Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23569

141 (2019) 269–278
February

Preparation of activated carbon from worn tires for removal of Cu(II), Ni(II) and Co(II) ions from synthetic wastewater

Somayeh Abbasi[a], Rauf Foroutan[b], Hossein Esmaeili[c,*], Feridun Esmaeilzadeh[d]

[a]*Department of Chemical Engineering, School of Chemical Engineering, Kherad Institute of Higher Education, Bushehr, Iran, email: sanaz.naz.abbasi@gmail.com (S. Abbasi)*
[b]*Young Researchers and Elite Club, Bushehr Branch, Islamic Azad University, Bushehr, Iran, email: rauf.foroutan@yahoo.com (R. Foroutan)*
[c]*Department of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran. Tel. +989179885692, Fax +987735683700, email: esmaeili.hossein@iaubushehr.ac.ir (H. Esmaeili)*
[d]*Department of Chemical and Petroleum Engineering, School of Chemical and Petroleum Engineering, Enhanced Oil and Gas Recovery Institute, Enhanced Gas Condensate Recovery Research Group, Shiraz University, Shiraz, Iran, Tel. 7134551154, email: Esmaeil@shirazu.ac.ir (F. Esmaeilzadeh)*

Received 11 May 2018; Accepted 5 December 2018

ABSTRACT

In this study, activated carbon was produced through pyrolysis process from worn tires and applied as an effective and low-cost adsorbent to remove heavy metal ions of copper, nickel and cobalt from aqueous solutions. Scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and Brunauer–Emmett–Teller (BET) analyses were utilized to investigate the characteristics of the adsorbent. The specific surface area of activated carbon by BET analysis was reported as 32.39 m^2/g which shows activated carbon has a suitable porous surface. The adsorption process of metal ions carried out discontinuously and effects of parameters like pH, temperature, contact time and adsorbent dosage on adsorption efficiency were examined. The results showed that adsorption efficiency increased by increasing initial pH (from 2 to 6), contact time and adsorbent dosage. But increasing the temperature, reduced adsorption efficiency showing that the adsorption process is exothermic. Besides, isotherm behavior of adsorption processes was studied using Langmuir and Freundlich isotherm models. According to correlation coefficient (R^2), the Freundlich isotherm model was more capable to describe isotherm behavior of adsorption process of metal ions in comparison with the Langmuir model. The maximum adsorption capacity (q_{max}) based on Langmuir isotherm model was determined as 109.89 mg/g, 74.626 mg/g and 90.09 mg/g for nickel, copper and cobalt adsorption, respectively which are significant amounts. The values of parameters n and R_L showed that the adsorption process is physical and desirable. Also, thermodynamic behavior showed that adsorption process was exothermic and spontaneous. Additionally, kinetic models showed that the pseudo second-order model has a greater ability to describe the kinetic behavior of the process.

Keywords: Activated carbon; Worn tires; Adsorption; Aqueous solution; Heavy metals

---

1. Introduction

Although heavy metal ions are available within the environment in low concentrations, human activities increased their concentrations and they are known as a contaminant agent these days. Transport and accumulation of metal ions in food chains cause harmful effects on human health and other creatures on earth [1,2]. Heavy metal ions contamination can be separated from other types of contaminations as they are not degradable and can be stored within living tissues and enter into food chains [3]. Nickel, copper and cobalt are toxic and non-biodegradable heavy metal cations which are frequently used in industries like galvanizing, melting, mining, battery manufacturing and additional operations

---

*Corresponding author.

of metals [4,5], electroplating and electronics. These ions are expelled to the environment through the wastewaters of these industries [6]. High consumption of nickel metal can lead to illnesses such as diseases of the brain, skin, liver, pancreas, heart [7], kidney damage, capillary trauma, gastrointestinal irritation, anemia [8], vomiting, muscle cramps and seizures [9]. Cobalt is another heavy metal ion which is necessary for the body in low quantity, but high concentrations of this ion can cause different diseases like paralysis, diarrhea, chronic blood pressure, pulmonary discomfort, bone defect [10], vomiting, shortness of breath, nausea, cardiac failure, kidney damage and thyroid disabilities [11]. Therefore, it is necessary to remove these metal ions from industrial wastewaters and the environment to increase the health of human and living organisms.

Removing metal ions from aqueous solutions are carried out through different methods such as chemical treatments [12], ion exchange, adsorption [13], membrane processes [14], coagulation and electrochemical methods. Amongst aforementioned methods, adsorption is highly attended for metal ion removal from aqueous solutions due to the simplicity of the process, low cost and cost-effectiveness, adsorption capability and recovery of the adsorbent, high efficiency and operational speed [15]. Different materials are used for the adsorption process, but activated carbon is one of the most frequently used adsorbent all over the world for adsorption of metal ions from wastewaters. Although this adsorbent is expensive with the high cost of production [16], in the recent decade this cost decreased by using various types of activated carbon produced from agricultural wastes like coconut charcoal, walnut and hazelnut shells [17]. In all, very low-cost material with high organic content and low inorganic content within its structure can be used as a raw material of activated carbon production [18]. The wood of some plants, charcoal, brown charcoal, lignin, coconut shell, shells of fruits such as hazelnuts, walnuts are the most regular raw materials used to produce activated carbon. In addition to these materials, worn tire is another raw material highly considered for activated carbon production since high amount of tires are produced and released in the nature annually and its accumulation within the environment is accompanied by some problems like increasing the number of insects such as flies and rodents, as well as causing fires [19]. Therefore, recovery and conversion of this material to other sorts of substances and their recycling are very significant and essential.

In this research study, worn tires were employed for the preparation of activated carbon and its ability in nickel, copper and cobalt ions removal from synthetic wastewater was elucidated. The characteristics of produced activated carbon were analyzed by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and Brunauer–Emmett–Teller (BET) and scanning electron microscope (SEM). Effects of some parameters were fully investigated including initial pH of the solution, contact time, adsorbent dosage and temperature on adsorption efficiency. Isotherm models of Freundlich and Langmuir were applied to inspect equilibrium behavior of the adsorption process. Besides, the adsorption process regime was studied at different temperatures by thermodynamic parameters like enthalpy, entropy and Gibbs free energy. To the best of author's knowledge, there is no published research regarding heavy metals removal by activated carbon prepared with worn tires.

