Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21523

92 (2017) 196–204
October

The effect of modified zeolite, activated carbon and peat with cationic surfactant and sodium hydroxide on removing anions from irrigation saline waters

M. Ghasemi*, J. Abedi Koupai, M. Heidarpour

Water Engineering Department, College of Agriculture, Isfahan University of Technology, Isfahan, Iran, Tel./Fax: +98 9134550160; email: ghasemi1860@yahoo.com (M. Ghasemi), Tel. +98 3133913432; email: koupai@cc.iut.ac.ir (J. Abedi Koupai), Tel. +98 3133913436; email: heidar@cc.iut.ac.ir (M. Heidarpour)

Received 4 June 2017; Accepted 4 October 2017

ABSTRACT

The high salinity of irrigation water is harmful for plants and soil; therefore, finding low-cost methods to reducing salinity ions of irrigation water is inevitable. The aim of this study was to modify zeolite, peat and activated carbon produced from pine cone trees by using a cationic surfactant of hexadecyltrimethylammonium bromide (HDTMABr) and sodium hydroxide (NaOH) to reduce chloride (Cl^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) from saline irrigation waters. The characteristics of adsorbents were determined by X-ray diffraction, Fourier transform infrared spectroscopy and Brunauer–Emmett–Teller. Adsorption experiments were conducted in a batch system, and the effects of contact time, the initial concentration of anions, adsorption kinetic and adsorption isotherms were evaluated. The adsorbents adsorbed some anions which were between 11.05 and 143.23 mg/g; among the absorbents, the maximum anions adsorption was related to modified peat, such that its adsorption capacities in waters with the electrical conductivity of 5.58, 10.41 and 20.4 dS/m were 18.4, 54.84 and 143.23 mg/g, respectively. In all salinity levels and for all absorbents, the adsorption percentage of HCO_3^- ion (49%–82.4%) was greater than those of Cl^- (3.8%–20.8%) and SO_4^{2-} (6.4%–46.6%). Changes in pH after adsorption for all salinity levels were between 0.3 and 0.7. For all adsorbents, Freundlich isotherm showed the best fit with the experimental data. Also, the pseudo-second-order kinetic model was found to be the best adsorption kinetic model.

Keywords: Zeolite; Activated carbon; Peat; Cationic surfactant; Anion removal; Irrigation saline waters

1. Introduction

Due to limited water resources in arid and semi-arid areas, the use of saline water resources is very important and finding new methods to reduce the salinity of saline waters is essential. Water salinity is mainly due to the presence of anions and cations including Cl^-, SO_4^{2-}, HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, and, rarely, NO_3^- or K^+. Salinity of the irrigation water adversely affects plant growth, such that a large amount of bicarbonate in the irrigation water causes the sedimentation of calcium and magnesium, the increase of the sodium adsorption ratio, root growth reduction, and the decrease of the absorption of some elements by the plant. Chloride is toxic to plants when it is in high concentrations in irrigation water, slowing their growth [1]. However, a very high amount of salinity ions in irrigation water increases the osmotic pressure and adversely affects water uptake by the roots. Various methods have been applied to reduce salt ions from the aqueous phase, including electrodialysis, reverse osmosis, evaporation and ion-exchange. Most of these methods are costly and consume a lot of energy; therefore, developing a new method to reduce the irrigation water salinity is inevitable [2]. One solution to this problem is using low-cost natural adsorbents such as zeolite, peat moss and activated carbon. Because saline water causes serious problems in the environment, several researches have been conducted on the removal of anions and cations from saline water resources.

---

* Corresponding author.

Ghorbani et al. [2] evaluated the impact of some natural adsorbents on some physical and chemical properties of the aqueous salt solution. They found that the highest adsorption of Ca^+ (30.5%), Cl^- (20%) and Mg^{2+} (17.5%) ions and the maximum reduction of water hardness (23%) were achieved by passing saline water throughout a mixture of sand plus rice shell filters. Rostamian et al. [3], on the other hand, used the biochar produced from rice paddy in irrigation water desalination, concluding that the pyrolysis temperature of 600°C led to the highest adsorption of saline ions. Aghakhani et al. [4] also applied some combined adsorbents to remove salinity from the drainage water.

Activated carbon is a highly porous material produced from the burning of materials containing carbon in the absence of oxygen. Activated carbon is usually produced from materials such as coal, wood, coconut shell, walnut shell, pine cones and other plant residues [3,5]. Activated carbon is widely used to remove impurities from water. Peat moss is a cheap and abundant material that has many pores and is widely used in the adsorption of heavy metals from aqueous solutions [6]. Peat moss, which has a high cation exchange capacity, is found in countries such as Iran, Finland, Brazil and the UK [6,7]. Zeolites are hydrated aluminosilicate minerals which have a large internal and external surface area with the net negative surface charge. Among several types of zeolite, clinoptilolite is one of the most important ones. Natural clinoptilolite is the most widely used type due to its high adsorption rate and cation exchange [8,9]. Zeolites and peat moss are widely used to remove cationic heavy metals from aqueous solutions, but their external surface charge can be changed by a cationic surfactant to adsorb anions [9,10]. Several authors have reported the adsorption of heavy metals on the surfactant modified zeolite, activated carbon and peat moss [11–13]. For example, the surface of natural clinoptilolite can be modified with a cationic surfactant such as HDTMABr. Under suitable conditions, the enhanced loading of HDTMABr on natural clinoptilolite can form bilayers (admicelle) that have the capability of adsorbing arsenic molecules within themselves, by hydrophobic or ionic interactions [14].

The aim of this study was modifying the natural Iranian zeolite, peat and activated carbon by the cationic surfactant of HDTMABr and NaOH to adsorb anions including Cl^-, SO_4^{2-} and HCO_3^- from saline irrigation waters. The kinetics and adsorption isotherms were also investigated using batch equilibrium techniques.

2. Materials and methods

2.1. Materials

All chemicals, including sodium hydroxide and HDTMABr, were purchased from Merck Co. (Germany). Natural zeolite was obtained from Afrand Tooska Co. (Iran). Peat moss was purchased from Novarbo Oy Co. (Finland). Saline water samples were obtained from Roodasht drains (Esfahan, Iran). Saline water properties have been illustrated in Table 1.

