Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20822

83 (2017) 47–55
July

Evaluation of humic acid removal efficiency in aqueous solution by feather protein granules

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Received 21 July 2016; Accepted 12 April 2017

ABSTRACT

The use of cheap adsorbent has been studied as an alternative substitution of activated carbon for the adsorption of the organic pollutant from aqueous solution. In the present study, the effect of contact time, pH, initial concentration of humic acid, and temperature was tested for investigation of the humic acid removal efficiency of the feather protein granule as a low-cost adsorbent. The equilibrium time was 120 min. It was found that the removal efficiency depended on pH and the highest removal was 68.3 % at pH of 3.0. The equilibrium adsorption data fitted with linear of Freundlich and Langmuir isotherm models. The thermodynamic studies revealed the endothermic and spontaneous process in 298°C. The feather protein granules were successfully used for the adsorption of humic acid from aqueous solution.

Keywords: Feather protein; Humic acid; Removal efficiency; Aqueous solution

1. Introduction

Humic acid is one of the main pollutants of organic substances and of the humic substances components which are presented in water resources [1]. Humic acids cause bacteria growth, undesirable color, taste and smell and result in a decrease of water quality [2,3]. Also, humic acids tend to form complexes with heavy metals and pesticides which lead to the transmission of the pollutants in water resources [4,5]. Humic acids react with chlorine and produce disinfection byproducts such as trihalo methanes, halo acetic acids, and halo ketone during water treatment [6–8]. Toxicity, carcinogenicity and mutagenic effect of disinfection by-products and their complications have caused public concern [9,10]. The Environmental Protection Agency (EPA) has approved 100 ppb of trihalo methanes in the drinking water quality as maximum level standard [7]. The epidemiological studies have been proven disinfection by-products effects on the bladder cancer, colon and rectal cancers [11]. According to aesthetic and health effects of humic substances in water, removal of these compounds are very important before disinfection by chlorine [12]. Conventional water treatment processes are not able to remove natural organic substances in low concentrations and humic acid removal efficiency of these processes is about 10% to 15% so, these substances must be removed from water systems by a secondary process to achieve standards in polluted waters [13,14]. Com-

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1944-3994 / 1944-3986

mon methods to remove natural organic substances include chemical coagulation, membrane filtration, and advanced oxidation which is limited to high costs [4,5,12–15]. Among the various treatment technologies, adsorption is considered as a quick, cheap, efficient, and easy method that studies have rapidly evolved to develop a low-cost adsorbent, in recent years [16,17]. Adsorption is one of the effective ways to remove humic acids and various adsorbents such as activated carbon, clay, zeolite, chitosan, and metal oxides have been studied to remove humic acids [4,18,19]. A study by Tashauoei et al. was conducted to remove humic acid from aqueous solution under different conditions using modified nano zeolite A. Their results indicated that the maximum humic acid removal of 83.16% on nano zeolite occurred at pH 3 and contact time of 30 min [20]. Zhu et al. conducted a study for adsorption of humic acid by activated carbon from natural water. Their results showed that powder activated carbon had a good performance in removing of humic acid at high concentrations, low pH, and low temperature. The absorption model followed the pseudo-second-order kinetic equation [21]. Kamari et al. studied the sawdust adsorbent for adsorption of humic acid from aqueous solutions. They found that sawdust adsorption capacity was 68.4 mg·L^{-1} at pH 2 and humic acid initial concentration of 80 mg·L^{-1} [22]. Peng et al. used the Bentonite column as an adsorbent to remove humic acids at acidic conditions. Bentonite column had a high adsorption capacity (537 mg·g^{-1}) in removing of humic acid and it can be an effective adsorbent to remove humic acids from water [23]. Humic acid adsorption kinetics and mechanisms on chitosan granules were studied by Zhang et al. This study indicated that humic acid adsorption depended on pH strongly and it significantly decreases with an increase of pH so humic acid adsorption occurred in a high percent in acidic and neutral conditions. The adsorption process was followed by the Langmuir model at different concentrations of humic acid and constant pH [24].