2. Materials and methods

2.1. Preparing activated carbon

In this work, activated carbon was prepared by the thermochemical method and through the pyrolysis process. The worn tire was split into small fragments and for chemical activation soaked within potassium hydroxide for three hours. The process was accomplished in 250 ml Erlenmeyer by mixing the sample of the worn tire with potassium hydroxide and ethanol as solvent. This mixture was kept in an oven for 24 h at 110°C. Afterward, the activated tire was placed in the furnace with 700°C temperature to do the pyrolysis process. The product of this stage was washed with 0.5% normal chloride acid at 85°C and distilled water in order to completely neutralize it and then again placed in the oven for 24 h and 110°C to completely dry it up. The activated carbon was then powdered and separated with sieve No. 25.

2.2. Devices and instruments

FRIR (Broker Victor 22) was applied in order to investigate functional groups in produced activated carbon and the changes on the surface after removing copper, nickel and cobalt ions. The structure and morphology of the adsorbent were studied by XRD (Siemens D500 type) and SEM (Hitachi S4160), respectively. Also, the specific surface area, pore volume, and pore size of the adsorbent were determined by BET (Micrometrics/Asap2020, USA). Additionally, the amount of residual metal ions within the solution after the tests was measured by a flame atomic absorption device (type SpectrAA-10 Plus) with acetylene-air fuel made by Varian Manufacturing Company. Measuring surface features, porosity and available pores of activated carbon were done by Micrometrics/Asap 2020 made in USA. Initial pH of the solutions was measured by a digital pH meter (Metrohm 744).

2.3. Preparing stock solution and undertaking the tests

In this study, all the above-mentioned materials and devices were purchased from Merck company (Germany). The solutions with nickel (II), cobalt (II) and copper (II) contents were prepared from $Ni(NO_3)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $CuSO_4{\cdot}5H_2O$, respectively. The stock solution with 1000 mg/L initial concentration was obtained by dissolving certain amounts of the mentioned compounds in double distilled water. In order to achieve definite molarity of the solutions for the experiments, the stock solution was diluted with double distilled water. The adjustment of initial pH of solutions for the adsorption process was performed using HCl and NaOH (1 M).

The experiments for the adsorption of metal ions from synthetic wastewater using activated carbon produced from worn tires were discontinuously performed inside a 250 ml Erlenmeyer containing 100 ml working volume. The effects of parameters like initial pH of the solution, contact time, adsorbent dosage and temperature were thoroughly investigated on the adsorption process. In order to check the effect of initial pH, the adsorption tests were performed at pH range of 2–11, 25°C temperature, 60 min contact time, 10 mg/l initial concentration of metal ions, 3 g/l adsorbent dosage and 300 rpm mixing rate. After determination of optimal pH, the effects of other parameters including temperature (25–55°C), contact time (5–200 min) and adsorbent dosage (1–10 g/l) at optimum pH were studied.

Flame atomic absorption device employed for the measurement and determination of residual metal ions within the solutions after the adsorption process. In all samples, the amount of adsorbed heavy metal ions (R%) and adsorption capacity (q_e) were defined by Eqs. (1) and (2) [4]:

$$R(\%) = \left(\frac{C_i - C_o}{C_i}\right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_i - C_o}{W}\right) \times V \quad (2)$$

where C_i and C_o are the initial and equilibrium concentration of metal ions (mg/l), respectively. V is the volume of the solution (L), M is the weight of dried adsorbent used in the experiments (g), R is the percentage of heavy metal ions adsorption and q_e is the adsorption capacity per gram of dried bio-adsorbent (mg/g).

3. Results and discussion

3.1. Adsorbent properties

In order to investigate the changes on the surface of activated carbon produced from worn tire before and after adsorption process, the surface of activated carbon was covered with a thin layer of gold in a vacuum condition and the surface was inspected by SEM. Fig. 1 shows SEM images of this adsorbent before and after adsorption of metal cations. As shown in this figure, there are a number of pores and holes with different sizes on the surface of the adsorbent which is the primary requirement for the metal ion adsorption. After the adsorption process, it is clearly seen that these pores filled to a great extent which can be the effect of metal ions.

Fig. 2a shows FT-IR analysis of the powdered activated carbon before and after adsorption of copper, nickel and cobalt ions. In the range of 3440–3738 cm^{-1}, there are weak but sharp peaks showing the vibrations of OH and N-H functional groups [20]. There is also a sharp peak at 1644 cm^{-1} with low intensity as a result of C=C vibrations during carbonization process [21]. FT-IR analysis showed a dramatic peak with high intensity at 1521 cm^{-1} incorporated with C=O functional group within carbon structure [22]. There were also other vibrations in the range of 1000–1300 cm^{-1} mainly due to C-O group vibrations in produced activated carbon [20].

Fig. 2b shows the spectrum of XRD analysis for the activated carbon produced from the worn tire. The results revealed that this adsorbent has a complex structure of crystalline and amorphous shape [23]. Different peaks are observed in the range of 2θ = 25° and 2θ = 43° which represent the amount of dispersion associated with the graphite structure in activated carbon [24].

In order to study some properties of size, surface and volume of nano-particles, BET analysis was applied and the results are shown in Table 1. Specific surface area and pore volume in the activated carbon produced from worn tire were determined as 32.39 m^2/g and 0.098 cm^3/g, respectively. Other parameters including active sites, the size of the pores and holes are mentioned in Table 1. According to Table 1, the adsorbent is a mesoporous material. All these values show that metal ions of copper, nickel and cobalt