2.2. Activated carbon production

In order to produce the activated carbon, initially pine cones were collected and washed several times with distilled water to remove dust and impurities; then they were dried in an oven for 24 h at 80°C. Next, the pine cones were crushed by a mechanical mill and separated to a particle size of 105–500 μm by using US standard sieves (Nos. 35 and 140). 20 g of particles was placed within a fixed bed reactor and the reactor temperature was increased to 400°C at a rate of 10°C/min under nitrogen gas; this was kept at this temperature for 1 h. In the next step, the reactor temperature was increased from 400°C to 850°C at a rate of 10°C/min, and activation was carried out for 2 h at this temperature under water vapor. Finally, the reactor temperature was reduced slowly to reach room temperature under nitrogen gas. Activated carbon was washed several times with distilled water and dried in an oven [3].

2.3. Modification of the sorbent

Zeolites were initially crushed and sieved to a particle size of 105–500 μm. Then, the materials were washed several times with distilled water to remove impurities and dried in an oven at 105°C for 24 h. Adsorbents were modified in two steps by the cationic surfactant and NaOH. For this purpose, in the first step, 50 g zeolite, 10 g peat and 10 g activated carbon were separately left in contact with 500 mL of 50 mmol/L HDTMABr for 24 h, at room temperature (298 K) and 150 rpm. Then, the solids were washed by distilled water for 10 times and dried in an oven at 80°C for 24 h. In the second step, the adsorbents prepared in the previous step were left in contact with 500 mL of 1 mol/L NaOH and the mixtures were shaken for 4 h, at room temperature. Then, the adsorbents were separated from the solutions and washed with distilled water for 10 times. Finally, the solids were dried in an oven at 80°C for 24 h. Modified zeolite, modified peat and modified activated carbon are represented by symbols of MZ, MP and MAC, respectively.

2.4. Analyses

X-ray diffraction (XRD) patterns of the adsorbents were determined with a Philips X'PERT MPD diffractometer to determine the crystalline phases. Fourier transform infrared spectroscopy (FTIR) analysis was done to determine the

Table 1
Some properties of saline water used for tests

EC (dS/m)	pH	Cl^- (mg/L)	HCO_3^-(mg/L)	SO_4^{2-} (mg/L)	Total anions (mg/L)	TDS (mg/L)
20.4	8.2	5,918.0	671.1	2,469.8	9,058.9	13,869.6
10.41	8.2	2,718.0	366.1	1,114.6	4,198.6	6,415.5
5.58	8.2	1,418.0	207.4	508.9	2,134.3	3,253.8

effective functional groups in adsorption. The FTIR spectra of the adsorbents were obtained by using Bruker Tensor 27. Adsorbents surface areas were determined with the Brunauer–Emmett–Teller theory. In order to determine the zero point charge (pH_{pzc}), 0.1 g of each adsorbent was mixed with 50 mL of potassium nitrate (0.1 mol/L) and the mixtures were shaken in a mechanical shaker (Dragon-SK-330-Pro) for 24 h, at the room temperature (25°C ± 2°C). The initial pH of the solutions was adjusted between 2 and 12 by HCl (0.1 mol/L) and NaOH (0.1 mol/L). By drawing the difference between the initial and final pH ($pH_i - pH_f$) vs. the initial pH (pH_i), pH_{pzc} was determined [15].

2.5. Adsorption experiments

In order to evaluate the adsorption of Cl^-, SO_4^{2-} and HCO_3^- from saline water, batch experiments were used. Ion concentrations of Cl^-, SO_4^{2-} and HCO_3^- in different electrical conductivities (ECs) of 5.58, 10.41 and 20.4 dS/m are presented in Table 1. From the perspective of irrigation, the EC of brackish water, saline water and more saline water is about 5, 10 and 20 dS/m, respectively [16]. So salinity levels of 5.58, 10.41 and 20.4 dS/m were selected to evaluate the effect of the salt concentration on the anions absorption. The salinity of Roodasht drains water was about 30 dS/m. In order to provide water with specific salinities, certain volumes of distilled water were added to saline water until the salinity reached the desired level. 1 g adsorbents of MZ, MP and MAC were added to 50 mL saline water, and the mixtures were then agitated in a mechanical shaker (Dragon-SK-330-Pro) for 4 h, at room temperature (298 K). Then, the adsorbents were separated from the solutions using 5B filter papers. The EC, pH, Cl^- concentration, SO_4^{2-} concentration and HCO_3^- concentration were determined before and after absorption using the standard analytical procedures. Titration method was used to measure Cl^- and HCO_3^- ions, and the turbidimetric method was employed to measure SO_4^{2-} ions [17]. Kinetic experiments were carried out at the temperature of 298 K, water EC of 20.4 dS/m, the pH of 8.2; this was done for a fixed adsorbent amount of 1 g/50 mL and the agitation rate of 150 rpm, which was withdrawn after 15, 30, 45, 60, 75, 90, 120, 180 and 240 min. Isotherm tests were conducted at the temperature of 298 K, water EC of 5.58, 8, 10.41, 15 and 20.4 dS/m, the pH of 8.2; this was done for a fixed adsorbent amount of 1 g/50 mL and the agitation rate of 150 rpm. In isotherm tests, the concentration of anions (mg/L) in saline water samples was as follows: Cl^- 1,418–5,918 mg/L, SO_4^{2-} 508.9–2,469.8 mg/L and HCO_3^- 207.4–671.1 mg/L. All the experiments were conducted in triplicate, and the mean values were used for data analysis. The removal efficiency (R%), and the amounts of Cl^-, SO_4^{2-} and HCO_3^- adsorbed onto the modified adsorbents per unit mass of the sorbent at equilibrium (q_e, mg/g) at time t (q_t, mg/g) were determined using the following equations [18,19]:

$$R(\%) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{\left(C_0 - C_e\right)V}{W} \tag{2}$$

$$q_t = \frac{\left(C_0 - C_t\right)V}{W} \tag{3}$$

where C_0 and C_e (mg/L) are the initial and equilibrium anions concentrations in the solution, respectively; and C_t (mg/L) is the residual concentration at the time t. Also, V is the volume of the solution (L), and W is the used mass of the adsorbent (g).

2.6. Kinetic and isotherm models

The anion adsorption kinetic data were correlated with the kinetic models:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \quad \text{(pseudo-firtst-order kinetic model)} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{(pseudo-second-order kinetic model)} \tag{5}$$

$$\frac{q_t}{q_e} = k.t^{0.5} + C \quad \text{(intra-particle diffusion kinetic model)} \tag{6}$$

where k_1 (min^{-1}) and k_2 (g/mg min) are the adsorption rate constants, C is the intercept, and k is the intra-particle diffusion rate constant (mg/g $min^{1/2}$) [20,21].

