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Investigation the efficiency of Mch/Fe-Zr nano-composite for adsorption of humic acid

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ABSTRACT

Organic material, including humic acid, is a matter that affect water quality through increasing coagulates and disinfectants and results in production of complex materials and increasing re-growth in distribution systems and provides a background for production of by-products resulted from disinfection. The aim of this study is to study the synthesis and efficiency of Mch/Fe-Zr nano-composite to remove humic acid from aqueous solutions. Synthesis of nano-composite was carried out as co-precipitation method and to identify its characterizations SEM, FTIR, XRD and VSM techniques were used. The effect of different variables including initial pH (3–11), contact time (0–120 min), initial concentration of pollutants (10–50 mg /L), adsorbent dosage (0.4–2 g/L) and temperature (15–35ºC) were studied. The results of the research indicated that highest efficiency of humic acid removal was in pH = 5 (100%). In addition, as the adsorbent dosage increases, adsorption efficiency increases and increased concentration results in decreased removal efficiency. Adsorption follows Freundlich isotherm and the kinetic model of the pseudo-second order. According to the obtained results, it was clear that synthesized adsorbent has high capability in humic acid adsorption and can be used as a cost effective and accessible adsorbent.

Keywords: Magnetic nano-composite; Mch/Fe-Zr; Adsorption; Humic acid

1. Introduction

Water pollution is a basic environmental problem that has attracted global considerations during recent years, especially noticing that several pollutants enter water resources as a result or urbanization and industrialization [1]. Underground waters are important sources of drinking water, because they have high quality [2]. Considering that in many parts of the world underground resources are the source of drinking water, we are facing the crisis of water resources [3]. Worldwide water contains natural organic materials (NOM) that result from the interaction between the geospher, hydrosphere and biosphere cycle [4]. Natural organic materials including humic acid is a material that affects water quality through increasing coagulates and disinfectants and result in production of complex materials and provide a background for by-products resulted from disinfectant (DBP: disinfection by-products) [5]. Humic material include 50–80% of organic materials in soil and water [6]. Molecule weight of acid humic is different from some to several thousand g/mol (500–250000 g/mol) [7]. The structure of humic material include aromatic circles with carboxyl groups (COOH) and hydroxide groups (OH) [8]. When the concentration of humic acid in aqueous environments increases, it changes the aesthetic properties [8].

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Humic acid molecules ,make removal of existing contaminants in the water difficult [9]. Although humic acid compounds are not carcinogenic, but create secondary problems in purification of drinking water including taste, color and smell in water [10], unfavorable effect on membrane performance [11,12], corrosion of metal equipments [13] and re-growth of micro-organisms in water supply and water reservoirs [14].

Increasing use of disinfectants in water purification, reaction of humic acid compounds with disinfectants is the cause of 600 types of DBPs including halo acetic acid and tri halo-methans that cause cancer, among which colorectal and bladder cancer are the most important [15]. Humic acid removal from drinking water is carried out by different processes including adsorption, coagulation, advanced oxidation, membrane processes, ion exchange, chitosan adsorption. Due to easy design and operation, adsorption process is better than other methods [7]. Today, adsorption with adsorbents that produced from natural waste material is cost effective, has high application in research works [16]. Chitosan is a polymer adsorbent that is obtained from sea crustaceans' shell including the shrimp. Chitin and chitosan are natural amino polysaccharides that have complex operations, unique structure and vast applications in industrial and biotechnological fields [17]. Due to poly cationic characteristics of chitosan, amine groups can take part in adsorption reaction to anion materials including humic acids. Anyway, chitosan is tempted to closure and hardening of aqueous solutions [18]. Results of similar studies for removal of organic material showed that chitosan is a suitable substitute for aluminum salts and with mixture of chitosan and Poly Aluminium Chloride with 1:1 ratio is suitable for elimination of humic acid [19].

In another study the adsorption of humic acid by chitosan covered with granules was investigated, and results showed that it was a suitable adsorbent for elimination of organic compounds from aqueous solutions [20].

In another research that carried out by Saeedi et al., regarding cadmium adsorption by chitosan and nano chitosan it was shown that both have good adsorption potential, but nano chitosan has higher adsorption capacity and follows from second order kinetic [21]. Soluble organic material have high tendency for adsorption on the minerals' surface such as aluminum and iron oxides [22]. Chitosan alone does not have magnetic property, so a material with magnetic property must be added to it, in order to separate chitosan from aqueous media. In recent years, modified zero-capacity iron nano-particles, with the size smaller than 100 nm are considered. Modified zero-capacity iron nano-particles have high surface energy and reactivity that is due to their high specific surface area [23]. In addition, Fe_3O_4 magnetic particles have high application due to consistent biological and chemical stability and high magnetic property, so magnetic chitosan nano-particles are used as a promising adsorbent for elimination of material. These materials in addition to having hydroxyl and amine groups in chitosan chain have high nano-magnetic capability, therefore considering its magnetic properties, it can easily be separated in adsorption process by using magnetic field [24], so the aim of this research is to study the efficiency of Mch/Fe-Zr nano-composite for adsorption humic acid from aqueous environments.

2. Materials and methods

The materials used in this research were acetic acid, NaOH, HCl and Fe_2SO_4, $FeCl_3$ and $ZrOCl_2$ salts, all of them products of Merck Company. The apparatus used include Spectrophotometer (model UV/Vis T80$^+$), FTIR (model AVATAR 370 made in America), with spectrometer range in 400–4000 cm^{-1} (UV/Visible), XRD (X Pert Pro, PANalytical Company, Nederland) and FESEM (SIGMA VP-500, Zeiss, Germany) and VSM (model LAKE shore 7404 made in U.S).