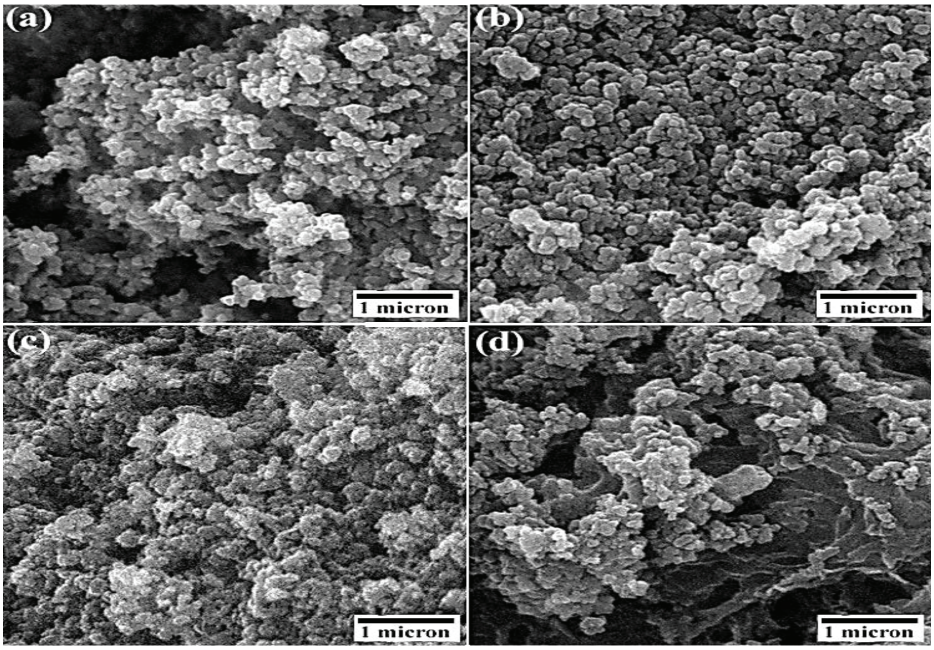

Fig. 1. SEM images a) AC, b) AC-Ni(II), c) AC-Cu(II), d) AC-Co(II).

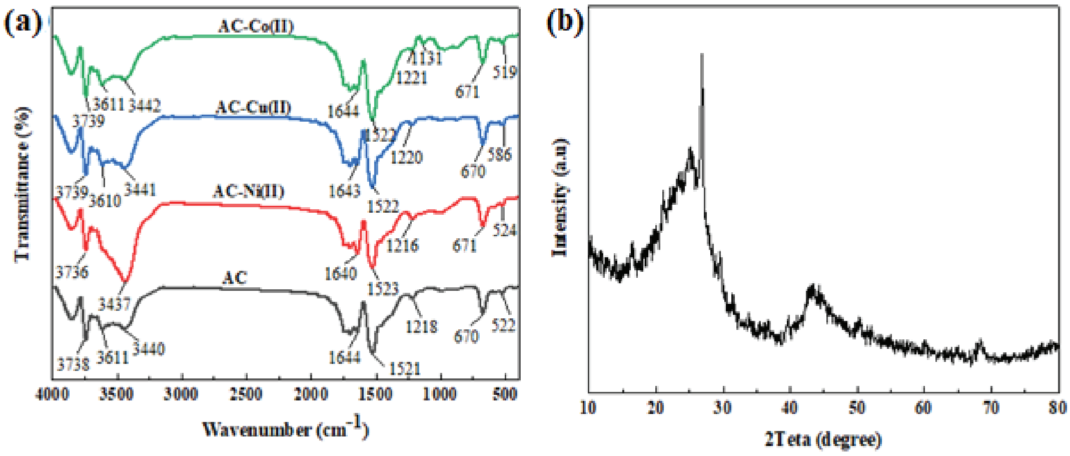

Fig. 2. a) FT-IR analysis b) XRD of activated carbon produced from worn tire.

Table 1
Properties of active carbon prepared from worn tire based on BET data

Surface area	Single point surface area at p/p°	29.61 m²/g
	BET surface area	32.39 m²/g
	Langmuir surface area	46.54 m²/g
	t-Plot external surface area	37.11 m²/g
Pore volume	Single point adsorption total pore volume of pores less than 703.576 Å diameter at p/p°	0.098 cm³/g
	t-Plot micropore volume	–0.003 cm³/g
	BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.25 cm³/g
	BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.25 cm³/g
Pore size	Adsorption average pore width (4 V/A by BET)	120.74 Å
	BJH adsorption average pore width (4 V/A)	300.91 Å
	BJH desorption average pore width (4 V/A)	281.45 Å

can penetrate into activated carbon pores. It is worth mentioning that the pores on the surface of activated carbon can cause transport and adsorption of metal ions from aqueous solution towards the adsorbent.

3.2. Initial pH

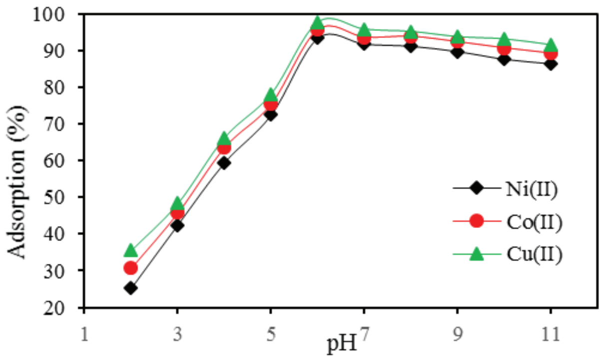

Fig. 3. The effect of pH on adsorption efficiency (temperature = 25°C, initial concentration of metal ions = 10 mg/l, contact time = 60 min and adsorbent dosage = 3 g/l).

Initial pH is a very significant and critical parameter in the adsorption process of metal ions from aqueous solutions. The effect of pH on the adsorption process of nickel, copper and cobalt cations performed in the pH range of 2–11, 25°C, the initial concentration of metal ions of 10 mg/l, 60 min contact time, 300 rpm mixing rate and 3 g/l adsorbent dosage. The results are illustrated in Fig. 3 proving that increasing initial pH from 2 to 6 increases the adsorption efficiency of nickel, cobalt and copper from 25.18%, 30.78% and 35.50% to 93.36%, 95.68% and 97.72%, respectively. At a pH value greater than 6, the adsorption efficiency decreased. Low adsorption efficiency at lower pH values can be dedicated to the high concentration of H^+ in aqueous solution; as this cation competes with metal cations to relocate on the surface of the adsorbent and as it has a positive charge, it causes a repulsive electrostatic force on other cations [25]. All these incidents decrease the efficiency of adsorption for metal cations. At higher pH values (pH > 6), the adsorption efficiency decreased again as the concentration of OH^- anions increased in the solution which makes a complex with other ions within the solution and makes sedimentation on the surface of the adsorbent. This reduces the contact of metal ions with the adsorbent surface and thus reduces the efficiency [26].

3.3. Effect of contact time and temperature

The effect of contact time on adsorption efficiency of nickel, cobalt and copper aqueous solutions using worn tire made activated carbon is shown in Fig. 4a. The results show that the adsorption process took place during two stages: the first stage is very rapid and the second one is a very slow rate. The first stage completed very fast up to 40 min of contact time and during this period the adsorption efficiency of nickel, cobalt and copper reached 93.25%, 95.46% and 97.58%, respectively. At the second one, the adsorption process was investigated up to 200 min and during this period the adsorption efficiency of nickel, cobalt and copper increased to 94.04%, 96.27% and 98.42%, respectively. At early contact times, the high speed of adsorption can be dedicated to frequent active sites and availability of these sites for metal cations to relocate. At later contact times (more than 40 min), the adsorption rate decreases due to saturation of active sites by metal ions [27] and reduction in the concentration of metal ions within the aqueous solution. Therefore, 40 min contact time was reported as the optimum time.