Three adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms, are widely used. In the Langmuir isotherm model, it is assumed that the adsorption is monolayer, and the Freundlich isotherm explains the heterogeneous surface energies by multilayer adsorption. The linear forms of these isotherms can be represented by the following equations [22,23]:

$$\frac{1}{q_e} = \frac{1}{K_L.q_{\max}}.\frac{1}{C_e} + \frac{1}{q_{\max}} \quad \text{(Langmuir adsorption model)} \tag{7}$$

$$\log(q_e) = \log K_F + \frac{1}{n}\log(C_e) \quad \text{(Freundlich adsorption model)} \tag{8}$$

$$q_e = \frac{RT}{b_T}\ln\left(A_T\right) + \frac{RT}{b_T}\ln(C_e) \quad \text{(Temkin adsorption model)} \tag{9}$$

where K_L is the constant related to the energy or the net enthalpy of adsorption, $q_{\max}$ (mg/g) is the maximum adsorption capacity for forming the single layer, K_F is an indicator of the adsorption capacity, $1/n$ is a measure of the intensity of adsorption, A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is the universal gas constant (8.314 J/mol/K) and T is the temperature (298 K).

3. Results and discussion

3.1. Adsorbents characteristics

Physical and chemical properties of the adsorbents are shown in Table 2. Among the adsorbents, MP and MAC had the highest cation exchange capacity (CEC) and specific area, respectively. XRD pattern of the adsorbents is shown in Fig. 1 in two cases of before and after modifications. The absence of clear peaks in the XRD patterns of peat and activated carbon showed that they were amorphous materials. According

Table 2
Physical and chemical properties of the adsorbents

Parameter	MZ	MP	MAC
Particle size (mm)	0.1–0.5	0.1–0.5	0.1–0.5
Specific weight (g/cm^3)	0.87	0.16	0.41
EC (dS/m) in water	0.13	0.11	0.06
pH$_{pzc}$	7.43	6.83	7.75
CEC (meq/g)	1.48	1.68	1.42
Specific area (m^2/g)	9.09	26.2	64.65

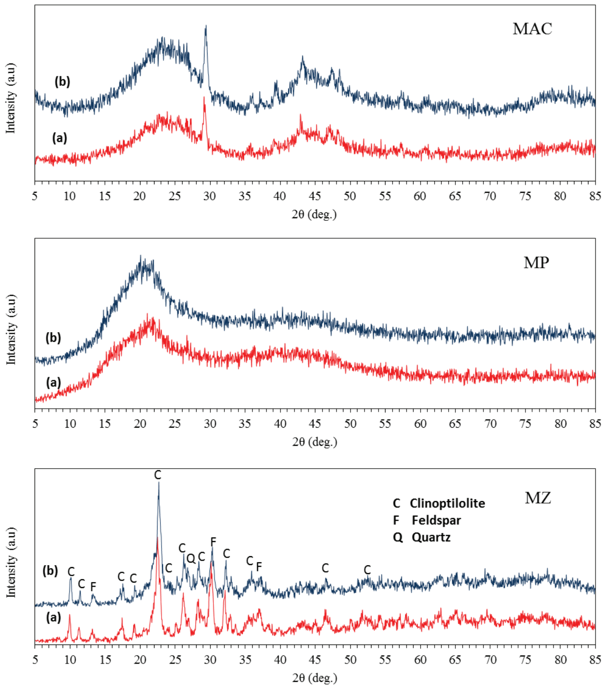

Fig. 1. XRD of adsorbents (a) before modification and (b) after modification.

to diffraction peaks, zeolite sample contained clinoptilolite (82.76%), feldspars (16.09%), quartz (0.56%), goethite (0.28%) and other minerals (<1%). Based on Fig. 1, after the modification of adsorbents, the sharpness of the peaks and the negligible variation of their positions suggested a high crystallinity degree and the structural stability of the materials. FTIR analysis was done to determine the effective functional groups in adsorbing anions. FTIR spectra of the adsorbents before modification, and before and after adsorptions are illustrated in Fig. 2. According to Fig. 2 MAC, the observed peak at 3,443 cm^{-1} corresponded to the presence of H$^+$ or OH$^-$ in alcohols, phenols or carboxylic acids [3,24]. The peaks at 2,922, 1,630 and 1,437 cm^{-1} were related to the stretching vibration bonding of C–H, C=C vibrating and CH$_3$ bending, respectively [25]. After modification, these peaks reached 3,445, 2,922, 1,630 and 1,435 cm^{-1}, respectively; after the adsorption test, they reached 3,449, 2,930, 1,628 and 1,439 cm^{-1}, respectively. According to Fig. 2 MP, the peaks at 3,424, 2,920, 2,581, 1,684, 1,630, 1,458 and 1,018 cm^{-1} corresponded to H$^+$ or OH$^-$ group, C–H stretching bonded, CH$_2$ or CH$_3$ stretching bonded, C=O stretching bonding of carboxylic acids, C=O stretching bonding of rotational and non-rotational combinations, C–H and C–O, respectively [21,26,27]. After the modification of peat, these peaks reached 3,424, 2,918, 2,581, 1,684, 1,630, 1,458 and 1,018 cm^{-1} respectively; after adsorption test of anions, they reached 3,432, 2,928, 2,576, 1,682, 1,632, 1,458 and 1,018 cm^{-1}, respectively. Based on Fig. 2 MZ, the observed peaks at 3,433, 1,626, 1,045, 789, 1,630, 604 and 465 cm^{-1} corresponded to symmetric stretching vibration of OH$^-$, flexural vibration of water molecules, asymmetric stretching vibration of Al–O, T–O and Si–O, T–O internal vibration, O–T–O bonded and TO4 internal bonded, respectively [28]. The peaks reached after the modification of zeolite were 3,431, 1,628, 1,045, 789, 1,630, 604 and 645 cm^{-1}, respectively; and after the adsorption experiment they were 3,441, 1,634, 1,049, 789, 1,626, 604 and 645 cm^{-1}, respectively.