2.1. Synthesis and preparation of Mch/Fe-Zr nano-composite (Mch/Fe-Zr)

In this study, in the first step $FeCl_2$ and $FeCl_3$ with the ratio of 1:2 were solved in a two-necked flask with a magnet, and then sodium hydroxide were added to solution, then was exposed to N_2 for deoxidation in 80ºC. Then, 30 ml of $ZrOCl_2$ (0.5 M) was added and mixed for 8 h on a heater. The dark sediment is washed with deionized water and then dried in oven in 70ºC [25].

2.2. Preparation of Fe_3O_4@$Zr(OH)_4$ nano-composite covered on chitosan bed(Mch/Fe-Zr)

In the first step, 4 g of chitosan was solved in 400 ml acetic acid 4% and was mixed with a shaker for 1 h. Then, 2.5 g of magnetic nano-composite of Fe_3O_4@ $Zr(OH)_4$ were added to chitosan gel. Then this step was repeated so that it takes a slurry form. Sodium hydroxide (2 M) was added to this solution drop by drop by a glass syringe while mixing severely. We let the gel to stay stable for 1 h in NaOH solution. Then, it is washed with deionized water to neutralize the pH. Then, Mch/Fe-Zr nano- composite was dried in an oven in 40ºC for 24 h [26].

2.3. Adsorption tests

In order to determine the equilibrium time of the Fe-Zr/chitosan nano-particle process, batch adsorption experiments were performed at the room temperature (25±1ºC) and effect of different variable included the pH (3–11); Mch/Fe·Zr dose (0.4–2 g/L); humic acid concentration (10–50 mg/L), contact time (0–120 min), and temperature (15–35ºC) [27]. In each step one parameter were changed and others were fixed.

During the experiment steps, specified amount of Mch/Fe-Zr nano-composite was added to a 200°C of humic acid (10 ppm) and placed on the shaker at 250 rpm. To adjust Ph, HCl (0.1 M) and NaOH (1 M) were used. The residual humic acid concentration was achieved using a spectrophotometer at 254 nm wavelengths based on the standard methods [28]. To calculate removal efficiency (%R) and balance adsorption capacity (q_e) of the adsorbent, Eqns. (1), and (2) were used.

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

where, C_0 and C_f are respectively initial and final concentration of humic acid (mg/L).

$$q_e = \frac{V}{M} \times (C_{in} - C_{out}) \tag{2}$$

where, q_e is the equilibrium capacity of adsorbent mg/g, V is the volume of solution (L), M: adsorbent mass (g), C_{in} and C_{out}, is the initial and final concentration of humic acid (mg/L), respectively.

In order to calculate thermodynamics of humic acid adsorption by synthesized nano-composite, Eqns. (3) and (4) were used. In Eq. (3), ΔG is variations of Gibbs free energy; R is gasses constant value and equal to 8.314 J/mol/k, T temperature based on K and K_d thermodynamic balance constant. In Eq. (4), ΔS is standard entropy (J/mol K), ΔH standard enthalpy variations (KJ/mol) and R is gasses constant value (J/mol K).

$$\Delta G = -RT \ln K_d \tag{3}$$

$$\text{Ln } k_d = \Delta S/R - \Delta H/RT \tag{4}$$

After calculation of thermodynamic balance constant for different temperatures and calculation of related free energy, ln K_d chart against 1/T was plotted. The slope and width of the origin of this graph are used to determine the values of ΔS and ΔH [28].

In order to study adsorption isotherms, experiment data were analyzed by Freundlich and Langmuir isotherm equations. Linear forms of these equations can be defined as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{5}$$

$$LnQ_e = \left(\frac{1}{n}\right) LnC_e + LnK_f \tag{6}$$

In these studies q_e is the concentration of balancing pollutant in solid phase in mg/g, q_{max} is maximum surface adsorption in mg/g, k_L Langmuir surface adsorption balance constant in 1/mg, K_f Freundlich constant in $\text{mg}^{1-1/n}\text{]}^{1/n}$/g that indicates surface adsorption capacity and n is a constant indicating surface adsorption.

To study adsorption kinetic, two common models of pseudo-first order and pseudo-second order were used to survey balance data. Correlation coefficient (R^2) was considered as a criteria of consistence between empirical data and two proposed models. pseudo-first order kinetic model or Lagergren 1989 equation is as follows [29]:

$$\log(q_e - q_t) = \log q_e - K_1 t \tag{7}$$

In this equation q_t and q_e are respectively the amount of adsorbed material on adsorbent in time t and in balance time (mg/g) and K_1 is pseudo-first order speed constant (1/min).

log ($q_e - q_t$) chart in time t is used to determine k constant value and R^2 coefficient. Pseudo-second order equation is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \tag{8}$$

In this equation K_2 is pseudo-second order adsorption speed constant (g/mg min). T/q_t chart in time t is used to obtain speed parameters and the results propose consistence of this kinetic model with empirical data. q_e and K_2 values are plotted from calculation of slope and y-intercept [30].

3. Results and discussion

3.1. Determining the properties and structure of Fe-Zr/chitosan nano-composite

In order to study magnetic properties of Mch/Fe-Zr nano-composite, VSM (vibrating sample magnetometer) was used.

Magnetic moment against magnetic field (M-H ring) for Mch/Fe-Zr is presented in Fig. 1. Magnetic curve shows that Mch/Fe-Zr is super-magnetic and its magnetic saturation value is 12.77 emu/g synthesized adsorption are as disperse and can be redistributed. These particles have high magnetic properties and can be separated by means of a magnet.

By XRD(X-ray diffraction), crystalline structure of Mch/Fe-Zr nano-composite was studied (Fig. 2).

