell	–	–	–	4.445	[26]
Sawdust	–	–	–	5.080	[26]
Wheat Shell	–	–	–	8.255	[27]
Anaerobic granular biomass	–	–	26.000	55.000	[28]
Olive stone waste	–	–	0.517	0.565	[29]
Malch	–	–	–	20.574	[30]
Grape stalks	–	–	10.627	10.097	[30]
Cork bark	–	–	4.111	4.445	[30]
Reed biomass	–	–	7.926	9.906	[30]
Carrot residues	–	–	–	32.740	[31]
Grape stalk waste	–	–	18.100	15.900	[32]
Kaolinite	0.446	0.919	1.669	10.787	[33]
Black carrot residues	3.871	5.350	5.745	8.877	Present work
Prolyzed coffee residues	–	–	11.000	31.200	[34]
Sunflower leaves	–	–	–	89.370	[13]
Paper mill	–	–	–	19.300	[35]
Ballclay	–	–	0.410	–	[36]
Coir pith	–	12.82	15.950	–	[37]
Turkish lignite	–	–	13.000	17.800	[38]
Hazelnut shell act. carbon	–	–	5.983	–	[39]
Coir pith act. carbon	–	–	62.500	–	[40]
Ceiba pentadra hulls act. carbon	–	–	–	20.800	[41]
Broiler manure granular act. Carbon	–	–	–	1.920	[42]

Table 8
Thermodynamics parameters related to adsorption of Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solutions onto MCR

Metal ions	Mean ΔH (kJ mol ⁻¹)	R^2	ΔG (kJ mol ⁻¹)			ΔS (kJ mol ⁻¹ K ⁻¹)		
			293 K	313 K	333 K	293 K	313 K	333 K
Mn(II)	27.18	0.9903	6.15	5.37	4.94	0.072	0.070	0.067
Co(II)	23.94	0.9969	5.01	4.94	4.72	0.065	0.061	0.058
Ni(II)	26.88	0.9989	4.93	3.68	2.03	0.075	0.074	0.075
Cu(II)	26.23	0.9998	4.15	2.81	1.22	0.075	0.075	0.075

lational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity of adsorbent at higher temperatures may be attributed to the strong affinity between adsorbate and adsorbent [33,43].

4. Conclusion

In this study, the order of biosorption of Cu(II), Ni(II), Co(II), and Mn(II) ions were determined onto MCR in batch system. The heavy metals removal (>70%) were achieved at low contact times (less than 1 h). Kinetics of heavy metals sorption on MCR is observed to confirm Lagergren first-order rate

expression. The rate constants were higher at higher temperature. The activation energies were determined to be same order of magnitude as the activation energy of chemisorption. The sorption data adapted to Langmuir model. The values of Langmuir constants q_m and b are order of the sorption capacity: Cu(II) > Ni(II) > Co(II) > Mn(II). The increases in q_m and b with increasing temperature from 20 up to 60 °C at pH 5.25, suggest that are an endothermic process. The values of thermodynamic parameter obtained such as the ΔH , ΔG and ΔS related to adsorption of Cu(II), Ni(II), Co(II), and Mn(II) onto MCR. The results indicate that the positive values of (ΔH) indicated the adsorption process was endothermic. The values of ΔG are very small and positive, and decrease with an increase of temper-

ature, and better adsorption is obtained at higher temperature, and the positive values of ΔS showed the increased randomness at solid–solution interface during adsorption. It may be concluded that the MCR, being a cheap and easily available material, can be successfully used as alternative adsorbent for many costly adsorbents for Cu(II), Ni(II), Co(II), and Mn(II) in wastewater treatment process. MCR biosorbent may be used as a low-cost and abundant source for removal of heavy metal ions and it may be an alternative to many costly methods such as active carbon adsorption, solvent extraction and chemical oxidation.