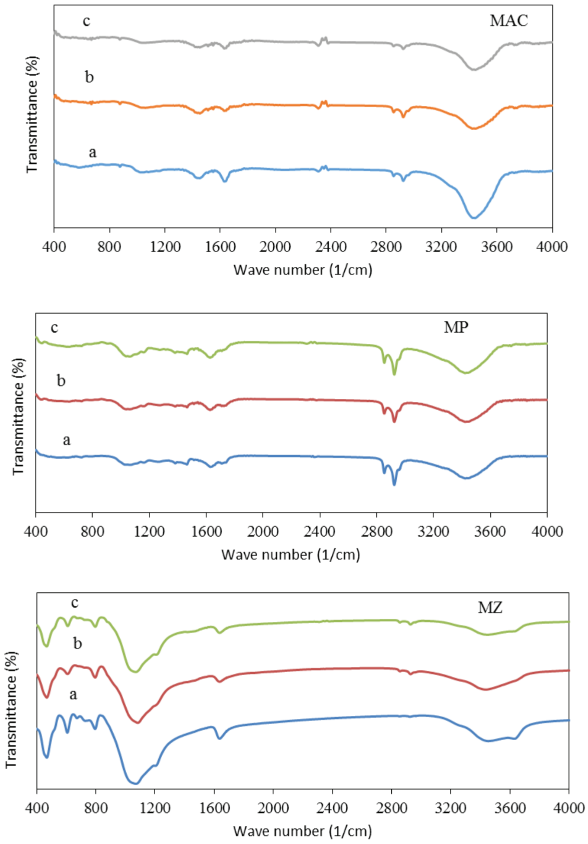

Fig. 2. FTIR of adsorbents (a) before modification, (b) before adsorption and (c) after adsorption.

3.2. The effect of anion concentrations on the adsorption rate

Figs. 3 and 4 show the adsorption rate and the adsorption percentage of Cl$^-$, SO$_4^{2-}$, HCO$_3^-$ and total anions on the basis of using 1 g adsorbent in 50 cc of saline water with the EC of 5.58, 10.4 and 20.41 dS/m. According to Fig. 3(a), in the EC of 20.4 dS/m, Cl$^-$ adsorption onto MAC, MP and MZ adsorbent was 54.6, 61.5 and 57.6 mg/g, respectively. As shown in Fig. 4(a), with the EC of 20.4 dS/m, the adsorption percentage of Cl$^-$ onto MAC, MP and MZ adsorbent was 18.5%,

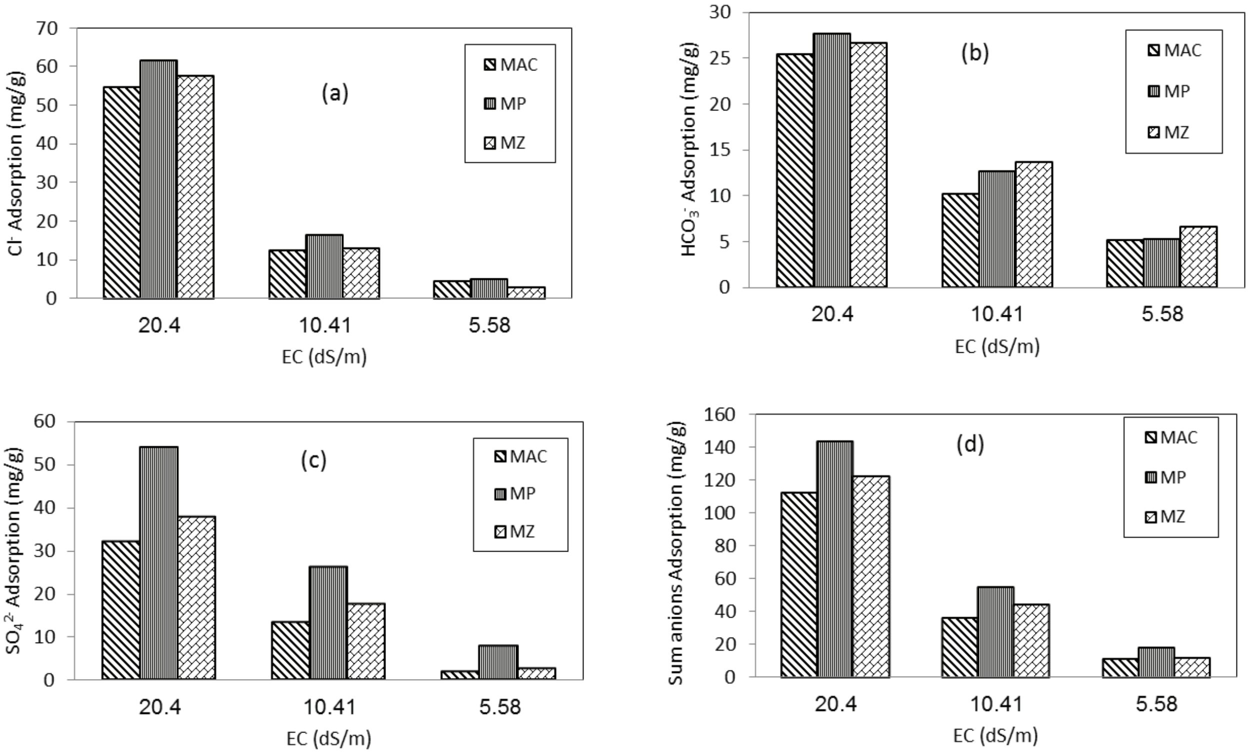

Fig. 3. Adsorption of (a) Cl$^-$, (b) HCO$_3^-$, (c) SO$_4^{2-}$ and (d) sum anions on adsorbents. Adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