According to Fig. 2, a characteristic peak at 2θ = 25° are observed which correspond to its amorphous shape

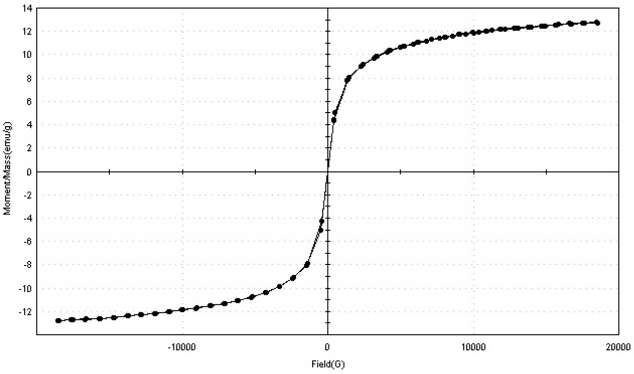

Fig. 1. VSM curve of magnetic Mch/Fe-Zr nano-composite.

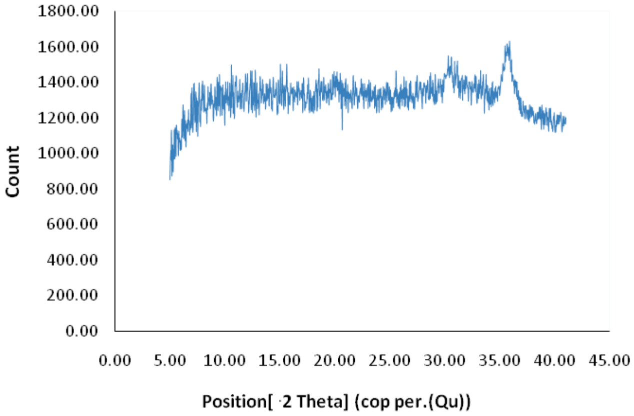

Fig. 2. XRD spectrum of Mch/Fe-Zr nano-composite.

of Mch/Fe-Zr nano-composite, which is due to the presence of amino groups (NH_2). Two peaks between 15 and 25° refer to the crystalline structure of the biopolymer, as a result of packing the polymer chains due to their interactions. The peak at $2\theta = 35.72°$ refer to iron-oxide [31]. The results also indicate crystallization of Mch/Fe-Zr nano-composite particles.

FTIR (Fournier transform infrared spectroscopy) method was used to identify existing functional groups in the Mch/Fe-Zr nano-composite, as shown in Fig. 3.

As shown in Fig. 3, existence of below frequencies approves the existence of considered functional groups in the structure of Fe-Zr/chitosan. Frequency in 3415.85 cm^{-1} is related to O-H tension bond, 2924.4 cm^{-1} frequency is adsorption band resulted from tension bond of alkans (indicating sitting organic compounds on considered adsorbent), 1626.85 cm^{-1} frequency is the result of tension bond of C=C, 1377.73–1417.48 cm^{-1} frequency is contributed to strong alkans' bond and 578.43 cm^{-1} is related to Fe-O cm^{-1} tension bond in Mch/Fe-Zr nano-composite. The peaks at 637 and 451.91 cm^{-1} can be related for the vibration of the Zr–OH and Zr–O–Zr, in the Mch/fe-Zr nano-copmosite respectively [32].

Scanning electron microscope (SEM) was used to study average diameter of the particles, shape and surface details that are shown in Fig. 4.

The shape and the size of magnetic nano-composite were determined by means of scanning electron microscope (SEM). Fig. 4 shows SEM figure related to these nano-composite that are spherical Fe_3O_4 particles attached to the surface of Mch/Zr particles that have specifications such as high density and irregular shape. The size of magnetic nano-particles was in the range of 16.5–18.92 nm.

3.2. Results of humic acid adsorption process by Mch/Fe-Zr nano-composite

3.2.1. pH effect

In this study, the effect of the initial pH of the solution on the adsorption of humic acid by the Mch/Fe-Zr nano-composite, was investigated in the range pH (3–11) [26], the results of which are shown in Fig. 5. The highest removal efficiency at pH = 5 was obtained (98.5%) and the lowest in pH = 11 (32%), and it became clear that by increasing pH, adsorption efficiency decreased.

pH is one of the most important parameters in the removal process of various pollutants. The results of the pH test showed that the humic acid absorption efficiency on Mch/Fe-Zr nano-composite decreases by increasing pH, and the highest removal was obtained at pH = 5 (98.5%). The reason for these changes can be described as absorption of soluble ions in the environment being largely dependent on the protonation of carboxylic and amine groups found in chitosan nano-composite [33]. Humic acid have a high solubility in acidic conditions, which affects on adsorption process. Also, pH influences the adherence and surface density of nano-composite.

In addition, with increasing pH, the size of humic acid molecules is altered from spherical to linear shape, therefore, the adsorption of humic acid reduced [34]. Moreover at low pH values (3–5), the protonation of the amino groups

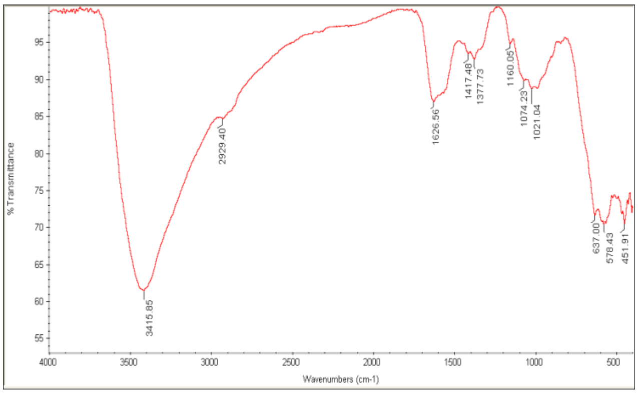

Fig. 3. FTIR range of Mch/Fe-Zr nano-composite.