One of the natural and cheap adsorbents is chicken feathers. Chicken feathers have been recently used to produce keratin nanoparticles and have had a good performance in removing of pollutants. Moreover, using chicken feathers as an adsorbent for removing of subsequent pollution from the environment is environment-friendly manner. It has been determined that chicken feather protein is mostly insoluble and has non-toxic keratin, which has very high adsorption ability [25,26]. In previous studies, chicken feathers have been used to remove water pollutants such as heavy metals like arsenic, cadmium, chromium, copper, zinc etc. [25,27,28]. Zhou et al. conducted a study to adsorb oil from aqueous solutions by a keratin porous sponge prepared from chicken feathers. Their results showed that the modified material had high adsorption capacity for oil derivatives [29]. Eslahi et al. investigated to assess the feasibility of producing nanoparticles from feathers waste after modifying by ultrasonic and enzymatic hydrolysis. The findings indicated that particle size decreased after ultrasonic treatment. Also in this research, crystallization and thermal stability of feathers nanoparticles increased by enzymatic hydrolysis during the ultrasonic treatment [30]. A study was conducted by Pandima et al. to apply chicken feathers as an adsorbent to remove acid brown dye from aqueous solutions. In that study, adsorption capacity was investigated in optimal conditions such as pH, contact time, temperature, amount of adsorbent, and adsorbate concentration. The data of study was consistent with Freundlich and Langmuir isotherm model [31]. The modified feathers with 5% tannic acid were applied by Yang et al. to remove metal cations from aqueous solutions. Metal cations adsorption by modified and unmodified feather fibers was examined as a function of fiber weight, temperature, and pH. The adsorption rate was increased at alkaline pH, ambient temperature and increasing of tannic acid. The maximum adsorption of metal cations occurred at pH 11 whereas at acidic pH, cations adsorption was negligible. The findings indicated that feather fibers modified by tannic acid had good adsorption of metal cations and can be used as the metal adsorbent from aqueous solutions [32].

In the present study, chicken feathers obtained from slaughter houses and breeding centers was used as the new bio-availability adsorbent which is unusable. For this purpose, the porosity of chicken feathers was increased by pretreatment and thermal modification and then it was studied for humic acid adsorption from aqueous solutions.

2. Experimental

2.1. Materials and instruments

This descriptive study was conducted in a chemistry laboratory at the School of Public Health Yazd. The humic acid absorption spectra in different concentrations were scanned by UV-Vis spectrometer at wavelength ranges of 200–700 nm in various concentrations to determine the maximum wavelength of humic acid absorption

All chemicals used in the experiments were of analytical grade. In this study, humic acid from Sigma-Aldrich Company was used to prepare the stock solution. Other materials were purchased from The German Company, Merck. The used devices include water distillation device, sensitive analytic scale model of R200 with the precision of 0.0001 g (A&D Company, Japan) pH meter model of Mi 151 for measuring the pH (Wagtech Company, U.K.), Ultrasonic baths model of TI-H-5 (Elma Company, Germany) for homogenizing the samples, orbital shaker model GFL 137 For proper mixing of adsorbent and humic acid solution and also to control the temperature of the suspension, the scanning electron microscopy (SEM) model Phenom (Holland) for observation of surface morphology and UV-Vis spectrometer model of SP-3000 PLUS (OPTIMA Company, Japan) to measure humic acid concentration before and after the adsorption process.

2.2. Bio-sorbent preparation

Chicken feathers were obtained from slaughterhouses. It was washed with detergent, rinsed with distillate water 3 times, and dried at 70°C overnight. The chicken feathers were heated in the furnace at 120°C for an hour to increase the amount of porosity and to remove organic pollutants sticking to the feathers. The obtained chicken feathers were grind by an electric grinder and then the grind feathers were sized by standard sieves with the pore size of 60–100 mesh (diameter of 250 and 149 µ). The isolated granules were washed with 20% ethanol and then 5 times with distilled water to remove organic materials. The porous granules obtained from chicken feathers as adsorbent were stored in the desiccators for the next adsorption experiments after drying at laboratory temperature.

2.3. Determination of pHzpc

The first stage of the experiment consisted of determining the pH_{ZPC}, for this purpose, the 50 ml of the 0.005 M solution of NaCl as the electrolyte was poured into six 150 ml flasks and the initial pH solutions were adjusted to values of 2, 4, 6, 8, 10 and 12 by using 0.1 M NaOH or HCl solution. Then, 0.1 g of adsorbent was added to each sample. The mixtures were stirred at 125 RPM by an orbital shaker for 24 h. The end of 24 h, the final pH solutions were measured by using a pH meter, again. The same experiments were carried out without adsorbent and the curve of final pH changes was plotted against the initial pH for obtaining of pHzpc.

2.4. Adsorption experiments

A stock solution of 50 mg·L^{-1} of humic acid was prepared by dissolving of the appropriate amount of humic acid in the 15% ethanol-water. The required concentrations of samples and standards were prepared daily by diluting the stock solution with distilled water. Several different experiments were performed to optimize the effective parameters such as solution pH, initial concentration of humic acid, contact time and solution temperature on the adsorption process.

