Synthesis of walnut shell modified with titanium dioxide and zinc oxide nanoparticles for efficient removal of humic acid from aqueous solutions

Ali Naghizadeh, Habibeh Shahabi, Fatemeh Ghasemi and Ahmad Zarei

ABSTRACT

The main aim of this research was to study the efficiency of modified walnut shell with titanium dioxide (TiO_2) and zinc oxide (ZnO) in the adsorption of humic acid from aqueous solutions. This experimental study was carried out in a batch condition to determine the effects of factors such as contact time, pH, humic acid concentration, dose of adsorbents (raw walnut shell, modified walnut shell with TiO_2 and ZnO) on the removal efficiency of humic acid. pH_{zpc} of raw walnut shell, walnut shell modified with TiO_2 and walnut shell modified with ZnO were 7.6, 7.5, and 8, respectively. The maximum adsorption capacity of humic acid at concentration of 30 mg/L, contact time of 30 min at pH = 3 in an adsorbent dose of 0.02 g of walnut shell and ZnO and TiO_2 modified walnut shell were found to be 35.2, 37.9, and 40.2 mg/g, respectively. The results showed that the studied adsorbents tended to fit with the Langmuir model. Walnut shell, due to its availability, cost-effectiveness, and also its high adsorption efficiency, can be proposed as a promising natural adsorbent in the removal of humic acid from aqueous solutions.

Key words | adsorption, humic acid, titanium dioxide, walnut shell, zinc oxide

Ali Naghizadeh (corresponding author)
Habibeh Shahabi
Fatemeh Ghasemi
Department of Environmental Health Engineering,
    Faculty of Health,
Birjand University of Medical Science (BUMS),
Birjand,
Iran
E-mail: aliinaghizadeh@gmail.com

Ali Naghizadeh
Medical Toxicology and Drug Abuse Research
    Center (MTDRC),
Birjand University of Medical Sciences (BUMS),
Birjand,
Iran

Ahmad Zarei
Department of Environmental Health Engineering,
    Faculty of Health,
Gonabad University of Medical Science,
Gonabad,
Iran

INTRODUCTION

Humic and fulvic acids are known as the main precursors of trihalomethanes and other disinfection by-products in water (Graham 1999). Humic acid is a major component of organic compounds originating from decomposition of dead plant materials, animal bodies, and biological activities of microorganisms (Jiahong *et al.* 2014) which exists in a yellow to black color in almost all natural waters (Corin *et al.* 1998). Humic acid may cause water to have an undesirable taste and color. Moreover, it acts as a nutrient for the growth of bacteria in water distribution systems. Humic acid can cause blockage of membranes in membrane treatment processes, and therefore, increase the operational costs. Furthermore, humic acid can form complexes with chlorine, heavy metals, pesticides, and herbicides, creating carcinogenic compounds (Graham 1999; Rubia *et al.* 2006; Naghizadeh 2016). Thus, even low levels of humic acid can cause major problems in water.

Various processes, such as chemical coagulation, advanced oxidation, membrane separation, adsorption and bio-degradation, have been studied for the removal of humic acid from water. Among these, adsorption is most used due to its simplicity and cost-effectiveness. Due to its characteristics, many studies have been carried out in order to develop a suitable adsorbent for the removal of humic acid from water (Duan *et al.* 2003; Lorenc-Grabowska & Gryglewicz 2005; Salman *et al.* 2007; Wang *et al.* 2010, 2011). Recently, a great deal of attention has been paid to the adsorption process. Adsorption efficiency depends on several operating variables, such as solution pH, adsorbent dosage, contact time, type of adsorbent and organics (Dehghani *et al.* 2013; Naghizadeh 2015). In the case of expensive adsorbent application, the adsorption process will also be expensive. Therefore, it is better to use natural adsorbents such as agricultural wastes which are

inexpensive and abundantly available. There are many studies in the literature regarding the adsorption of humic acid onto different adsorbents, but few studies have been done on the removal of humic acid by natural adsorbents. Therefore, in this study, we attempted to experimentally investigate the effectiveness of walnut shell, due to its several advantages in water treatment, in the removal of humic acid from aqueous solutions using batch adsorption method.

MATERIALS AND METHODS

This research is a practical study carried out experimentally on a batch basis. The raw material used in this study was walnut shell. Initially, the raw walnut shell was washed to remove any dust and dirt, ground, sieved and then used in the experiments. Also, ZnO and TiO_2 were used as catalysts.

Synthesis of walnut shell

The synthesis of modified walnut shell with TiO_2 and ZnO nanoparticles was performed in environmental health engineering laboratories of Birjand University of Medical Sciences in Iran. 0.75 g of TiO_2 and ZnO powders were carefully weighed and placed separately into 500 mL Erlenmeyer flasks. Then, 200 mL of deionized water was added and the suspension stirred for 30 min (agitation speed = 200 rpm) until the solution turned colorless. 15 g of the prepared adsorbents were then added separately to each of the solutions and stirred again for 12 hours at 200 rpm. After that, they were dried in an oven at 110 °C for 8 hours. Then, the temperature of the oven was fixed at 185 °C for 2 hours to dry the adsorbent completely. The dried powder was washed with double distilled water and filtered. Finally, the filter cake was placed in a beaker and then dried in an oven at 100 °C for 12 hours.