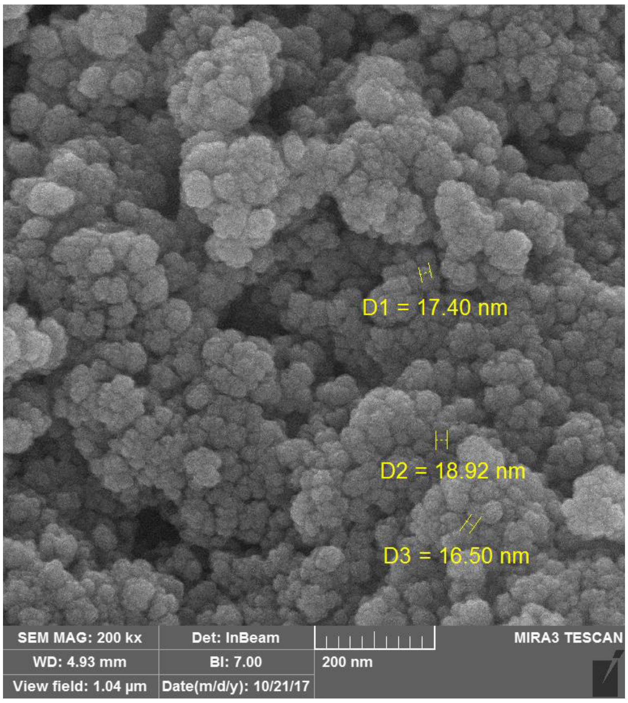

Fig. 4. FE-SEM spectrum of Mch/Fe-Zr nano-composite.

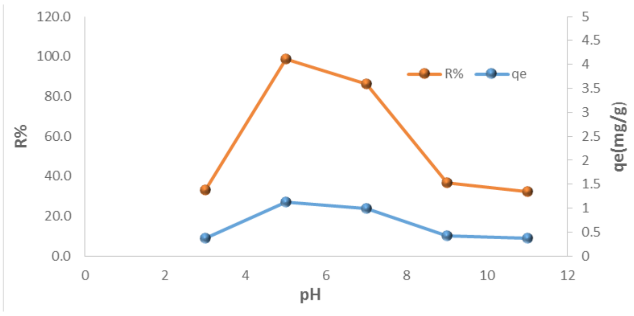

Fig. 5. Effect of pH variation by Mch/Fe-Zr nano-composite (concentration of humic acid 10 ppm, adsorbent dosage 1 g/L, temperature = 25°C, and time = 30 min).

in Mch–Fe/Zr beads causes electrostatic attraction between RCOO– groups of humic acid and NH_3^+ groups of Mch/Fe-Zr nano-composite. AS a result adsorption rate of humic acid significant increased [35].

However at higher pH however, the concentration of H+ declined, thus humic acid adsorption decreased. The study conducted by Ghafoori and Naghizadeh showed that the optimum pH was 4 and at this condition, occurred higher adsorption of humic acid [28]. In a study performed by Saeedi et al, adsorption of cadmium by chitosan and nano chitosan, the results showed that highest adsorption capacity for chitosan and nano-chitosan are respectively at 153.85 mg/g (in pH = 7) and 357.14 mg/g (in pH = 4.6) [21]. In a study performed by Hanafiah et al., on adsorption of humic acid from aqueous solution on chitosan, results showed the maximum adsorption capacity was at pH = 6 was 44.8 mg/g [35].

3.2.2 The effect of contact time

The comparison of various contact time on efficiency of humic acid adsorption and capacity of adsorption by Mch/Fe-Zr nano-composite in pH = 5, humic acid concentration 10 ppm, temperature 25ºC, adsorbent dosage 2 g/L were studied, that the results are provided in Fig. 6. It showed that by increasing contact time, elimination increases. Optimum time of 60 min was selected and after that, adsorption efficiency was constant.

Generally, it is obvious that in the first moments absorption is fast and a steep slope is observed in the diagram, which is related to physical absorption, then the slope is slightly milder, which is also due to the resistance against penetration, so that after a while that empty sites are occupied by metal ions, repulsive forces are formed between the fluid bulk and the absorbing molecules, and the absorption efficiency decreases, finally, the adsorption reaches to saturation, and after that, by increasing the time, adsorption does not increase. This is balance time and adsorption level is stable or slightly decreases after that, and the decrease in adsorption may be due to desorption [36]. The results showed that by increasing contact time from 15 to 60 min, adsorption efficiency has increased, but after that, did not increase significantly, so optimal time of 60 min was selected.

In a study performed by Liang Peng titled modification of nano particles with humic acid for elimination of Rhodamine, the results showed that optimum time of rhodamine adsorption was 15 min with Fe_3O_4/HA nano-particles [37]. In the study of Hanafiah et al. subjected adsorption of humic acid from aqueous environment on chitosan, the optimum time was 50 min and maximum capacity was 44.8 mg/g [35]. These two studies are consistent with the present research.

3.2.3. The effect of initial concentration of humic acid on adsorption efficiency

In order to determine the effect of the initial concentration of humic acid on adsorption efficiency, the concentration of humic acid (10–50 mg/L) was selected. Based on Fig. 7, the changes in humic acid concentration with Fe-Zr/chitosan concentration have a reverse relation with the adsorption efficiency. The more pollutant concentration in a contact time and absorbent dose at optimum pH, the removal efficiency will be reduced.