To determine the effect of time, the experiments were performed in different contact times of 15, 30, 60, 120 and 180 min while all other parameters were 0.1 g adsorbent in 50 ml of 5 mg·L^{-1} humic acid at pH 3 and 25°C. For investigation of pH effect on humic acid removal efficiency by feathers protein granules, experiments were performed at four levels of 3, 5, 7 and 9 were adjusted by a buffer solution in the initial concentration 5 mg·L^{-1} and 0.1 g adsorbent while contact time of 120 min and a temperature of 25°C were constant. At the next stage, to determine the effect of initial concentration on removal efficiency, all parameters were constant and removal efficiency was investigated by changing the initial concentration at four levels of 5, 10, 25 and 50 mg·L^{-1}. Then the effect of temperature was investigated by varying of temperature from 25 to 65°C at the obtained optimum condition that was initial concentration 5 mg·L^{-1}, 0.1 g adsorbent, pH 3 and contact time of 120 min.

Ultimately, the flasks were excluded from the shaker after a required time. The adsorbent was separated from the suspension by Whatman filter No. 42 and the clear solutions were analyzed by spectrometer UV-Vis at 292 nm to obtain the concentration of remaining humic acid. All experiments were done triplicate and the mean of data was calculated. Finally, the humic acid removal efficiency and adsorption capacity were calculated for each experiment using the following equations [33].

$$\%RE = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q = \frac{(C_o - C_e)}{m} \times V \quad (2)$$

In these equations, RE is removal efficiency, q is adsorption capacity, C_0 and C_e are initial and final humic acid concentrations in the solution (mg·L^{-1}) respectively, V is the volume of solution (L), and m is adsorbent mass (g).

2.5. Isotherm and thermodynamic studies

The equilibrium studies conducted at different initial concentrations, 0.1 g fixed adsorbent dose and pH of 3. Then, the obtained results were fitted into the linearized Langmuir and Freundlich adsorption isotherms, which linear form of isotherms was applied for adsorption equilibrium are of the Eqs. (3) and (4):

$$\frac{C_e}{q_e} = \frac{1}{Q_m \cdot b} + \frac{C_e}{Q_m} \quad (3)$$

$$In(q_e) = InK_F + \frac{1}{n} InC_e \quad (4)$$

where q_e is the amount of pollutant adsorbed in the unit of adsorbent mass (mg·g^{-1}), C_e is the equilibrium concentration (mg·L^{-1}), Q_m and b are Langmuir constants related to maximum adsorption efficiency and energy of adsorption and K_F and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively.

Finally, the four experiments were done by adding a fixed amount of 0.1 g adsorbent to a series of 150 ml flasks filled with 50 ml of 5 mg·L^{-1} of humic acid which were placed in the temperature programmable orbital shaker at 125 RPM in different temperatures of 25, 45, 55 and 65°C to obtain thermodynamic parameters. Then, the thermodynamic parameters were calculated by Eqs. (5) and (6) as below:

$$\Delta G = -RTInK_c \quad (5)$$

$$InKc = \frac{\Delta S}{R} + \frac{\Delta H}{R} \times \frac{1}{T} \quad (6)$$

where R is the gas constant (8.314 J·mol^{-1} °K^{-1}), K_c is the equilibrium constant, T is the absolute temperature °K. The ΔH and ΔS parameters were calculated from the slope and intercept of the plot of lnK_c vs. $1/T$ according to Eq. (6).

3. Results

3.1. Characteristic of adsorbent

3.1.1. UV-Vis spectra

The scanning graphs for determining of a maximum wavelength at different concentrations are shown in Fig. 1. According to Fig. 1, maximum wavelength of 292 nm was determined for further measurement of humic acid in ethanol-water solution.

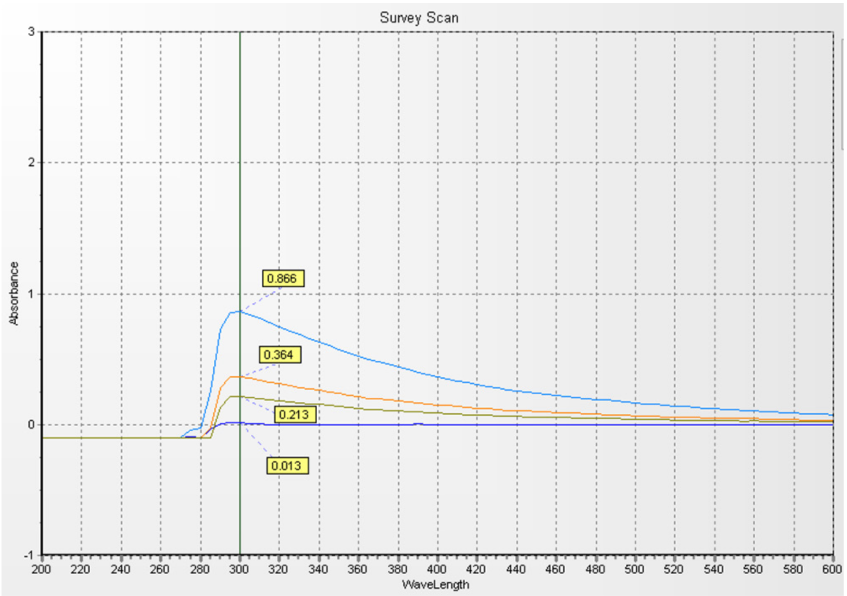

Fig. 1. Spectrum of scanning wavelength of humic acid at various concentrations**.**