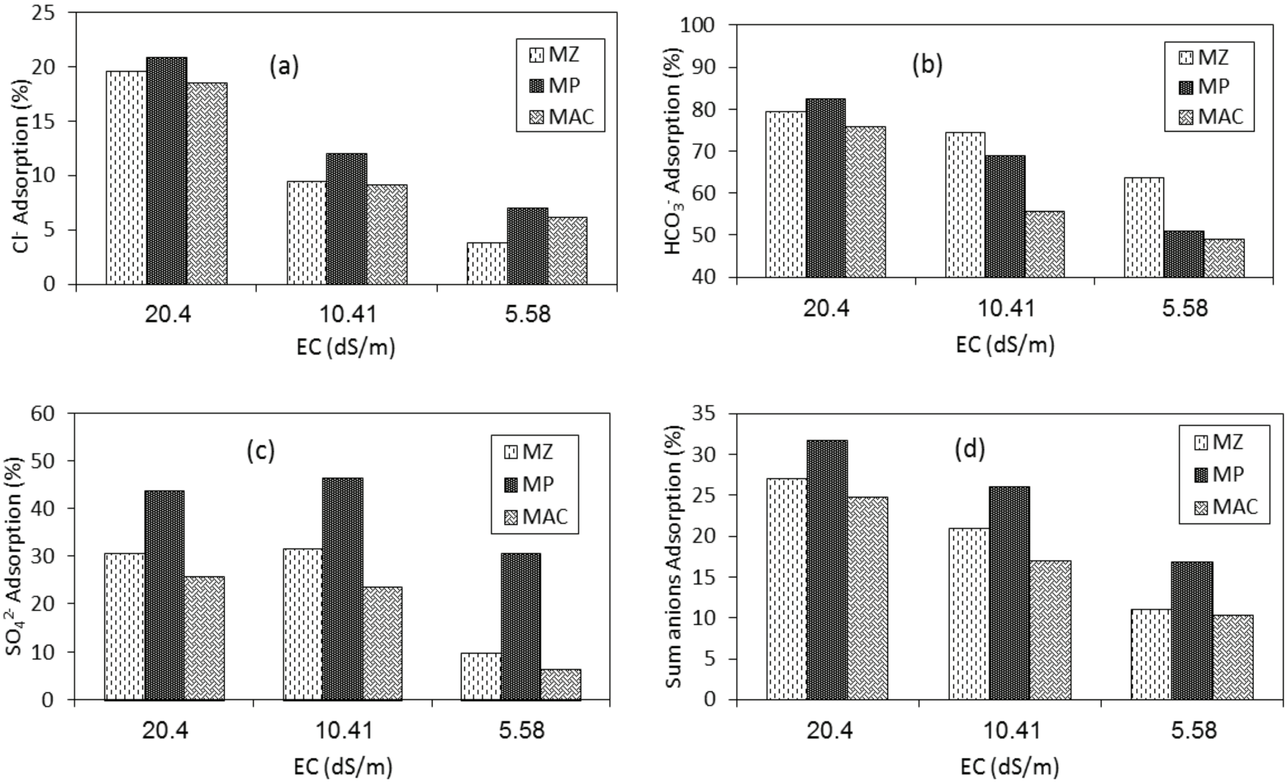

Fig. 4. Adsorption percentage of (a) Cl$^-$, (b) HCO$_3^-$, (c) SO$_4^{2-}$ and (d) sum anions on adsorbents. Adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

20.8% and 19.5%, respectively. By reducing the water salinity from 20.4 to 10.41 dS/m, the adsorption of Cl^- for these adsorbents was decreased to 12.3, 16.2 and 12.8 mg/g, respectively. Fig. 3(a) shows that the lowest rate of the adsorption of Cl^- happened in the EC of 5.58 dS/m. Fig. 3(b) shows that at the EC of 20.4 dS/m, the maximum adsorbed HCO_3^- was 27.6 mg/g, which was related to MP adsorbent, but in the EC of 10.41 and 5.58 dS/m, the MZ adsorbent absorbed more bicarbonate, as compared with the MAC and MP adsorbent. As shown in Fig. 4(b), the maximum HCO_3^- adsorption percentage at the EC of 5.58 and 10.4 dS/m was related to MZ (63.7% and 74.4%), whereas at the EC of 20.4 dS/m, the maximum HCO_3^- adsorption percentage was related to MP (82.4%). According to Fig. 3(c), at the EC of 5.58, 10.41 and 20.4 dS/m, the maximum adsorbed SO_4^{2-} was 7.8, 26 and 54 mg/g, respectively, which was related to MP. Anions adsorption capacity, as shown in Fig. 4(d), at all salinity levels of MP and MAC adsorbents, had the highest and lowest adsorption, respectively. Based on Fig. 3(d), at the EC of 20.4 dS/m, the anions adsorption capacity of MAC, MP and MZ adsorbents was 112.2, 143.2 and 122.1mg/g, respectively. It seemed with increasing the salinity levels, anions were more accessible, and absorbents could adsorb more. Comparison of the anions adsorption showed that the MP adsorbent absorbed more anions at all levels of salinity, as compared with other adsorbents, and the activated carbon also absorbed the lowest amount of anions. In different salinity levels, the water sample of Cl^- was about 6.8–8.8 times of HCO_3^-, while the ratio of the adsorption of Cl^- to HCO_3^- for different adsorbents and salinity levels was between 0.4 and 2.23. Comparison of Cl^- adsorption and HCO_3^- adsorption showed that with decreasing the salinity level, the amount of HCO_3^- adsorption was increased, as compared with Cl^- adsorption. Figs. 3 and 4 show that although the value of HCO_3^- ions in the tested water was less than those of other ions, its adsorption percentage was higher than that of SO_4^{2-} and Cl^- ions in all treatments. From the results, it could be concluded for all treatments, adsorption priority was $HCO_3^- > SO_4^{2-} > Cl^-$. Aghakhani et al. [4] concluded that in the adsorption of salinity ions onto some adsorbents, bicarbonate adsorption has been the first priority.

3.3. Changes in the pH and adsorption mechanism

A general model representing the modification of adsorbents by the cationic surfactant and sodium hydroxide is shown in Fig. 5. One of the most important parameters in determining the mechanism of adsorption is considering the changes in the solution's pH. Adsorbents were modified with sodium hydroxide after modifying with the cationic surfactant, so after adsorbing anions, hydroxide ions were released in the solution and the final pH of the solution was increased. In Fig. 6, the final pH of water after adsorbing has been shown. The initial pH was 8.2 at all salinity levels; according to Fig. 6, in all treatments; the pH of the solution after adsorbing was increased. At the EC of 20.4 dS/m, the highest pH increase belonged to MZ treatment; where the pH value was 8.93. Also, the maximum pH increase at the salinity levels of 10.41 and 5.58 dS/m was related to MP treatment, where the final solution pH reached 8.83 and 8.79, respectively. pH changes at all levels of salinity indicated that in all treatments, the ion-exchange had occurred [4]. However, low pH changes indicated that mechanisms such as adsorption could have a significant impact on the removal of anions by the adsorbents. In addition, attracting more anions at the higher salinity levels showed that adsorption process could be more effective at these salinity levels [3].

3.4. The effect of the contact time and the kinetic study

The effect of adsorbent's contact time on the total anions adsorption at the EC of 20.4 dS/m is presented in Fig. 7. According to the results for the MP adsorbent, in the first 15 min, the curve slope was high; in fact, it was 96.7 mg/g (67.5%) of the total adsorption that had occurred. After 90 min, the adsorption rate reached a fixed value

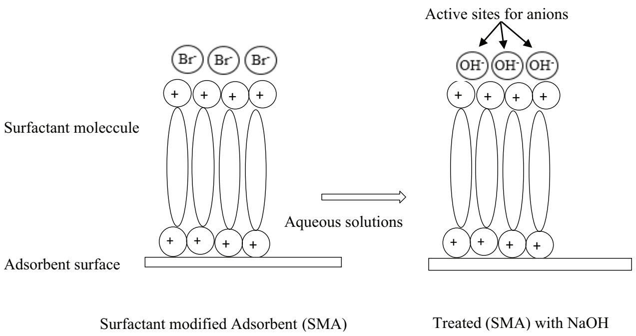

Fig. 5. A model of modification of adsorbents by HDTMABr and NaOH [14].