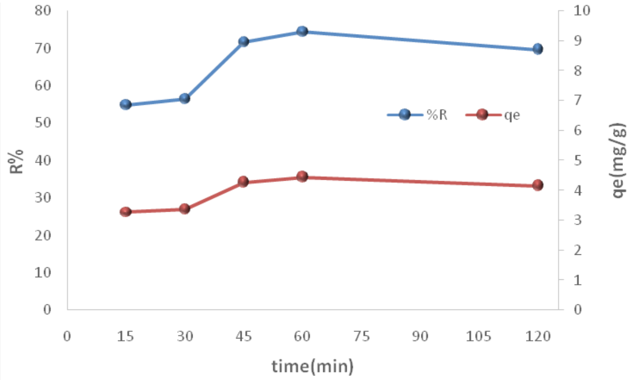

Fig. 6. Effect of contact time on efficiency of humic acid adsorption by Mch/Fe-Zr nano-composite (pH = 5, humic acid concentration = 10 ppm, temperature = 25ºC, adsorbent dosage = 2 g/L).

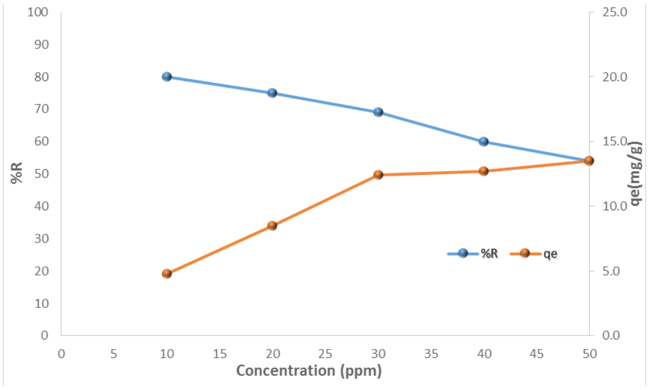

Fig. 7. Comparison of concentration variations by Mch/Fe-Zr nano-composite (temperature = 25ºC, adsorbent dosage = 2 g/L, time = 60 min and pH = 5).

The initial humic acid concentration results in decreased absorption. At low concentrations, all humic acid ions react to adsorption sites, but there are still free adsorption sites at the adsorbent surface. In higher concentrations, the absorption capacity is almost constant, which is due to the saturation of adsorption sites [38]. In a study by Zareie et al. on the removal of copper using nano-chitosan, the range was 10–100 mg and with the increase of pollutant concentrations, the removal efficiency has decreased [39]. In another study performed by Caliani et al. adsorption of copper ions by chitosan/perlite combination were studied. According these results by increasing pollutant concentration, adsorption capacity has increased [40].

3.2.4. The effect of adsorbent dosage of Mch/Fe-Zr nano-composite on adsorption of humic acid

In order to determine the effective dose of adsorbent, the absorbance dose was in the range of 0.4–2 g/L and the highest adsorption rate in adsorbent dose 2 g/L (81.7%). Fig. 8 shows the variations in nano-composite dosage on humic acid adsorption.

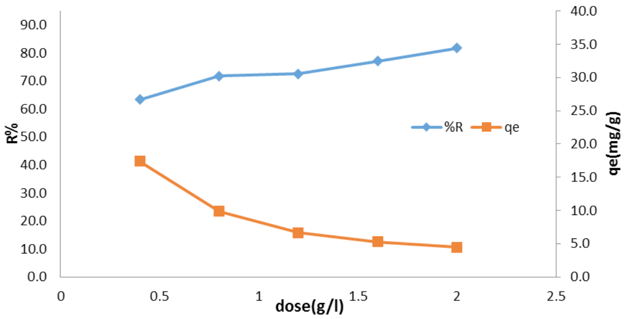

Fig. 8. Effect of adsorbent dose variations by Mch/Fe-Zr nano-composite (humic acid concentration 10 ppm, temperature = 25°C, time = 60 min and pH = 5).

By increasing adsorbent dosage, adsorbent surface has increased and as a result pollutant removal increases. By increasing adsorbent dosage from 0.4 to 2 g/L, adsorption capacities are respectively 17.4 and 4.48 mg/g and by increasing adsorbent dosage, removal percentage increases respectively as 63.4% and 81.7%.

In a study performed by Khodadadi et al. the removal of heavy metals by Fe-Zr/chitosan were investigated, the results showed that by increasing adsorbent dosage, removal efficiency increased from 63 to 96% [41]. In another study performed by Daifullah the results indicated that by increasing adsorbent dosage, elimination level increases due to increasing adsorption surface [42].

3.2.5. The effect of temperature and thermodynamic parameters of humic acid adsorption by Mch/Fe-Zr nano-composite

The results of the effect of solution temperature on efficiency of humic acid elimination process are presented in Fig. 9. As it is shown, increasing solution temperature has led to increasing adsorption of humic acid that indicates endothermic reaction of humic acid removal.

Fig. 9 shows the effect of temperature and thermo-dynamic of humic acid adsorption by Fe-Zr/chitosan. After calculation of the constant of thermo-dynamic balance for different temperatures and related free energy, ln k_d diagram against 1/T was plotted. If by increasing temperature, adsorption increases as well, it indicates endothermic reaction of removal of humic acid. As can be observed, in this experiment by increasing temperature from 15 to 35°C, efficiency of humic acid adsorption increased, that is approved.

3.2.6. Kinetic and thermodynamic survey of humic acid adsorption by Mch/Fe-Zr nano-composite

According to Table 1 the value of ΔS is 65.1 1 J/mol·k and ΔH value is 0.016 kJ/mol. The negative sign of the Gibbs free energy variations (ΔG) indicates that the adsorption process is spontaneous [43]. The positive values of ΔS represent the adsorbent tendency to the absorbing material in the solution and some structural changes in adsorbent and absorbing. The positive value of ΔH represents that absorption process is endothermic and the absorption capacity increases with increasing temperature.