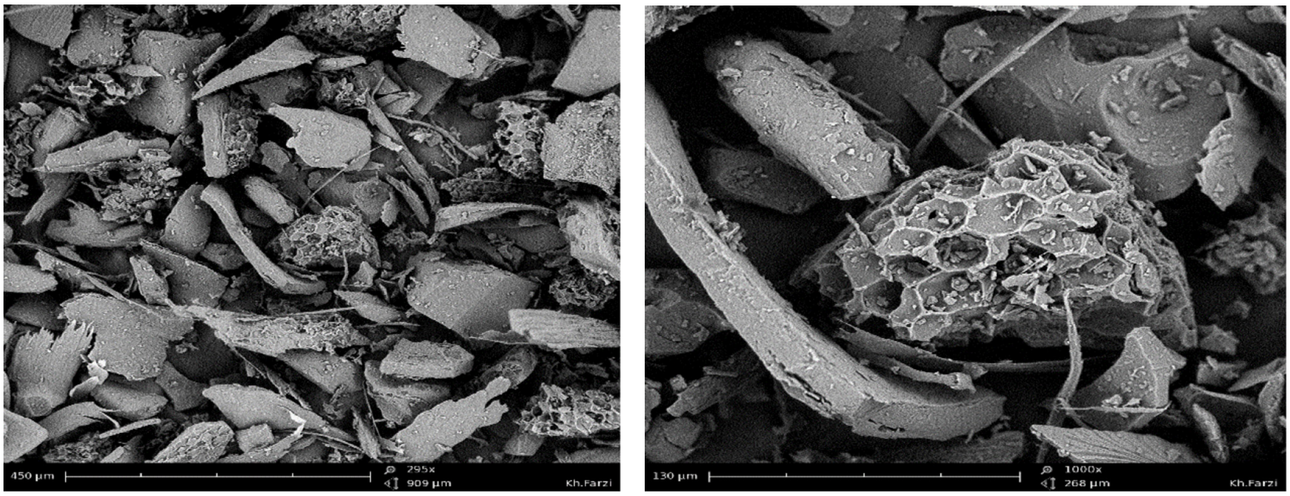

Fig. 2. SEM images of feather protein granule (a) 500× magnitude (b) 1000× magnitude.

3.1.1.1. SEM

The SEM observations were employed to obtain the surface physical morphology of adsorbent. Fig. 2 shows the image of the feather protein granules surface.

It can be found SEM image of the feather protein granule at 500× magnification that there are several pores on the adsorbent. Fig. 2b shows a magnified part of Fig. 2a at 1000× pore on the father protein granule.

3.1.1.2. pHzpc

The pH of zero point charge is the pH, which the net charge of surface is zero. The results for determining of pH_{ZPC} are shown in Fig. 3. The point of intersection of the curves of pH_f vs. pH_i was recorded as pHzpc which was set equal to 5.3 according to Fig. 3.

3.2. Optimization of effective parameters

Several adsorption experiments were carried out to obtain the best adsorption condition in sequential stages. At each stage of the experiment, one variable was changed while other experimental conditions were constant. The next stage, the obtained optimal parameter in the previous stage was constant and the experiments were performed by a variety of another parameter.

3.2.1. Effects of contact time

Fig. 4 shows the results for effect of contact time on adsorption process efficiency. As the figure shows, humic acid removal efficiency by feather protein granules increases with an increase in contact time. The removal efficiency was increased from 37% to 66% with an increasing of contact

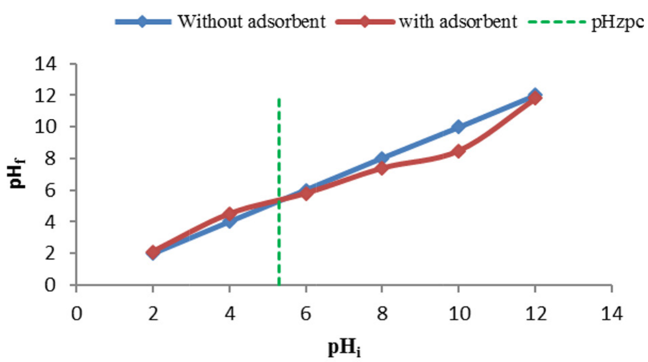

Fig. 3. The plots of pH_f vs. pH_i.