Temperature is another parameter with a very significant effect on the adsorption process [27]. Investigation of temperature effect on the adsorption process of metal ions was performed at the temperature ranges of 25–55°C and the results are shown in Fig. 4b. This figure confirms that the rise in temperature is associated with a decrease in adsorption, as the process is exothermic and no permanent chemical bond is formed during the process. Such condition can be due to numerous factors including the higher tendency of the adsorbed metal to detach from the adsorbent surface and releasing back to the aqueous solution [28] and providing required energy to break the bond between metal ions and active adsorbent sites. Accordingly, 25°C was selected as an optimum temperature for cobalt, nickel and copper adsorption by activated carbon produced from the worn tire. The adsorption efficiency of these metal ions at 25°C was determined as 93.25%, 95.46% and 97.58%, respectively.

3.4. Effect of adsorbent dosage

Adsorbent dosage is one of the effective parameters which is usually studied during adsorption, as it determines the adsorption capacity of the adsorbent at each concentration of metal ion [29]. Fig. 5 shows the effect of adsorbent dosage on the removal efficiency of nickel, cobalt and copper ions. Considering these results, as adsorbent dosage increased from 1 to 10 g/l, the adsorption efficiency of nickel, copper and cobalt increased from 73.23%, 79.66% and 75.38% up to 94.17%, 98.03% and 96.31%, respectively. Such an increase in efficiency is because of a higher number of active sites on the adsorbent surface. It should be reminded that increasing adsorbent dosage of more than 3 g/l, does not affect the adsorption process to a considerable extent. It proves that for a certain amount of adsorbents (optimum value), maximum adsorption occurs and after that adsorbed cations and free cations within the aqueous solution remain unchanged. This phenomenon can be justified by partial adsorbent accumulation at high concentrations and reduction in the active sites present in the adsorbent surface [15].

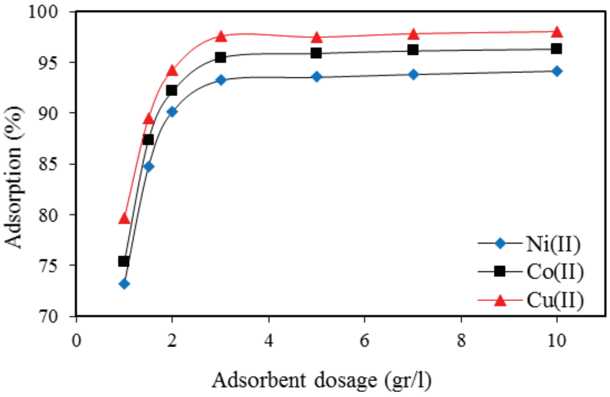

Fig. 5. Effect of adsorption dosage on removal efficiency (temperature = 25°C, initial concentration of metal ions = 10 mg/l, contact time = 40 min and mixing rate = 300 rpm).

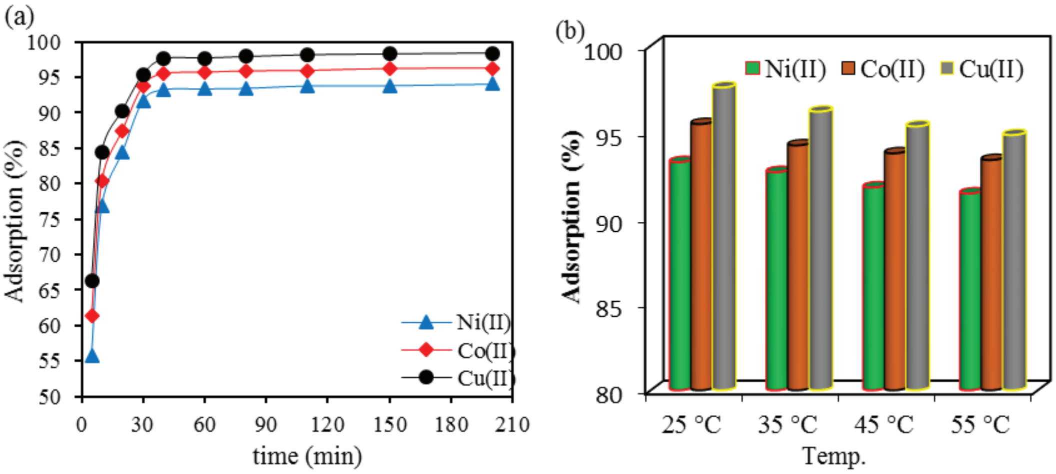

Fig. 4. Effect of a) contact time and b) temperature on cobalt, nickel and copper adsorption by activated carbon produced from worn tire.

3.5. Thermodynamic study

The thermodynamic parameters are important for describing the adsorption process and achieving an equilibrium state [30]. Thermodynamic parameters such as enthalpy, entropy and Gibbs free energy were studied in order to define if the process is endothermic or exothermic and/or if it is spontaneous or not. Gibbs free energy (ΔG°) was determined using the following equation [31,32]:

$$\Delta G^o = -RT\ln K_D \tag{3}$$

where R, T and K_D are the universal gas constant (8.314 J/mol K), the absolute temperature (K) and the equilibrium constant of the adsorption, respectively. The value of the adsorption equilibrium constant or K_D is defined as follows:

$$\mathrm{K}_D = \frac{\mathrm{C_A}}{\mathrm{C_S}} \tag{4}$$

where C_A and C_S are the amounts of adsorbed metal ion on the adsorbent surface at equilibrium time (mg/L) and residual metal ion within the solution at the equilibrium time, respectively.

Other thermodynamic parameters of enthalpy (ΔH°) and entropy (ΔS°) are calculated as follows:

$$\frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} = \ln K_D = \frac{-\Delta G^o}{RT} \tag{5}$$

The values of ΔH° and ΔS° are determined from the slope and intercept of Ln (K_D) vs. 1/T (Fig. 6). For ΔH° > 0 and ΔH° < 0, the adsorption process is endothermic and exothermic, respectively. Thermodynamic parameters for the adsorption of nickel, copper and cobalt ions using worn tire derived activated carbon are shown in Table 2. The value of Gibbs free energy at all temperatures and for each metal ion is a negative value showing that this adsorption process is desirable and spontaneous. Besides, Gibbs free energy reduced with increasing temperature confirming that the degree of spontaneously of the process decreases with increasing temperature. According to Fig. 6, the slope of the curve is negative (ΔH° < 0) and also, the value of ΔH° for nickel, copper and cobalt adsorption was obtained as –7.33, –10.52 and –21.15 KJ/mol, respectively. Negative values of enthalpy confirm that the interaction between the activated carbon and metal cations is exothermic. Similar results have been observed in previous studies [4,32].