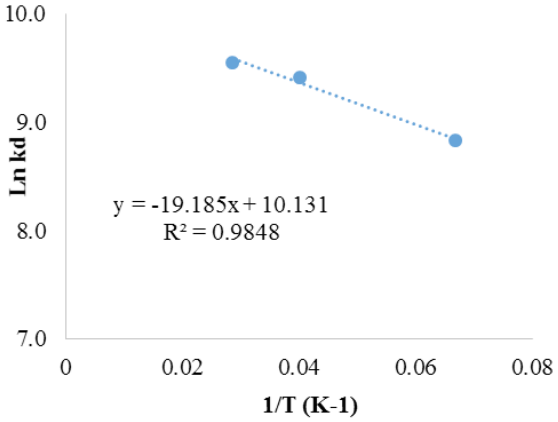

Fig. 9. Linear presentation of In k_d in 1/T for surface adsorption of humic acid on Mch/Fe-Zr nano-composite.

Table 1
Constants of acid humic adsorption kinetic model parameters by Mch/Fe-Zr nano-composite

T (k)	(K_d)	ΔG (kJ/mol)	ΔS (J/mol°k)	ΔH (kJ/mol)
288	8.8	–15.64	65.1	0.016
298	9.41	–17.62		
308	9.54	–18.54		

Kinetic parameters obtained from studying adsorption process are presented in Table 2. As can be seen in the table, considering comparison of R^2 correlation values in two kinetic models, adsorption process can be better defined by pseudo-second order model.

In Table 2, calculated thermo-dynamic parameters of humic acid adsorption by Mch/Fe-Zr nano-composite follows from pseudo-second order model. In this study the potential of application of pseudo-first order kinetic model in different times was surveyed by kinetic study.

In this study, the applicability of the pseudo-first and pseudo-second-order kinetics models was investigated by kinetic study at different initial concentrations of adsorbent material. Comparison of the values of the R^2 coefficient in the two studied kinetic models indicates the consistency of the adsorption of humic acid by the adsorbent studied from the pseudo-second order equation. Also, according to the results obtained (Table 2), adsorption capacity calculated according to kinetic equations in the pseudo-second order equation is closer to the adsorption capacity obtained from the adsorption experiments. This also confirms the adherence of the adsorption process to the pseudo-second-order kinetic model. Therefore, chemical adsorption is the process limiting step which is suggested to evaluate the reaction speed of this model.

In pseudo-first order kinetic model, ln ($q_e - q_t$) diagram against t was used to determine k_1 constant and R^2 coefficient and against t. t/q_t diagram was applied to calculate speed parameters in pseudo-second order model. q_e, k_2 values were determined to calculate y-intercept and slope of this diagram [40]. Comparison of the values of R^2 coefficient values in two studied model, indicates consistence of

Table 2
Thermo-dynamic parameters of acid humic adsorption by Mch/Fe-Zr nano-composite

Pseudo-first-order model			Pseudo-second order mode		
R^2	q_e (mg/g)	K_1 (min^{-1})	K_2 (g/mg min)	q_e (mg/g)	R^2
0.78	4.19	0.0653	0.0157	5.72	0.96

Table 3
Parameters of isotherm models of acid humic adsorption by Mch/Fe-Zr nano-composite

Langmuir			Freundlich		
R^2	q_{max} (mg/g)	K_L (L/mg)	R^2	n	Log K_f (L/mg)
0.11	–125	0	0.95	1.05	1.42

adsorption process with pseudo-second order model. The result of the study of Naghizadeh et al. showed adsorption kinetic and thermo-dynamic of elimination of Hydrophobic organic material from aqueous solutions by multi wall carbon Nano-tubes followed by pseudo-second order [44]. In addition, in a study by Wang titled humic acid adsorption from aqueous solution with polyaniline/attapulgite composite, humic acid adsorption followed from pseudo-second order model [45].

Based on Table 3, the study of the adsorption isotherms of Mch/Fe-Zr nano- composite in the elimination of humic acid showed that the data obtained follow from the Freundlich formula. Freundlich isotherm is an absorption isotherm that is empirically obtained and unlike the Langmuir model enthalpy absorption variation is independent from cover fraction and is based on heterogeneous absorption and multi-layer absorbing material on absorbent. According to the concentration of the study $R^2 = 0.95$ shows the value of the Freundlich regression, which is more suitable for this experiment.

According to the results of isothermic studies of the adsorption of humic acid by adsorbent in this study, the correlation coefficient of the Freundlich isotherm equation shows the best interpretation of the pollutant by the adsorbent. Therefore, the results indicate that the adsorbent surface is non-homogeneous or heterogeneous and has uneven and non-uniform energies. The parameters of $1/n$ and n in the Freundlich equation can determine the desirability of the adsorption process. If $1/n$ is less than 1 and n is between 1 and 10, it indicates the desirability of the adsorption process by the Freundlich isotherm model. According to Table 3, in the adsorption of humic acid by the adsorbent, the value of n is between 1 and 10 also, the value of $1/n$ is less than one, which indicates the appropriate adsorption of humic acid by the two studied adsorbents.

The parameter n in the Freundlich equation can determine the desirability of the adsorption process. If n is between 1 and 10, it indicates that the adsorption process is desirable by the Freundlich isotherm model, which is confirmed by the calculations.