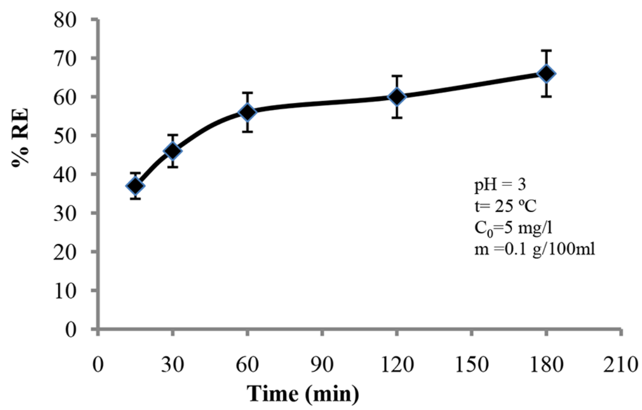

Fig. 4. Effect of contact time on removal of humic acid by feathers protein granules.

time from 15 to 120 min and was nearly constant in further increasing of time to 180 min.

According to the results, equilibrium time of 120 min was selected as the optimal contact time for humic acid removal and was considered constant in the next experiments.

3.2.2. Effect of pH

The results of the pH effect on the humic acid removal efficiency by feather protein granules are represented in Fig. 5. As the figure shows, removal efficiency decreased significantly from 57.2% to 5.6% with an increase in pH from 3 to 9. Hence, the best pH for removal of humic acid by this adsorbent was pH of 3 which was considered constant in the future experiments.

3.2.3. Effect of initial concentration

Fig. 6. shows the results related to the effect of humic acid initial concentration on removal efficiency. Based on Fig. 6, we can see that maximum humic acid removal is at the concentration of 5 mg·L^{-1}. The results indicated that an increase in the initial concentration of humic acid from 5 to 50 mg·L^{-1} led to a decrease in removal efficiency from 58% to 28.3%.

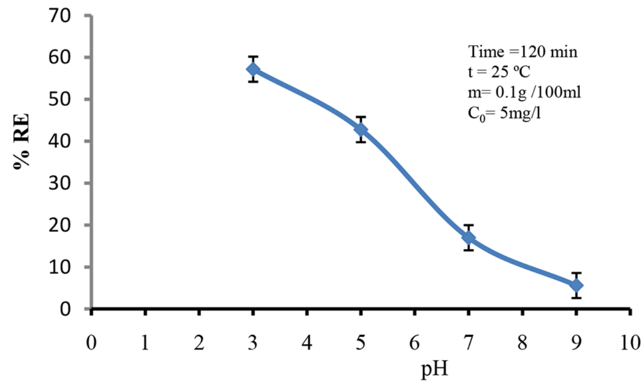

Fig. 5. Effect of pH on removal of humic acid by feather protein granules.

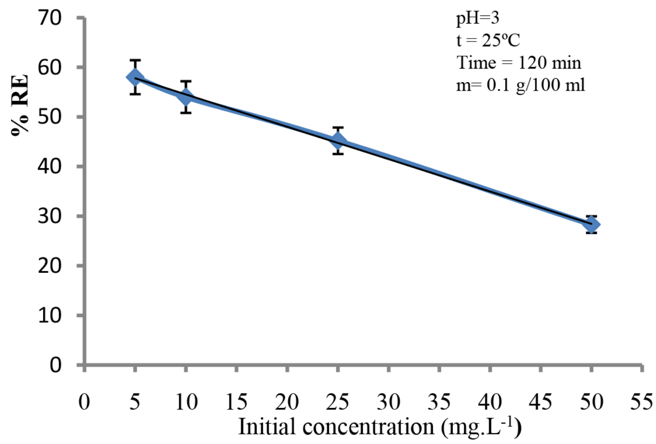

Fig. 6. Effect of initial concentration on removal of humic acid by feathers protein granules.

3.2.4. Effect of temperature

The findings for the effect of temperature on humic acid removal efficiency are shown in Fig. 7. As the results indicate the removal efficiency was decreased from 64% to 30% with an increase in temperature from 25°C to 65°C. Fig. 7 indicate that the best removal efficiency occurred in the temperature of 25ºC.

4. Adsorption isotherms

The plot of C_e/q_e vs. C_e obtained from a linear Langmuir isotherm model that is shown in Fig. 8. The Langmuir constant of Q_m and b were determined from the slope and intercept of the linear and found to be 18.67 mg/g and 0.11 L / mg, respectively.

The linear plot of log q_e vs. log C_e is shown in Fig. 9 that is a linear form of Freundlich isotherm. The Freundlich constants K_F and n were determined from the slope and intercept of the linear and were 2.14 mg·g^{-1} and 1.78, respectively.