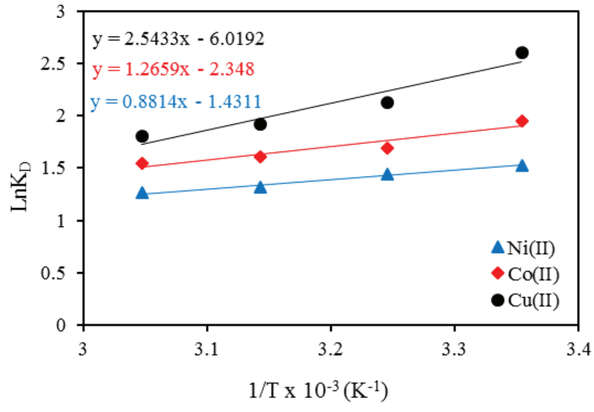

Fig. 6. Linear relationship between ln K_D versus 1/T in order to determine the thermodynamic parameters of nickel, copper and cobalt ions with activated carbon.

3.6. Equilibrium study

To explain the interaction between adsorbent and contaminants, adsorption isotherms are widely used and play an important role in the optimal use of adsorbents [4,31]. Commonly used equilibrium models are Langmuir and Freundlich models. Freundlich model is an empirical model which is utilized as a criterion describing the isothermal behavior of adsorbent in adsorption process of heavy metal ions in aqueous solutions. This model is applied to describe multi-layer adsorption on heterogeneous surfaces. The linear form of this model is as follows [33,34]:

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

In this equation, q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration of metal ions within the solution (mg/L), K_f and n the constants of Freundlich model showing the relationship between adsorption capacity and adsorption intensity which are determined as slope and intercept of lnq_e vs. lnC_e (Fig. 7-a). The value of 'n' shows the degree of deviation from the linear model. For $n = 1$, $n > 1$ and $n < 1$ the process is linear, physical and chemical, respectively [35].

The Langmuir isotherm model assumes that adsorption of metal ions occurs on a single and homogeneous layer of adsorbent and the number of active sites on the adsorbent is constant. This model expresses the information about the adsorption capacity as well as the equilibrium behaviour of the adsorption process [36]. The linear form of this model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{7}$$

Table 2
Constant values and thermodynamic parameters of adsorption process by worn tire activated carbon

Metal ions	ΔH° (KJ/mol)	ΔS° (J/molK)	ΔG° (KJ/mol)			
			298.15 K	308.15 K	318.15 K	328.15K
Ni(II)	–7.3279	–11.898	–3.7852	–3.6852	–3.4759	–3.4612
Co(II)	–10.524	–19.5212	–4.8266	–4.3363	–4.2626	–4.2187
Cu(II)	–21.1449	–50.0436	–6.4401	–5.4502	–5.0659	–4.9341

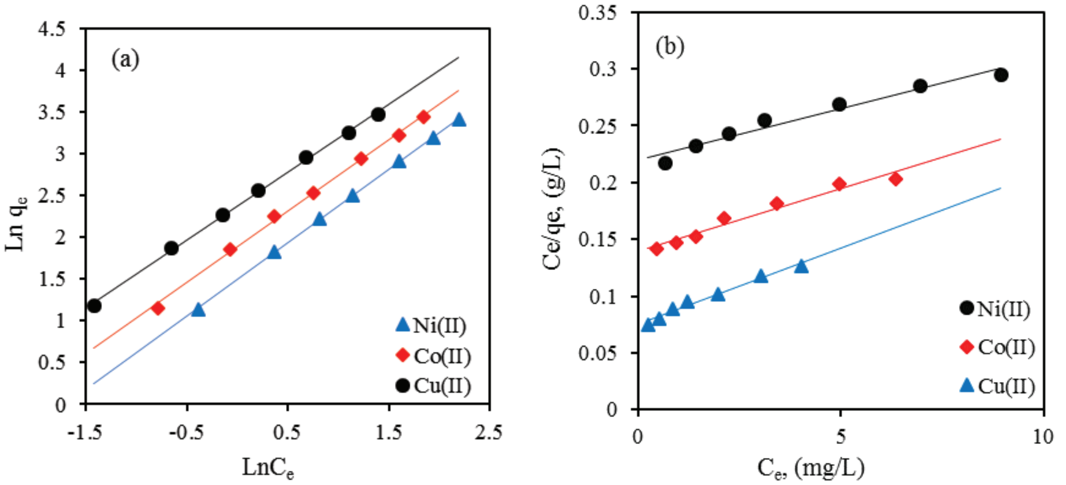

Fig. 7. Isotherm models of a) Freundlich and b) Langmuir for the adsorption of copper, nickel and cobalt ions using activated carbon produced from worn tire.

Table 3
Constants and parameters of Langmuir and Freundlich models for the adsorption of metal ions using activated carbon produced from worn tire

Models	Parameters	Ni(II)	Co(II)	Cu(II)
Langmuir	q_m (mg/g)	109.89	90.09	74.626
$C_e/q_e = C_e/q_m + 1/K_Lq_m$	K_L (L/mg)	0.0414	0.0797	0.1784
	R^2	0.9605	0.9632	0.976
	R_L	0.1945–0.7072	0.1114–0.5564	0.053–0.3591
Freundlich	n	1.1371	1.1732	1.235
$\ln q_e = \ln K_f + 1/n \ln C_e$	K_f (mg/g) (L/mg)$^{1/n}$	4.464	6.566	10.719
	R^2	0.9998	0.998	0.9983

In Eq. (7), q_m and K_L are the maximum adsorption capacity (mg/g) and the adsorption energy (L/g), respectively. These values are the constants of the Langmuir model which are calculated as slope and intercept of C_e/q_e versus C_e, respectively (Fig. 7-b). Adsorption intensity (R_L) is one of the most important parameters recounting the characteristics and feature of the Langmuir model. This value shows mode and how the adsorption isotherm model is. If $R_L > 1$, $R_L = 0$, $R_L = 1$ and $0 < R_L < 1$, the process is categorized as undesirable, irreversible, linear and desirable, respectively. The value of R_L is determined by the following equation [34]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

The parameters of Langmuir and Freundlich isotherm models extracted from Fig. 7 are reported in Table 3. The results revealed that the correlation coefficient (R^2) for the Freundlich model was higher than that of the Langmuir model showing that this model is better fitted with the experimental data and heterogeneous surfaces play important roles in ion removal process. The value of parameter '*n*' for Freundlich model was 1.14, 1.24 and 1.17 for nickel, copper and cobalt, respectively. These values of '*n*' describe that the adsorption process of metal ions are physical and desirable which these results are observed in previous studies [4,32]. Also, the adsorption energy by the Langmuir model was calculated 0.0414, 0.0797 and 0.1784 L/mg for Ni (II), Co (II) and Cu (II), respectively.