In the study of Malekutian and Kalankesh titled "surveying the efficiency f silicon nanoparticles in adsorption of water humic acid", the results showed that adsorption of humic acid follows from Freundlich isotherm, the speed of which follows from second order kinetic with correlation coefficient respectively 0.8872 and 0.9936 [46]. In addition in a study performed by Khodadadi et al. about elimination of heavy metal by Fe-Zr/chitosan, it followed both isotherm models, but Freundlich isotherm was better [41].

4. Conclusion

Based on the results obtained, it can be concluded that Mch/Fe-Zr nano-composite, due to the presence of carboxylic and amine groups and having a high surface area can be effective in removal of humic acid. In addition, chitosan due to its environmental compatibility, non-toxicity and high absorption capacity has lots of applications. Chitosan is also used due to its flocculation properties in the industrial wastewater, which causes the trapping of contaminant from the solution. Variables such as adsorbent amount, pH, and initial concentration of humic acid affect on adsorption capacity and removal efficiency. Maximum removal of humic acid was at (pH = 5, adsorbent amount 2 g/L, concentration 10 mg/L, was equal to 98.5%), so it is cost-effective and suitable for adsorption of humic acid from aqueous solutions.

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References

[1] D.H.K. Reddy, S.M. Lee, Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions, Adv. Colloid Interface Sci., 201 (2013) 68–93.

[2] M. Polemio, V. Dragone, P. Limoni, Monitoring and methods to analyse the groundwater quality degradation risk in coastal karstic aquifers (Apulia, Southern Italy), Econ. Gol., 58 (2009) 299–312.

[3] O. Schmoll, G. Howard, J. Chilton, I. Chorus, Protecting groundwater for health: managing the quality of drinking-water sources, World Health Organization., (2006).

[4] C.A. Murray, S.A. Parsons, Removal of NOM from drinking water: Fenton's and photo-Fenton's processes, Chemosphere, 54 (2004) 1017–1023.

[5] M. Kabsch-Korbutowicz, K. Majewska-Nowak, T. Winnicki, Water treatment using MIEX® DOC/ultrafiltration process, Desalination, 221 (2008) 338–344.

[6] M.N. Jones, N.D. Bryan, Colloidal properties of humic substances, Adv. Colloid Interface Sci., 78 (1998) 1–48.

[7] D. Doulia, C. Leodopoulos, K. Gimouhopoulos, F. Rigas, Adsorption of humic acid on acid-activated Greek bentonite, J Colloid Interface Sci., 340 (2009) 131–141.

[8] J. Liu, H. Huang, R. Huang, J. Zhang, S. Hao, Y. Shen, H. Chen, Mechanisms of CPB modified zeolite on mercury adsorption in simulated wastewater, Water Environ. Res., 88 (2016) 490–499.

[9] C. Li, Y. Dong, D. Wu, L. Peng, H. Kong, Surfactant modified zeolite as adsorbent for removal of humic acid from water, Appl. Clay Sci., 52 (2011) 353–357.

[10] D.A. Fearing, J. Banks, S. Guyetand, C.M. Eroles, B. Jefferson, D. Wilson, P. Hillis, A.T. Campbell, S.A. Parsons, Combination of ferric and MIEX® for the treatment of a humic rich water, Water Res., 38 (2004) 2551–2558.

[11] S.C. Fan, Y.C. Wang, C.L. Li, K.R. Lee, D.J. Liaw, H.P. Huang, J.Y. Lai, Effect of coagulation media on membrane formation and vapor permeation performance of novel aromatic polyamide membrane, J. Membr. Sci., 204 (2002) 67–79.

[12] M. Khodadadi, M.H.E. Ehrampoush, A. Allahresani, M.T. Ghaneian, M.H. Lotfi, A.H. Mahvi, $FeNi_3@SiO_2$ magnetic nanocomposite as a highly efficient Fenton-like catalyst for humic acid adsorption and degradation in neutral environments, Desal. Water Treat., 118 (2018) 258–267.

[13] Y. Yoon, R.M. Lueptow, Removal of organic contaminants by RO and NF membranes, J. Membr. Sci., 261 (2005) 76–86.

[14] B. Panyapinyopol, T.F. Marhaba, V. Kanokkantapong, P. Pavasant characterization of precursors to trihalomethanes formation in Bangkok source water, J. Hazard. Mater., 120 (2005) 229–236.

[15] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interface Sci., 159 (2010) 189–197.

[16] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 97 (2006) 1061–1085.

[17] B. Tanhaei, A. Ayati, M. Lahtinen, M. Sillanpää, Preparation and characterization of a novel chitosan/Al_2O_3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorption, Chem. Eng. J., 259 (2015) 1–10.

[18] H.Y. Zhu, Y.Q. Fu, R. Jiang, J. Yao, L. Xiao, G.M. Zeng, Novel magnetic chitosan/poly (vinyl alcohol) hydrogel beads: preparation, characterization and application for adsorption of dye from aqueous solution, Bioresour. Technol., 105 (2012) 24–30.

[19] C.Y. Chen, C.Y. Wu, Y.C. Chung, The coagulation characteristics of humic acid by using acid-soluble chitosan, water-soluble chitosan, and chitosan coagulant mixtures, Environ. Technol., 36 (2015) 1141–1146.

[20] X. Zhang, R. Bai, Mechanisms and kinetics of humic acid adsorption onto chitosan-coated granules, J. Colloid Interface Sci., 264 (2003) 30–38.

[21] S.M. Seyedi, B. Anvaripour, M. Motavassel, N. Jadidi, Comparative cadmium adsorption from water by nanochitosan and chitosan, Int. J. Eng. Innov. Technol., 2 (2013) 145–148.