Preparation of stock solution of humic acid

The stock solution of humic acid was prepared by dissolving 926 mg of humic acid (purchased from Acros Company) in 1 L of distilled water. The purity of the purchased humic acid was 54% and the concentration of the stock solution was 500 mg/L. The chemical structure of humic acid is shown in Figure 1.
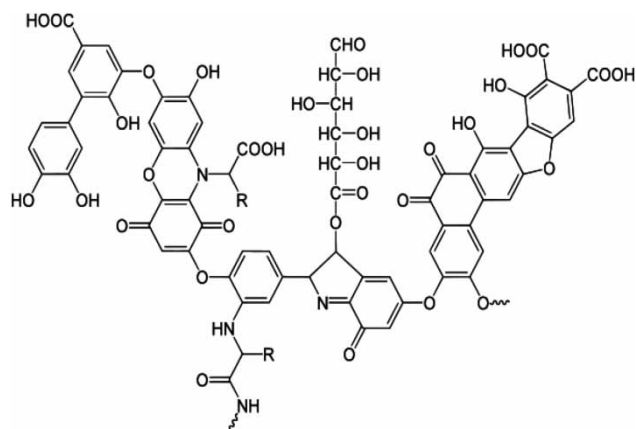

Figure 1 | Chemical structure of humic acid.

Adsorption experiments

In this study, the effects of various parameters such as initial concentration of humic acid, adsorbent dosage, contact time, and pH were studied. Several 250 mL Erlenmeyer flasks containing doses of walnut shell (20, 30, 50, and 100 mg), 100 mL of humic acid solution at various concentrations (10, 15, 20, 30 mg/L), pHs (3, 5, 7, 9, and 12), and contact times (5, 10, 15, 20, 30, and 40 min) were placed on shakers at 200 rpm to be mixed completely. Then, the samples were filtered and measured by a UV/VIS Spectrometer (+T80) at 254 nm. All the experiments were repeated twice to represent the normal cases. Adsorption efficiency of humic acid by walnut shell was calculated from the equation:

$$q_e = \frac{(C_0 - C_e)}{M} \times V$$

where C_o and C_e = initial and final concentration of humic acid (mg/L), M = weight of adsorbent (g) and V = volume of solution (L).

RESULTS AND DISCUSSION

Characteristics of the adsorbents

Scanning electron microscope (SEM) pictures of the raw walnut shell, walnut shell modified with ZnO, and walnut

shell modified with TiO_2 are shown in Figure 2. By comparing the surface structure of the adsorbents, it can be concluded that the walnut shell modification with ZnO and TiO_2 leads to a remarkable increase in the surface area and mesoporous volume of these adsorbents. Thus, walnut shell modified with ZnO and walnut shell modified with TiO_2 can be good adsorbents for humic acid removal.

Determination of pH_{zpc} of raw walnut shell, modified walnut shells with TiO_2 and ZnO

The results of pH_{zpc} measurement for adsorption of humic acid for the studied adsorbents are shown in Figure 3.

The pH of the zero point of charge (pH_{zpc}) is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. When the pH of the solution is higher than pH_{zpc}, the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species (Naghizadeh *et al.* 2013). According to Figure 3, pH_{zpc} of walnut shell activated carbon in three adsorbents including raw walnut shell, modified with TiO_2 and modified with ZnO was 7.6, 7.5, and 8, respectively. This observation is similar to that reported by Larimi & Ayati (2014) who studied feasibility of walnut shell and almond activated carbon in the removal of direct Blue71.