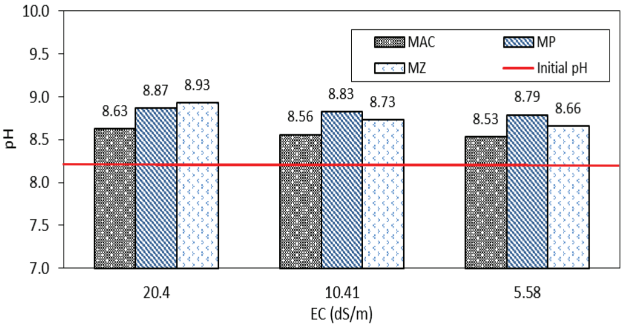

Fig. 6. The effect of anions adsorption on the pH of water. Adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

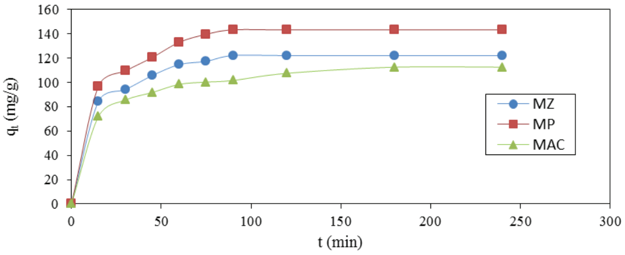

Fig. 7. Amount of anions adsorbed per unit mass of adsorbents MZ, MP and MAC. EC of water: 20.4 dS/m; adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

(143.23 mg/g), so it was not changed. So the equilibrium time for the MP treatment was 90 min. Also, according to Fig. 7, the equilibrium time for MAC and MZ treatments was 180 and 90 min, respectively. At the beginning of the adsorption process, many adsorption sites are available on the surface of the adsorbents and anions are adsorbed at these sites easily. For this reason, the adsorption rate at the beginning of the adsorption process was high and by reducing the adsorption sites gradually, the rate of adsorption was decreased [20]. Choi et al. [12] found that the time required to reach the equilibrium in the adsorption of chromium to activated carbon was 180 min.

In order to determine the adsorption kinetic of total anions, water with the EC of 20.4 dS/m and the pH of 8.2 was used, and the adsorbent to water ratio was 1 g/50 mL. For this purpose, kinetic models including the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion were used; the results are presented in Fig. 8 and Table 3. Based on the results presented in Table 3, the pseudo-second-order kinetic model could best describe the adsorption of anions among all adsorbents (R^2 value of 0.996, 0.993 and 0.999 for MZ, MP and MAC adsorbents, respectively). Besides, equilibrium adsorptions from the pseudo-second-order kinetic model ($q_{e,\mathrm{cal}}$ 133.33, 158.73 and 114.94 mg/g for MZ, MP and MAC adsorbents, respectively), as compared with the equilibrium adsorptions from experiments ($q_{e,\mathrm{exp}}$ 122.09, 143.23 and 112.56 mg/g for MZ, MP and MAC adsorbents, respectively) showed a slight difference. The better correlation of the pseudo-second-order kinetic model with the anions adsorption data showed that the adsorption process was controlled by the chemical adsorption [29,30]. Hemmati et al. [21] introduced the pseudo-second-order kinetic model as the best adsorption model to remove malachite green by using the modified sphagnum peat moss. Asgari et al. [10] concluded that in Cr(VI) adsorption on the surfactant modified by the Iranian zeolite, pseudo-second-order model could be the best kinetic model. Papari et al. [31] found that the pseudo-second-order model was the best kinetic model to remove the fluoride ion from the aqueous solution, groundwater and seawater by granular and powdered *Conocarpus erectus* biochar.

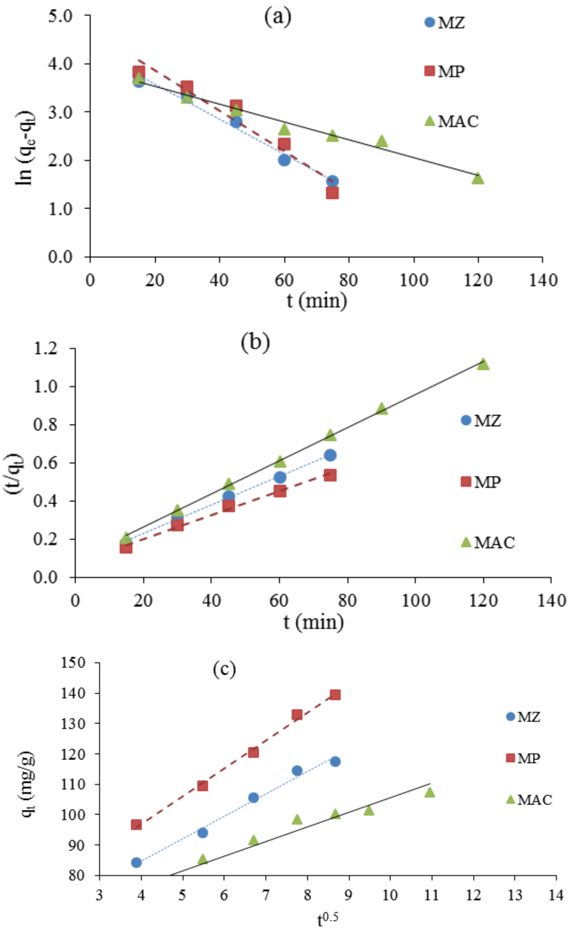

Fig. 8. Anions adsorption by MZ, MP and MAC according to (a) the pseudo-first-order model, (b) the pseudo-second-order model and (c) the intra-particle diffusion model. EC of water: 20.4 dS/m; adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