[22] P. Rao, M.S. Mak, T. Liu, K.C. Lai, I.M. Lo, Effects of humic acid on arsenic (V) removal by zero-valent iron from groundwater with special references to corrosion products analyses, Chemosphere, 75 (2009) 156–162.

[23] Y.P. Sun, X.Q. Li, J. Cao, W.X. Zhang, H.P. Wang, Characterization of zero-valent iron nanoparticles, Adv. Colloid Interface Sci., 120 (2006) 47–56.

[24] C. Yuwei, W. Jianlong, Preparation and characterization of magnetic chitosan nanoparticles and its application for Cu (II) removal, Chem. Eng. J., 168 (2011) 286–292.

[25] M. Faraji, Y. Yamini, E. Tahmasebi, A. Saleh, F. Nourmohammadian, Cetyltrimethyl ammonium bromide-coated magnetite nanoparticles as highly efficient adsorbent for rapid removal of reactive dyes from the textile companies' wastewaters, J. Iranian Chem. Soc., 7 (2010) 130–144.

[26] M. Samarghandi, A. Ahmadzadeh, Y. Yamini, G. Asgari, Synthesis of Fe_3O_4 nanoparticles and its performance on the removal of hexavalent chromium from aqueous solutions, J. Mazandaran Univ. Med. Sci., 22 (2013) 174–187.

[27] W.W. Ngah, S. Fatinathan, Adsorption of Cu (II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads, Chem. Eng. J., 143 (2008) 62–72.

[28] M. Ghafoori, A. Naghizadeh, Isotherm, kinetic and thermodynamics study of humic acid removal process from aquatic environment by chitosan nano particle, J. Birjand Univ. Med. Sci., 23 (2016) 222–234.

[29] A. Naghizadeh, M. Ghafouri, Synthesis and performance evaluation of chitosan prepared from Persian Gulf shrimp shell in removal of reactive blue 29 dye from aqueous solution (isotherm, thermodynamic and kinetic study), Iranian J. Chem. Chem. Eng., 36 (2017) 25–36.

[30] A. Naghizadeh, M. Ghafouri, A. Jafari, Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions, Desal. Water Treat., 70 (2017) 355–363.

[31] H. Rezaei, M.R. Narooie, R. Khosravi, M.J. Mohammadi, H. Sharafi, H. Biglari, Humic acid removal by electrocoagulation process from natural aqueous environments, Int. J. Electrochem. Sci., 13 (2018) 2379–2389.

[32] Q. Hu, N. Chen, C. Feng, W. Hu, H. Liu, Kinetic and isotherm studies of nitrate adsorption on granular Fe–Zr–chitosan complex and electrochemical reduction of nitrate from the spent regenerant solution, RSC Adv., 6 (2016) 61944–61954.

[33] K. Sreejalekshmi, K.A. Krishnan, T. Anirudhan, Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies, J Hazard. Mater., 161 (2009) 1506–1513.

[34] A. Naghizadeh, F. Momeni, H. Kamani, Study of ultrasonic regeneration and adsorption of humic acid on activated carbon, Health Scope., 7 (2018).

[35] W.W. Ngah, M. Hanafiah, S. Yong, Adsorption of humic acid from aqueous solutions on crosslinked chitosan–epichlorohydrin beads: kinetics and isotherm studies, Colloids Surfaces B: Biointerfaces, 65 (2008) 18–24.

[36] N. Nasseh, L. Taghavi, B. Barikbin, A.R. Harifi-Mood, The removal of Cr(VI) from aqueous solution by almond green hull waste material: kinetic and equilibrium studies, J. Water Reuse Desal., 7 (2017) 449–460.

[37] C. Dong, W. Chen, C. Liu, Y. Liu, H. Liu, Synthesis of magnetic chitosan nanoparticle and its adsorption property for humic acid from aqueous solution, Colloids Surf. A Physicochem. Eng. Asp., 446 (2014) 179–189.

[38] W.E. Federation, A.P.H. Association, Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA., 2005.

[39] C. Zareie, G. Najafpour, Preparation of nanochitosan as an effective sorbent for the removal of copper ions from aqueous solutions, Int. J. Eng.-Trans. B: Appl., 26 (2013) 829–836.

[40] K. Swayampakula, V.M. Boddu, S.K. Nadavala, K. Abburi, Competitive adsorption of Cu(II), Co(II) and Ni(II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent, J. Hazard. Mater., 170 (2009) 680–689.

[41] M. Khodadadi, M.H. Saghi, N.A. Azadi, S. Sadeghi, Adsorption of chromium VI from aqueous solutions onto nanoparticle sorbent: chitozan-Fe-Zr, J. Mazandaran Univ. Med. Sci., 26 (2016) 70–82.

[42] A. Daifullah, B. Girgis, H. Gad, A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material, Colloids Surf. A Physicochem. Eng. Asp., 235 (2004) 1–10.

[43] A. Eser, V.N. Tirtom, T. Aydemir, S. Becerik, A. Dinçer, Removal of nickel (II) ions by histidine modified chitosan beads, Chem. Eng. J., 210 (2012) 590–596.

[44] Z. Hubicki, A. Wołowicz, M. Leszczyńska, Studies of removal of palladium (II) ions from chloride solutions on weakly and strongly basic anion exchangers, J. Hazard. Mater., 159 (2008) 280–286.

[45] J. Wang, X. Han, H. Ma, Y. Ji, L. Bi, Adsorptive removal of humic acid from aqueous solution on polyaniline/attapulgite composite, Chem. Eng. J., 173 (2011) 171–177.

[46] M. Malakootian, L. Ranandeh Kalankesh, Assessing the performance of silicon nanoparticles in adsorption of humic acid in water, Iranian J. Health Environ., 6 (2014) 535–544.