The maximum adsorption capacity of nickel, copper and cobalt was reported as 109.89 mg/g, 74.63 mg/g and 90.09 mg/g, respectively. In previous studies, Foroutan et al. obtained a maximum adsorption capacity of 13.73 and 13.996 mg/g using *padina* algae for Co(II) and Cu(II), respectively [30]. Also, a maximum adsorption capacity of Ni(II) ion using bentonite/magnetite was obtained 0.9808 mg/g by Ahmadi et al. [32]. By comparing these results with previous studies, it can be concluded that a very high adsorption capacity is obtained in this study. Different values of R_L at initial concentrations of 10–100 mg/L achieved in the range of 0.1945–0.7072 for nickel, 0.053–0.3591 for copper and 0.1114–0.5564 for cobalt. Such values affirm that the adsorption process of these cations with the mentioned adsorbent is suitable and desirable.

3.7. Kinetic study

Kinetic study of adsorption is of paramount importance as it provides valuable information about the reaction path and adsorption process control mechanism [37]. Pseudo first order and pseudo second-order models were applied to study the kinetic mechanism of adsorption from aqueous solutions and laboratory data were analysed using these kinetic models. The linear form of the pseudo first-order model is like below [38]:

$$Ln(q_e - q_t) = Lnq_e - k_1 t \tag{9}$$

where q_t and k_1 are the amounts of adsorbed ions per one gram of the adsorbent during the time t (mg/g) and adsorption constant (1/min). The constants and parameters of the pseudo first-order model are obtained by plotting "ln $(q_e - q_t)$" vs. 't' and the values of k_1 and $q_{e.cal}$ are the slope and intercept of the graph, respectively (Fig. 8a). The constants and parameters of the pseudo first-order model are reported in Table 4. The values of the correlation coefficient (R^2) for the adsorption process of nickel, cobalt and copper using activated carbon derived from worn tire were 0.7686, 0.8364 and 0.8481, respectively. It should be pointed out that the pseudo first-order model has no proper ability to describe the kinetic behavior of the process and the analysis of the given data. Because the maximum adsorption capacity calculated by the pseudo first-order model ($q_{e.cal}$) was less than maximum adsorption capacity measured from the experimental data ($q_{e.exp}$).

The pseudo second-order model is another kinetic model which has been used in order to examine the kinetic of adsorption. The linear form of this model is like below [39–41]:

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

where k_2 in g/mg min is the rate constant of the pseudo second-order kinetic model. The constants and parameters of the pseudo second-order kinetic model obtained by plotting t/q_t versus t (Fig. 8b). Also, the calculated parameters for the pseudo second-order model are reported in Table 4.

Calculated adsorption capacity using the pseudo second-order model for the adsorption of nickel, cobalt and copper was 3.17 mg/g, 3.25 mg/g and 3.31 mg/g, respectively. Calculated values were close to measured quantities attained from the experiments ($q_{e.exp}$). Therefore, it can be resolved that the pseudo second-order kinetic model has higher ability to describe the kinetic behavior of absorption for cobalt, nickel, and copper ions using the above-mentioned adsorbent in comparison with the pseudo first-order kinetic model. Furthermore, the correlation coefficient (R^2) of the pseudo second-order kinetic model was higher than that of the pseudo first-order model.

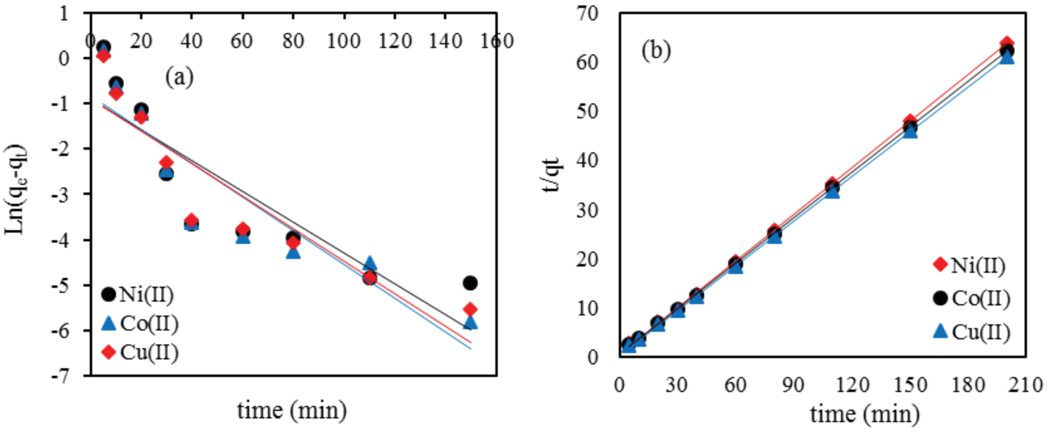

Fig. 8. Linear relationship between kinetic models a) pseudo first order b) pseudo second order model for the adsorption of nickel, cobalt and copper using activated carbon produced from worn tire.