The correlation coefficient (R^2) showed that the experimental data were obeyed both Freundlich and Langmuir

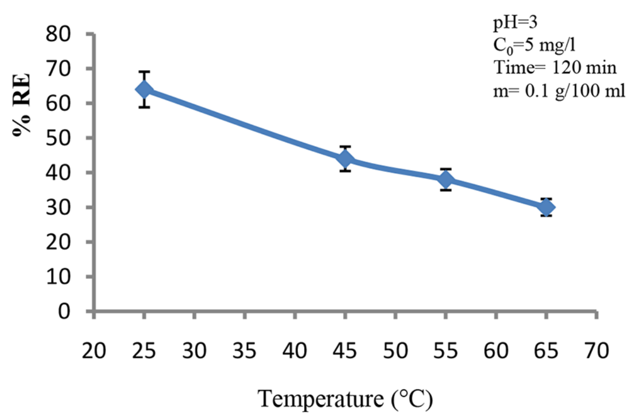

Fig. 7. Effect of temperature on removal of humic acid by feather protein granules.

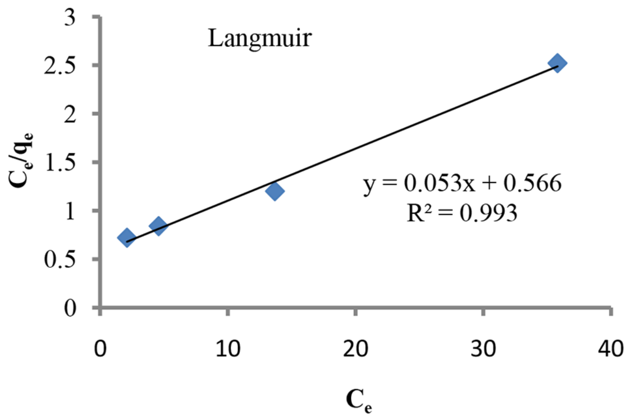

Fig. 8. Langmuir isotherm plot for adsorption of humic acid on feather protein granules.

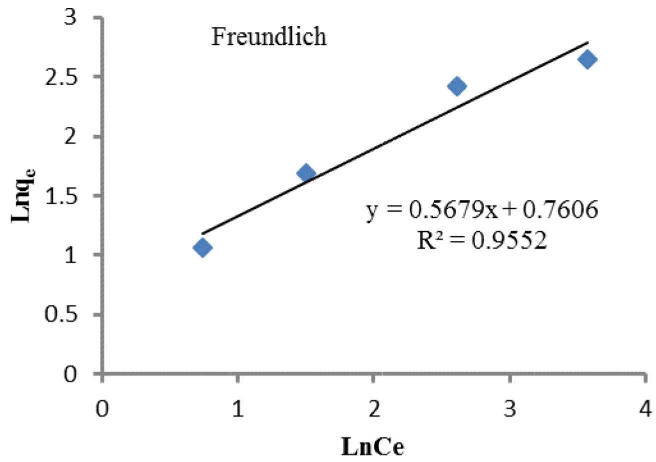

Fig. 9. Freundlich isotherm plot for adsorption of humic acid on feather protein granules.

Table 1
Parameters of Freundlich and Langmuir isotherm models for adsorption of humic acid

	Langmuir			Freundlich		
Parameters	Q_m	b	R^2	K_F	n	R^2
Values	18.67	0.11	0.99	2.14	1.78	0.95

models, exhibiting heterogeneous surface conditions and a monolayer adsorption [34]. The obtained parameters of two isotherm models are presented in Table 1.

5. Thermodynamic parameters

Fig. 10 indicates the effects of temperature on the removal efficiency of humic acid. The humic acid removal efficiency decreased with an increase in temperature from 25°C to 65°C.

Thermodynamic parameters, Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated and are represented in Table 2.

The Gibbs free energy increased from –1412.21 to 2360.51 J·mol^{-1} by rising of temperature from 25 to 65°C. The enthalpy and entropy changes of adsorption were 419.6 J·mol^{-1} and –1.32 kJ·mol^{-1}·K^{-1}, respectively.

6. Discussion

6.1. Effect of contact time on adsorption efficiency

According to Fig. 4, it is observed that the absorption rate is high and quick in the primary stages of the experiment (60 min). Over this time, the absorption rate had a constant process. This may be related to the large numbers of available vacant sites for adsorbent in the early stages. The humic adsorption rate decreases with time because of the accumulation of humic acid particles on unoccupied sites that cause to decrease of the number of active sites and also the number of absorbable particles in the solution. It can be noted that the concentration gradient between humic acid molecules in solution and adsorptive sites on the adsorbent surface is high in the primary contact times. It leads to the increase in humic acid adsorption in the early stages. More time, the concentration downturn gradually and causes a decrease in the concentration gradient in the later stages (after 120 min).