3.5. Adsorption isotherms

Three adsorption isotherm models (Freundlich, Langmuir and Temkin) were adopted for this study to choose the best model regression coefficient (R^2). In Fig. 9 and Table 4, the results of these isotherms for the total anions adsorption are presented. According to the regression coefficients (R^2 values of 0.98, 0.99 and 0.99 for MZ, MP and MAC adsorbents, respectively), Freundlich model had the highest correlation with experimental data for all adsorbents. Also, it could be deduced that anions adsorption onto all adsorbents had not been a kind of single layer adsorption. Also, the surface of adsorbents was heterogeneous, and adsorbent sites were non-uniform. Considering that in all treatments $1/n$ was greater than 1, the change in the adsorbed concentration was greater than that in the solution concentration [32]. The greater K_F for MP treatments (value of 9.52×10^{-5}), as compared with MZ and MAC treatments (the value of 1.54×10^{-5} and 7×10^{-6}), demonstrated that the adsorption intensity for the MP treatment was greater than that of MZ and MAC

Table 3
Kinetic parameters for the adsorption of anions onto MZ, MP and MAC

Kinetic model	Parameter	MZ	MP	MAC
Pseudo-first-order	$q_{e,\mathrm{exp}}$ (mg/g)	122.09	143.23	112.56
	k_1	0.036	0.042	0.019
	$q_{e,\mathrm{cal}}$ (mg/g)	74.43	110.04	49.33
	R^2	0.979	0.943	0.978
Pseudo-second-order	k_2	0.0007	0.0005	0.0008
	$q_{e,\mathrm{cal}}$ (mg/g)	133.33	158.73	114.94
	R^2	0.996	0.993	0.999
Intra-particle diffusion	k_{dif}	7.353	9.182	4.822
	C	55.426	60.2	57.369
	R^2	0.985	0.994	0.943

Note: EC of water: 20.4 dS/m; adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

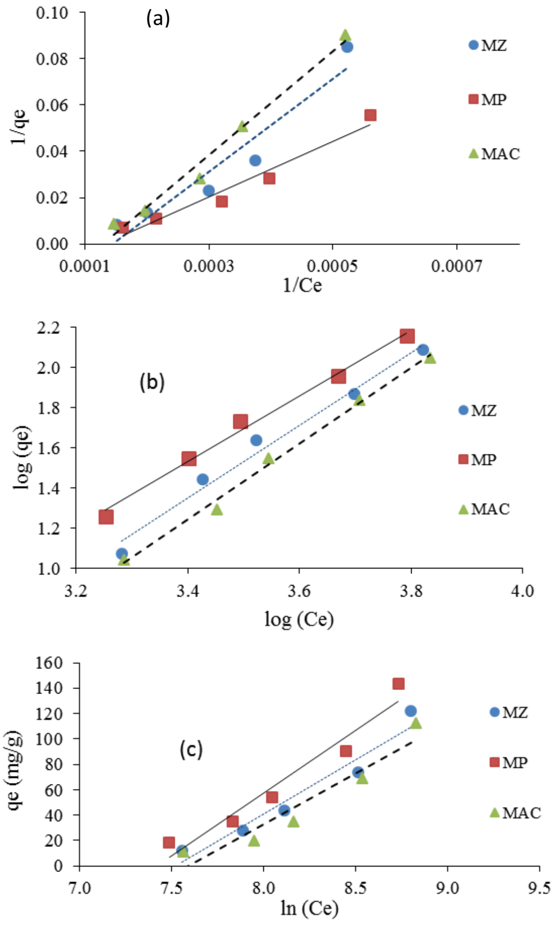

Fig. 9. Anions adsorption by MZ, MP and MAC according to the isotherm models (a) the Langmuir model, (b) the Freundlich model and (c) the Temkin model. EC range: 5.58–20.4 dS/m; adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

Table 4
Isotherm parameters for the adsorption of anions onto MZ, MP and MAC

Isotherm	Parameter	MZ	MP	MAC
Langmuir	q_m (mg/g)	34.36	63.29	34.48
	K_L	1.45×10^{-4}	1.31×10^{-4}	1.29×10^{-4}
	R^2	0.92	0.96	0.98
Freundlich	K_F	1.54×10^{-5}	9.52×10^{-5}	7×10^{-6}
	n	0.55	0.61	0.53
	R^2	0.98	0.99	0.99
Temkin	b_T	28.84	25.12	30.83
	A_T	5.4×10^{-4}	6.02×10^{-4}	5.04×10^{-4}
	R^2	0.94	0.95	0.92

Note: EC range: 5.58–20.4 dS/m; adsorbent dosage: 1 g/50 mL; temperature: 298 K; agitation rate: 150 rpm.

treatments [33]. In a study by Shams et al. [34] on phosphorus removal from the aqueous solution by cheap adsorbents, it was shown that Freundlich model was better fitted to the adsorption process than the Langmuir model.

4. Conclusion

In this study, removal of anions (Cl^-, SO_4^{2-} and HCO_3^- ions) from irrigation saline waters was evaluated using MZ, MAC and MP with the cationic surfactant and sodium hydroxide. Previous studies had been focused on the application of the surfactant modified adsorbents to adsorb heavy metals in aquatic environments, while this study also focused on the use of these adsorbents for the removal of anions from water. The results of this study showed that modified adsorbents could remove a significant part of anions from saline water. The results of this study could be summarized as follows:

- The most adsorption of MZ, MP and MAC adsorbents was in the salinity of 20.4 dS/m, such that their adsorption capacity was 122.09, 143.23 and 112.16 mg/g, respectively.
- For all adsorbents, the maximum adsorption in 20.4 dS/m was related to Cl^- ion, and for MZ and MAC adsorbents, the maximum adsorptions in 5.58 dS/m were related to HCO_3^- ions.
- The pseudo-second-order kinetic model and Freundlich adsorption isotherm model had the best fit with the experimental data.
- Ion-exchange and adsorption were the effective processes in removing anions by MZ, MP and MAC from saline water.
- For all adsorbents, HCO_3^- removal was more favorable than that of Cl^- and SO_4^{2-}.

References

[1] P.J. White, M.R. Broadley, Chloride in soils and its uptake and movement within the plant: a review, Ann. Bot., 88 (2001) 967–988.

[2] B. Ghorbani, R. Pourvaezi, S.J. Mirzaei, The impact of rice husk, activated carbon, almond shell, and sand filters on some physical and chemical properties of aqueous salt solution, Desal. Wat. Treat., 57 (2016) 10878–10885.

[3] R. Rostamian, M. Heidarpoor, S.F. Moosavi, M. Afyuni, Application of biochar produced from rice paddy in irrigation water desalination, Iran. Water Soil Sci. J., 71 (2015) 21–29 (In Persian).

[4] A. Aghakhani, S.F. Mousavi, B. Mostafazadeh-Fard, R. Rostamian, M. Seraji, Application of some combined adsorbents to remove salinity parameters from drainage water, Desalination, 275 (2011) 217–223.