Table 4
Kinetic parameters of copper, nickel and cobalt adsorption process using the activated carbon produced from worn tire

Models	Parameters	Ni^{+2}	Co^{+2}	Cu^{+2}
Pseudo-first-order:	k_1 (min^{-1})	0.034	0.0372	0.036
Ni: $y = -0.034x - 0.8963$	$q_{e(cal)}$ (mg/g)	0.408	0.4338	0.415
Co: $y = -0.0372x - 0.835$	R^2	0.7686	0.8364	0.8481
Cu: $y = -0.036x - 0.8794$				
Pseudo-second-order:	k_2 (g/mg min)	0.1603	0.1779	0.1947
Ni: $y = 0.3151x + 0.6195$	$q_{e(cal)}$ (mg/g)	3.173	3.245	3.312
Co: $y = 0.3081x + 0.5336$	R^2	0.9998	0.9999	0.9999
Cu: $y = 0.3019x + 0.4682$				
$q_{e(exp)}$ mg/g		3.134	3.209	3.28

4. Conclusions

The objective of this study was the use of worn tire as a low-cost source for the production of activated carbon through a chemical process. Besides, properties and ability of produced activated carbon in the removal of heavy metal ions of nickel, cobalt and copper from aqueous solutions were also inspected. The use of produced activated carbon by worn tire for removal of heavy metals is firstly employed. The results of BET analysis showed that the produced carbon has a specific surface area equal to 32.39 m^2/g which is within an acceptable range. For examining the adsorption of heavy metal ions, different parameters of initial pH, temperature, contact time and adsorbent dosage were investigated and the results showed that the maximum adsorption efficiency was obtained at pH of 6, adsorbent dose of 3 g/L, contact time of 40 min and temperature of 25°C which was 93.25, 95.46 and 97.58 for Ni (II), Co and Cu, respectively. A decrease in adsorption efficiency at higher temperatures showed that the process for the mentioned metal cations is exothermic. Isothermic models of Freundlich and Langmuir were selected to describe the adsorption behavior and the statistical results showed that Freundlich model can match data points better than the Langmuir model. Maximum adsorption capacity attained by Langmuir isotherm model was 74.63 mg/g, 90.09 mg/g and 109.89 mg/g for copper, cobalt and nickel cations, respectively. The kinetic behaviour of adsorption process was inspected using pseudo first-order and pseudo second-order models and the results showed that the pseudo second-order model can describe kinetic behaviour of metal ion adsorption better than the other one. The thermodynamic parameter of ΔH^o for the adsorption of nickel, copper and cobalt was reported as –7.33 KJ/mol, –10.52 KJ/mol and –21.15 KJ/mol, respectively. Negative values confirmed that the process was exothermic. The other thermodynamic parameter, Gibbs free energy, was negative for all three metal types showing that the process is spontaneous. Considering the experimental results as well as kinetic, equilibrium and thermodynamic behaviour of the process and also adsorption efficiency values revealed that the activated carbon produced from worn tire can be used as an effective and low-cost adsorbent for heavy metal cations removal.

Acknowledgment

The authors are grateful to the shiraz university and Islamic Azad University of Bushehr for supporting this research.

References

[1] A. Farghali, M. Bahgat, A.E. Allah, M. Khedr, Adsorption of Pb(II) ions from aqueous solutions using copper oxide nanostructures, Beni-Seuf Univ. J. Appl., 2 (2013) 61–71.

[2] H. Esmaeili, R. Foroutan, Investigation into ion exchange and adsorption methods for removing heavy metals from aqueous solutions, Int. J. Biol., Pharm. All. Sci., 4 (2015) 620–629.

[3] L. Shi, J. Du, Z. Chen, M. Megharaj, R. Naidu, Functional kaolinite supported Fe/Ni nanoparticles for simultaneous catalytic remediation of mixed contaminants (lead and nitrate) from wastewater, J. Colloid Interface Sci., 428 (2014) 302–307.

[4] F.S. Khoo, H. Esmaeili, Synthesis of CaO/Fe_3O_4 magnetic composite for the removal of Pb(II) and Co(II) from synthetic wastewater, J. Serb. Chem. Soc., 83 (2018) 237–249.

[5] T. Anirudhan, J. Deepa, J. Christa, Nanocellulose/nanobentonite composite anchored with multi-carboxyl functional groups as an adsorbent for the effective removal of Cobalt (II) from nuclear industry wastewater samples, J. Colloid Interface Sci., 467 (2016) 307–320.

[6] C. Borba, R. Guirardello, E. Silva, M. Veit, C. Tavares, Removal of nickel (II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves, Biochem. Eng. J., 30 (2006) 184–191.

[7] O.O. Ltaief, S. Siffert, S. Fourmentin, M. Benzina, Synthesis of Faujasite type zeolite from low grade Tunisian clay for the removal of heavy metals from aqueous waste by batch process: Kinetic and equilibrium study, C. R. Chim., 18 (2015) 1123–1133.

[8] R.R. Pawar, H.C. Bajaj, S.M. Lee, Activated bentonite as a low-cost adsorbent for the removal of Cu (II) and Pb (II) from aqueous solutions: Batch and column studies, J. Ind. Eng. Chem., 34 (2016) 213–223.

[9] G. Qiu, Q. Xie, H. Liu, T. Chen, J. Xie, H. Li, Removal of Cu (II) from aqueous solutions using dolomite–palygorskite clay: performance and mechanisms, Appl. Clay Sci., 118 (2015) 107–115.

[10] L.P. Lingamdinne, J.R. Koduru, H. Roh, Y.L. Choi, Y.Y. Chang, J.K. Yang, Adsorption removal of Co (II) from waste-water using graphene oxide, Hydrometallurgy, 165 (2016) 90–96.

[11] R. Kang, L. Qiu, L. Fang, R. Yu, Y. Chen, X. Lu, X. Luo, A novel magnetic and hydrophilic ion-imprinted polymer as a selective sorbent for the removal of cobalt ions from industrial wastewater, J. Environ. Chem. Eng., 4 (2016) 2268–2277.

[12] B.S. Zadeh, H. Esmaeili, R. Foroutan, Cadmium (II) removal from aqueous solution using microporous eggshell: Kinetic and equilibrium studies, Indones. J. Chem., 2018. Doi: 10.22146/ijc.28789.

[13] N. Gupta, A.K. Kushwaha, M. Chattopadhyaya, Adsorptive removal of Pb^{2+}, Co^{2+} and Ni^{2+} by hydroxyapatite/chitosan composite from aqueous solution, J. Taiwan. Inst. Chem. Eng., 43 (2012) 125–131.

[14] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: a comprehensive review, Desalination, 287 (2012) 2–18.

[15] R. Foroutan, F.S. Khoo, B. Ramavandi, S. Abbasi, Heavy metals removal from synthetic and shipyard wastewater using Phoenix dactylifera activated carbon, Desal. Water Treat., 82 (2017) 146–156.

[16] M. Hossain, H. Ngo, W. Guo, L. Nghiem, F. Hai, S. Vigneswaran, T. Nguyen, Competitive adsorption of metals on cabbage waste from multi-metal solutions, Bioresour. Technol., 160 (2014) 79–88.