6.2. Effect of pH on adsorption efficiency

The results (Fig. 5) showed that there was an inverse relationship between solution pH changes with removal efficiency. With regard to Fig. 3, zero point charge (pH_{ZPC}) of the adsorbent was equal to 5.3. As a result, the adsorbent surface charge is positive at pH lower than pHzpc and it creates the strong electrostatic force with negative molecules of humic acid and therefore, it leads to remove humic acid. At pH higher than pH_{ZPC}, the adsorbent charge is negative due to the OH^- adsorption which leads to an electrostatic repulsive force between humic acid ions in solution with the adsorbent surface so, the removal efficiency decrease at high pH values. Moreover, a decrease in removal efficiency with increasing of pH can be related to the effect of pH on the adsorbent surface charge and also on the ionization of

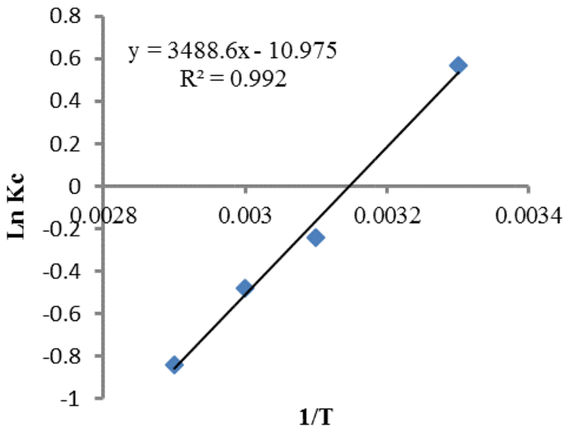

Fig. 10. The plot of LnK_C via 1/T plot for adsorption of humic acid on feather protein granules.

Table 2
Thermodynamic parameters for adsorption of humic acid on feather protein granules

T (k)	1/T*10^{-2}	LnK_c	ΔG (J·mol^{-1})	ΔS (kJ·mol^{-1} K^{-1})	ΔH (J·mol^{-1})
298	0.33	0.57	–1412.21	–1.32	419.6
318	0.31	–0.24	634.52		
328	0.30	–0.48	1308.95		
338	0.29	–0.84	2360.51		

humic acid molecules. Since the PK_a of carboxylic and phenolic groups in humic acid molecules is around 3 and 9. It is expected that carboxylic groups are without proton at pH above 3 and its negative charge leads to increase in repulsive force between humic acid molecules and the feather protein granule surface which had a negative charge at pH value higher than 5.3. These findings are consistent with the findings of Zhan et al. which was conducted to humic acid removal from aqueous solutions by zeolite modified with cetyl pyridinium bromide [18] and also with the findings of the study conducted by Hartono et al. which was studied on the layer structure of graphene oxide as a new adsorbent for removal of humic acid from aqueous solutions [35].

6.3. Effect of initial concentration on adsorption efficiency

According to Fig. 6, the removal efficiency increased at low concentrations of humic acid. It is due to the short diffusion path and adequate space that the adsorption on the vacant sites of the adsorbent surface occurs great quality. At high concentrations of humic acid, these vacant sites saturate fast and more adsorption requires penetration into deep areas of adsorbent by passing through a relatively long path which leads to a decrease in adsorption efficiency. In addition, at high concentrations, due to increase in electrostatic repulsive forces between the negative charges of humic acid molecules, adsorption rate decreases and the removal efficiency decreases, consequently. It seems that at high concentrations, the adsorbed molecules of humic acid on the surface of feather protein granules, due to the high molecular volume, cause to fill much space around the adsorbent surface that this phenomenon leads to the diminish of space for other molecules. It is a reason for decreasing in removal efficiency.

According to regression coefficient values presented in Table 1, the correlation coefficient for two models was higher than 0.95. It reveals that the both equations are capable of describing humic acid adsorption by feather protein granules but Langmuir was better than Freundlich. The Langmuir isotherm gives information about the maximum capacity of adsorption (Q_m) that it was 18.7 mg·g^{-1} for feather protein granule in the removal of humic acid. The b constant was 0.11 L·mg^{-1} that is related to the energy of adsorption. It has been shown that the b value between 0 and 1 indicates beneficial adsorption [36]. The values of constant parameters were determined to be K_F = 2.14 and n = 1.78. K_F is the adsorption capacity (mg·g^{-1}) and n is a constant for the adsorption intensity. The value of n larger than one suggests that the adsorption approach to a maximum.

6.4. Effect of temperature on adsorption efficiency

Fig. 10 shows that the humic acid removal decreased with an increase in temperature from 25°C to 65°C. This diminution in the efficiency may result in an increasing in the movement of humic acid molecules and thus a decrease in the attraction force between humic acid molecules and adsorbent surface. This means that some effective and active bands break down probability with an increasing in temperature. As a result of this reaction, the necessary attractive force to keep humic acid molecules on the vacant sites of the adsorbent was decreased and it causes humic acid removal efficiency decreases with temperature. These findings are consistent with the results of the study by Zhu et al. to evaluate of adsorption behaviors of humic acid by activated carbon from natural water [21].