[5] Z. Khademi, B. Ramavandi, M.T. Ghaneian, The behaviors and characteristics of a mesoporous activated carbon prepared from *Tamarix hispida* for Zn(II) adsorption from wastewater, J. Environ. Chem. Eng., 3 (2015) 2057–2067.

[6] A.N. Fernandes, C.A.P. Almeida, C.T.B. Menezes, N.A. Debacher, M.M.D. Sierra, Removal of methylene blue from aqueous solution by peat, J. Hazard. Mater., 144 (2007) 412–419.

[7] P. Fine, A. Scagnossi, Y. Chen, U. Mingelgrin, Practical and mechanistic aspects of the removal of cadmium from aqueous systems using peat, Environ. Pollut., 138 (2005) 358–367.

[8] A.H. Mahvi, M. Vosoughi, M.J. Mohammadi, A. Asadi, B. Hashemzadeh, A. Zahedi, S. Pourfadakar, Sodium dodecyl sulfate modified-zeolite as a promising adsorbent for the removal of natural organic matter from aqueous environments, Health Scope, 5 (2016) e29966.

[9] M.V. Niri, A.H. Mahvi, M. Alimohammadi, M. Shirmardi, H. Golastanifar, M.J. Mohammadi, M. Khishdost, Removal of natural organic matter (NOM) from an aqueous solution by NaCl and surfactant-modified clinoptilolite, J. Water Health, 13 (2015) 394–405.

[10] G. Asgari, B. Ramavandi, L. Rasuli, M. Ahmadi, Cr (VI) adsorption from aqueous solution using a surfactant-modified Iranian zeolite: characterization, optimization, and kinetic approach, Desal. Wat. Treat., 51 (2013) 6009–6020.

[11] S. Malamis, E. Katsou, A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: examination of process parameters, kinetics and isotherms, J. Hazard. Mater., 252 (2013) 428–461.

[12] H.D. Choi, W.S. Jung, J.M. Cho, B.G. Ryu, J.S. Yang, K. Baek, Adsorption of Cr(VI) onto cationic surfactant-modified activated carbon, J. Hazard. Mater., 166 (2009) 642–646.

[13] Y. Kalmykova, A.M. Stromvall, B.M. Steenari, Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations, J. Hazard. Mater., 152 (2008) 885–891.

[14] P. Chutia, S. Kato, T. Kojima, S. Satokawa, Adsorption of As(V) on surfactant-modified natural zeolites, J. Hazard. Mater., 162 (2009) 204–211.

[15] H. Deng, L. Yang, G. Tao, J. Dai, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution, J. Hazard. Mater., 166 (2009) 1514–1521.

[16] E.V. Maas, Salt Tolerance of Plants, B.R. Christie Ed., The Handbook of Plant Science in Agriculture, CRC Press, Boca Raton, Florida, 1984.

[17] A.E. Greenberg, L.S. Clasceri, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, D.C., USA, 1992.

[18] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon, J. Hazard. Mater., 124 (2005) 192–199.

[19] R. Malekian, J. Abedi-Koupai, S.S. Eslamian, Use of zeolite and surfactant modified zeolite as ion exchangers to control nitrate leaching, World Acad. Sci. Eng. Technol., 52 (2011) 715–719.

[20] S.M. Yakout, E. Elsherif, Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons, Carbon Sci. Technol., 1 (2010) 144–153.

[21] F. Hemmati, R. Norouzbeigi, F. Sarbisheh, H. Shayesteh, Malachite green removal using modified sphagnum peat moss as a low-cost biosorbent: kinetic, equilibrium and thermodynamic studies, J. Taiwan Inst. Chem. Eng., 58 (2016) 482–489.

[22] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, J. Appl. Chem., 3 (2012) 38–45.

[23] N. Jain, M.K. Dwivedi, A. Waste, Adsorption of Methylene Blue dye from Industrial effluents using coal fly ash, Int. J. Adv. Eng. Res. Sci., 3 (2016) 9–16.

[24] X. Hu, H. Zhang, Z. Sun, Adsorption of low concentration ceftazidime from aqueous solutions using impregnated activated carbon promoted by Iron, Copper and Aluminum, Appl. Surf. Sci., 392 (2017) 332–341.

[25] E. Altintig, G. Arabaci, H. Altundag, Preparation and characterization of the antibacterial efficiency of silver loaded activated carbon from corncobs, Surf. Coat. Technol., 304 (2016) 63–67.

[26] S.J. Lee, J.H. Park, Y.T. Ahn, J.W. Chung, Comparison of heavy metal adsorption by peat moss and peat moss-derived biochar produced under different carbonization conditions, Water Air Soil Pollut., 226 (2015) 9.

[27] A. Leon-Torres, E.M. Cuerda-Correa, C. Fernandez-Gonzalez, M.F.A. Franco, V. Gomez-Serrano, On the use of a natural peat for the removal of Cr(VI) from aqueous solutions, J. Colloid Interface Sci., 386 (2012) 325–332.

[28] M.K. Doula, Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity, Chemosphere, 67 (2007) 731–740.

[29] C.K. Ahn, D. Park, S.H. Woo, J.M. Park, Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants, J. Hazard. Mater., 164 (2009) 1130–1136.

[30] M.J. Amiri, J. Abedi-Koupai, S.S. Eslamian, M. Arshadi, Adsorption of Pb(II) and Hg(II) ions from aqueous single metal solutions by using surfactant-modified ostrich bone waste, Desal. Wat. Treat., 57 (2016) 16522–16539.

[31] F. Papari, P.R. Najafabadi, B. Ramavandi, Fluoride ion removal from aqueous solution, groundwater, and seawater by granular and powdered Conocarpus erectus biochar, Desal. Wat. Treat., 65 (2017) 375–386.

[32] A.U. Itodo, A. Usman, G. Akinrinmade, H.U. Itodo, V.C. Ugboaja, Performance assessment of received and formulated carbon animalis: a comparative adsorption isotherm test, Indian J. Environ. Prot., 3 (2012) 288–295.

[33] J.C. Igwe, A.A. Abia, Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co(II), Fe(II) and Cu(II) ions from waste water using modified and unmodified maize cob, Int. J. Phys. Sci., 2 (2007) 119–127.

[34] M. Shams, I. Nabipour, S. Dobaradaran, B. Ramavandi, M. Qasemi, M. Afsharnia, An environmental friendly and cheap adsorbent (municipal solid waste compost ash) with high efficiency in removal of phosphorus from aqueous solution, Fresenius Environ. Bull., 22 (2013) 723–727.