[17] G.P. Jin, X.H. Zhu, C.Y. Li, Y. Fu, J.X. Guan, X.P. Wu, Tetraoxalyl ethylenediamine melamine resin functionalized coconut active charcoal for adsorptive removal of Ni (II), Pb (II) and Cd (II) from their aqueous solution, J. Environ. Chem. Eng., 1 (2013) 736–745.

[18] C.S. Yuan, H.Y. Lin, C.H. Wu, M.H. Liu, C.H. Hung, Preparation of sulfurized powdered activated carbon from waste tires using an innovative compositive impregnation process, J. Air Waste Manag. Assoc., 54 (2004) 862–870.

[19] D.C. Ko, E.L. Mui, K.S. Lau, G. McKay, Production of activated carbons from waste tire–process design and economical analysis, Waste Manage., 24 (2004) 875–888.

[20] M.M. Rao, D. Ramana, K. Seshaiah, M. Wang, S.C. Chien, Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls, J. Hazard. Mater., 166 (2009) 1006–1013.

[21] T.A. Saleh, K.R. Alhooshani, M.S. Abdelbassit, Evaluation of AC/ZnO composite for sorption of dichloromethane, trichloromethane and carbon tetrachloride: kinetics and isotherms, J. Taiwan Inst. Chem. Eng., 55 (2015) 159–169.

[22] V.K. Gupta, A. Nayak, S. Agarwal, M. Chaudhary, I. Tyagi, Removal of Ni (II) ions from water using scrap tire, J. Mol. Liq., 190 (2014) 215–222.

[23] M. Karmacharya, V.K. Gupta, I. Tyagi, S. Agarwal, V. Jha, Removal of As (III) and As (V) using rubber tire derived activated carbon modified with alumina composite, J. Mol. Liq., 216 (2016) 836–844.

[24] S. Yao, J. Zhang, D. Shen, R. Xiao, S. Gu, M. Zhao, J. Liang, Removal of Pb (II) from water by the activated carbon modified by nitric acid under microwave heating, J. Colloid Interface Sci., 463 (2016) 118–127.

[25] J. Kong, Q. Yue, S. Sun, B. Gao, Y. Kan, Q. Li, Y. Wang, Adsorption of Pb (II) from aqueous solution using keratin waste–hide waste: equilibrium, kinetic and thermodynamic modeling studies, Chem. Eng. J., 241 (2014) 393–400.

[26] S. Venkateswarlu, S.H. Kumar, N. Jyothi, Rapid removal of Ni (II) from aqueous solution using 3-Mercaptopropionic acid functionalized bio magnetite nanoparticles, Water Resour. Ind., 12 (2015) 1–7.

[27] D. Gusain, V. Srivastava, Y.C. Sharma, Kinetic and thermodynamic studies on the removal of Cu (II) ions from aqueous solutions by adsorption on modified sand, J. Ind. Eng. Chem., 20 (2014) 841–847.

[28] U. Guyo, J. Mhonyera, M. Moyo, Pb (II) adsorption from aqueous solutions by raw and treated biomass of maize stover–a comparative study, Process Saf. Environ. Prot., 93 (2015) 192–200.

[29] R. Foroutan, H. Esmaeili, M. Abbasi, M. Rezakazemi, M. Mesbah, Adsorption behavior of Cu (II) and Co (II) using chemically modified marine algae, Environ. Technol., 39 (2018) 2792–2800.

[30] J. Romero-González, J.R. Peralta-Videa, E. Rodríguez, M. Delgado, J.L. Gardea-Torresdey, Potential of Agave lechuguilla biomass for Cr (III) removal from aqueous solutions: Thermodynamic studies, Bioresour. Technol., 97 (2006) 178–182.

[31] S. Hashemian, M. Salimi, Nano composite a potential low cost adsorbent for removal of cyanine acid, Chem. Eng. J., 188 (2012) 57–63.

[32] F. Ahmadi, H. Esmaeili, Chemically modified bentonite/Fe_3O_4 nanocomposite for Pb(II), Cd(II), and Ni(II) removal from synthetic wastewater, Desal. Water Treat., 110 (2018) 154–167.

[33] B. Kizilkaya, A.A. Tekinay, Y. Dilgin, Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones, Desalination, 264 (2010) 37–47.

[34] S.M. Mousavi, S.A. Hashemi, H. Esmaeili, A.M. Amani, F. Mojoud, Synthesis of Fe_3O_4 nanoparticles modified by oak shell for treatment of wastewater containing Ni(II), Acta Chim. Slov., 65 (2018) 750–756.

[35] A.M. Awwad, N.M. Salem, Kinetics and thermodynamics of Cd (II) biosorption onto loquat (Eriobotrya japonica) leaves, J. Saudi Chem. Soc., 18 (2014) 486–493.

[36] S. Rangabhashiyam, N. Selvaraju, Adsorptive remediation of hexavalent chromium from synthetic wastewater by a natural and $ZnCl_2$ activated Sterculia guttata shell, J. Mol. Liq., 207 (2015) 39–49.

[37] X. Xu, B. Gao, Q. Yue, Q. Li, Y. Wang, Nitrate adsorption by multiple biomaterial based resins: Application of pilot-scale and lab-scale products, Chem. Eng. J., 234 (2013) 397–405.

[38] R. Foroutan, R. Mohammadi, B. Ramavandi, Treatment of chromium-laden aqueous solution using $CaCl_2$-modified Sargassum oligocystum biomass: Characteristics, equilibrium, kinetic, and thermodynamic studies, Korean J. Chem. Eng., 35 (2018) 234–245.

[39] A. Teimouri, H. Esmaeili, R. Foroutan, B. Ramavandi, Adsorptive performance of calcined Cardita bicolor for attenuating Hg(II) and As(III) from synthetic and real wastewaters, Korean J. Chem. Eng., 35 (2018) 479–488.

[40] F.S. Sarvestani, H. Esmaeili, B. Ramavandi, Modification of Sargassum angustifolium by molybdate during a facile cultivation for high-rate phosphate removal from wastewater: structural characterization and adsorptive behavior, 3 Biotech, 6 (2016) 251.

[41] R. Foroutan, H. Esmaeili, S.M. Derakhshandeh Rishehri, F. Sadeghzadeh, S.R. Mirahmadi, M. Kosarifard, B. Ramavandi, Zinc, nickel, and cobalt ions removal from aqueous solution and plating plant wastewater by modified *Aspergillus flavus* biomass: A data set, Data Brief., 12 (2017) 485–492.