As shown in Table 2, the positive value of Δ*H* confirmed the endothermic adsorption by humic acid – feather granule system, whereas the negative ΔS values confirmed the randomness at the solid – solute interface decreased during adsorption. The negative Δ*G* values of humic acid adsorption onto feather granules at 298ºK was due to the fact that the adsorption processes were spontaneous with a high preference of humic acid onto feather granules. Also, the value of Δ*G* decreases with an increase in temperature which indicated the spontaneous nature of adsorption of humic acid was inversely proportional to the temperature and the adsorption process is favorable at low temperature.

6.4.1. Adsorption mechanism

The main interactions in physisorption process include hydrogen-bonding, Vander Waals forces, and diffusion into pores. Usually, in a batch experiment, different pHs are carried out in order to consider the mechanism of the adsorption process. Reactions (1)–(8) show the humic acid (HA) adsorption by feather protein (FP) can occur in the various pHs of the solution.

at pH < 3 $FP + H^+ \rightarrow FPH^+$ (1)

$HU + H^+ \rightarrow HUH^+$ (2)

in pH = 3–5.3 $HU \rightarrow HU^- + H^+$ (3)

$FPH^+ + HU^- \rightarrow FPH - HU$ (4)

in pH + 5.3–9 $FP + OH^- \rightarrow FPOH^-$ (5)

$-FPOH^- HU \rightarrow FP{-}HU^-$ (6)

at pH ≥ *9* $HU + OH^- \rightarrow HU^- + H_2O$ (7)

$-FPOH^{-+} HU^- \rightarrow$ no interaction (8)

Reactions (1) and (2) indicate the protonation of the functional groups of feather protein (FP) surface and humic acid at pH lower than 3. Reaction (3) shows the dissociation of the humic acid molecules to form Hu^- at pH values 3 until 9. The formation of surface complexes of humic acid anions with the protonated functional groups happen between pH 3 and pH 5.3, and the adsorption process is chemisorption according to reaction 4. With the conversion of more –FP groups to – FPH^+, there were more sites available on the feather protein surface for humic anions adsorption and removal efficiency increased. At pH more than 5.3, the adsorption of OH^- ions by FP from the solution appear through on the surface of FP that is presented in Reaction (5). Moreover, the electrostatic repulsion between the humic acid and the surfaces of the adsorbent increased with the formation of more $-FPOH^-$ sites on the surface. This effect would result in the decrease of humic acid adsorption on the feather protein with increasing solution pH values. On the other hand, with the increase of solution pH, Reaction (5) proceeded to the formation of anions, resulting in a decrease in the number of sites on the surface of feather protein for adsorption of humic anions and thus decreasing of removal efficiency. In this state, the adsorption of humic ions might occur through an outer complex (6). But at higher solution pH (basic pH), Reaction (7) might proceed. It indicates when the pH increases to values of 9, the humic acid react with hydroxide ions to form an anion. There were no Reaction (8) and the adsorption process decreases, vigorously.

6.4.2. Comparison of feather protein granules efficiency with other investigations

It is important to compare the efficiency of feather protein from this study with other adsorbents since this will suggest the effectiveness of feather protein as a low-cost adsorbent for humic acid removal. The experimental data of the contact time and pH investigations are lower than other values reported by Wang et al. [4] and Zhang and Bai [24]. The adsorption capacity varies and it depends on the characteristics of the extent of surface/surface modification and the initial concentration of the adsorbate. The experimental data of adsorption capacity in the present investigations are higher than other reported by Zhang and Bai [24] and Tao et al. [37]. Comparative results revealed that feather protein granules provides a better adsorbent property, with low cost and abundant availability in the environment, for humic acid removal in acidic pHs and could be used in water treatment.

7. Conclusion

Removal of humic acid on feather protein granules attained equilibrium after about 120 min of contact by agitation speed 125 RPM. The overall removal efficiency increased with a decrease in the pH, giving a maximum removal efficiency of feather protein granules of 57.2% at the pH value of 3. The obtained data well correlated with the Langmuir and Freundlich adsorption isotherm models and results showed maximum adsorption capacity based on Langmuir isotherm model to be 18.67 mg HA per g feather protein granules. The thermodynamic data of HA adsorption on feather protein granules indicated the spontaneous process for HA adsorption at 25ºC. The Gibbs free energy change (DG) for the HA adsorption onto feather protein granules was calculated to be about –1.412 $kJ \cdot mol^{-1}$. Feather protein granule represented the most suitable adsorbent for HA adsorption and could be utilized as low-cost adsorbent for removal of humic acid from aqueous solution at low concentrations.

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