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References

- [1] J. Bajpai, R. Shrivastava, A.K. Bajpai, Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary biopolymeric beads of cross linked alginate and gelatin, *Colloids Surf. A: Physicochem. Eng. Aspects* 236 (2004) 81–90.
- [2] E. Okoniewska, J. Lach, M. Kacprzak, E. Neczaj, The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon, *Desalination* 2006 (2007) 251–258.
- [3] D. Lison, M.D. Boeck, Update on the genotoxicity and carcinogenicity of cobalt compound, V. Verougstheate, M. Kirsh-Volders, *Occup. Environ. Med.* 58 (2001) 619–625.
- [4] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, *J. Hazard. Mater.* B97 (2003) 49–57.
- [5] F.A. Abu Al-Rub, M.H. El-Naas, I. Ashour, M. Al-Marzouqi, Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions, *Process Biochem.* 41 (2006) 457–464.
- [6] İ. Uzun, F. Güzel, Adsorption of some heavy metal ions from aqueous solution by activated carbon and comparison of percent adsorption results of activated carbon with those of some other adsorbents, *Turk. J. Chem.* 24 (2000) 291–297.
- [7] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421–1430.
- [8] D. Park, Y.-S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp., *Chemosphere* 60 (2005) 1356–1364.
- [9] V. Taty-Costodes Christian, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater.* B105 (2003) 121–142.
- [10] A. Özer, D. Özer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats, *J. Hazard. Mater.* B100 (2003) 219–229.
- [11] W.-C. Oh, M.-H. Yum, Silver loading effect for the activated fiber pretreated with acid, *Bull. Korean Chem. Soc.* 25 (8) (2004) 1189–1194.
- [12] C. Namasivayam, K. Ranganathan, Removal of Fe(II) by waste Fe(III)/Cr(III) hydroxide from aqueous solutions and electroplating industry wastewater, *Ind. J. Chem. Technol.* 1 (2005) 351–355.
- [13] H. Benaïssa, M.A. Elouchi, Removal of copper ions from aqueous solutions by dried sunflower leaves, *Chem. Eng. Process.* 46 (2007) 614–622.
- [14] S.K. Srivastava, V.K. Gupta, S. Anurpam, D. Mohan, Removal of some anionic detergents using an inorganic gel adsorbent, *Ind. J. Chem.* 34A (1995) 342–350.
- [15] I. Langmuir, The adsorption gases on the plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [16] Z. Aksu, S. Tezer, Biosorption of reactive dyes on the green alga *Chlorella vulgaris*, *Process Biochem.* 40 (2005) 1347–1361.
- [17] E.H. James, *Inorganic Chemistry Principles*, Harper International Edition, Harper & Row, 1978, pp. 235–237.
- [18] A.D. John, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1973, pp. 440–442.
- [19] J.E. Huheey, *Inorganic Chemistry*, Harper International Edition, New York, 1978, pp. 278–280.
- [20] X.-S. Wang, J. Huang, H.-Q. Hu, J. Wang, Y. Qin, Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite, *J. Hazard. Mater.* 142 (2007) 468–476.
- [21] Y. Sağ, T. Kutsal, Determination of the biosorption activation energies of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*, *Process Biochem.* 35 (2000) 801–807.
- [22] M.F. Sawalha, J.R. Peralta-Videa, J. Romero-Gonzalez, M. Duarte-Gardea, J.L. Gardea-Toresdey, Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (*Altriplex canescens*), *J. Chem. Thermodyn.* 39 (2007) 488–492.
- [23] M.N. Zafar, R. Nadem, M.A. Hanif, Biosorption of nickel from protonated rice bran, *J. Hazard. Mater.* 143 (2007) 478–485.
- [24] Y.P. Kumar, P. King, V.S.R.K. Prasad, Equilibrium and kinetic studies for the biosorption system of copper (II) ion from aqueous solution using *Tectona grandis* L. F. leaves powder, *J. Hazard. Mater.* B137 (2006) 1211–1217.
- [25] T. Akar, S. Tunali, Biosorption performance of *Botrytis cinerea* fungal by-products for removal Cd (II) and Cu(II) ions from aqueous solutions, *Miner. Eng.* 18 (2005) 1099–1109.
- [26] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, *Sep. Purif. Technol.* 43 (2005) 1–8.
- [27] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of copper(II) from aqueous solutions by wheat shell, *Desalination* 164 (2004) 135–140.
- [28] A.H. Hawari, C.N. Mulligan, Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass, *Bioresource Technol.* 97 (2006) 692–700.
- [29] N. Fiol, I. Villaescusa, M. Martínez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone wastes, *Sep. Purif. Technol.* 50 (2006) 132–140.
- [30] B. Southichak, K. Nakano, M. Nomura, N. Chiba, *Phragmites australis*: a novel biosorbent for the removal of heavy metals from aqueous solution, *Water Res.* 40 (2006) 2295–2302.
- [31] B. Nasarnejad, E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Comparison for biosorption modeling of heavy metals (Cr(II), Cu(II), Zn(II)) adsorption from wastewater by carrot residues, *Process Biochem.* 40 (2005) 1319–1322.
- [32] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalk wastes, *Water Res.* 38 (2004) 992–1002.
- [33] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, *Water Res.* 37 (2003) 948–952.
- [34] V. Noonamnuayvitaya, C. Chaiya, W. Tanthapanichakoon, S. Jarudilokkul, Removal of heavy metals by adsorbent prepared from prolyzed coffee residues and clay, *Sep. Purif. Technol.* 35 (2004) 11–22.
- [35] S.K. Lister, M.A. Line, Potential utilization of swage sludge and paper mill waste for bisorption of metals from polluted waterways, *Bioresource Technol.* 79 (2001) 35–39.
- [36] V. Chontawong, N.W. Harvey, V.N. Bashkin, Comparison of heavy metal adsorption by Thai kaolin and ballclay, *Water Air Soil Pollut.* 148 (2003) 111–125.
- [37] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium of Co(II), Cr(III), and Ni(II) onto coir pith, *Process Biochem.* 41 (2006) 609–615.
- [38] E. Pehlivan, G. Arslan, Removal of metal ions using lignite in aqueous solution – low cost biosorbents, *Fuel Process. Technol.* 88 (2007) 99–106.
- [39] E. Demirbaş, M. Kobya, S. Öncel, S. Şencan, Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon; equilibrium studies, *Bioresource Technol.* 84 (2002) 291–293.

- [40] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from coir pith, *Sep. Purif. Technol.* 24 (2001) 497–505.
- [41] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *cerbera pentandra* hulls, *J. Hazard. Mater.* B129 (2006) 123–129.
- [42] I.M. Lima, W.E. Marshall, Granular activated carbons from *broiler manure*: physical, chemical and adsorptive properties, *Bioresource Technol.* 96 (2005) 699–706.
- [43] S.S. Tahir, N. Rauf, Thermodynamics studies of Ni(II) adsorption onto bentonite from aqueous solution, *J. Chem. Thermodyn.* 35 (2003) 2003–2009.