Effect of pH on the adsorption of humic acid by these adsorbents

The results of the effect of pH on the adsorption of humic acid by the adsorbents raw walnut shell, modified walnut
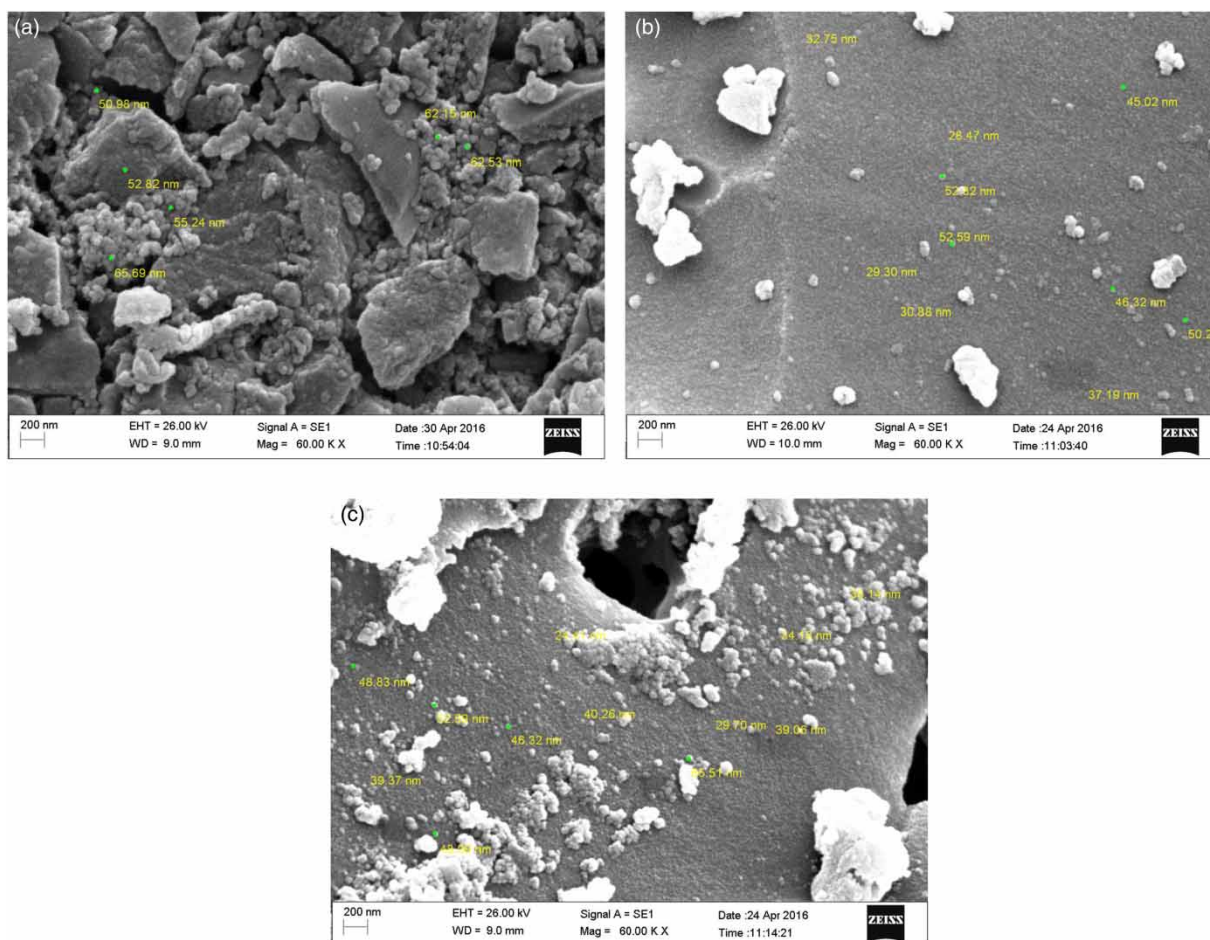

Figure 2 | SEM images of raw walnut shell (a), walnut shell modified with ZnO (b), and walnut shell modified with TiO_2 (c).
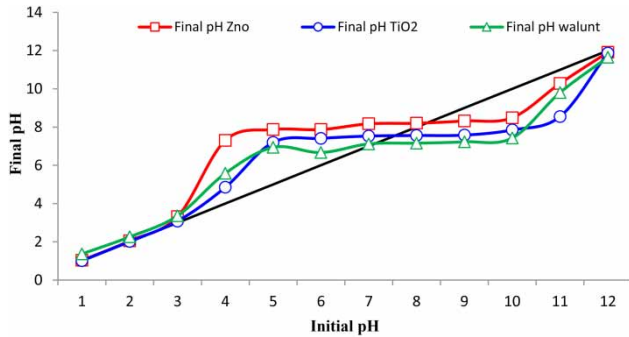
Figure 3 | Determination of pH_{zpc} for adsorption of humic acid by adsorbents (raw walnut shell, walnut shell modified with TiO_2, and walnut shell modified with ZnO).

shell with TiO_2, and modified walnut shell with ZnO are graphically presented in Figure 4.

According to Figure 4, the removal efficiency (adsorption capacity) of the three adsorbents raw walnut shell, walnut shell modified with ZnO, and walnut shell modified with TiO_2, at concentration of humic acid = 10 mg/L, pH = 3 was 8.14, 6.44, and 6.90 mg/g, respectively. The results also demonstrated that at pH = 3, all these adsorbents demonstrated maximum adsorption efficiency, which decreased with any increase in pH value. Asgari *et al.* (2009) studied the performance of modified zeolite with hexadecyltrimethyl ammonium bromide for the removal of humic acids from aqueous solutions and found that the adsorption efficiency of humic acid decreased with any increase in pH value. According to Lu & Su (2007), adsorption efficiency of natural organic matters (NOM) increased with an increase in initial concentration of NOM and decreased with an increase of pH value.
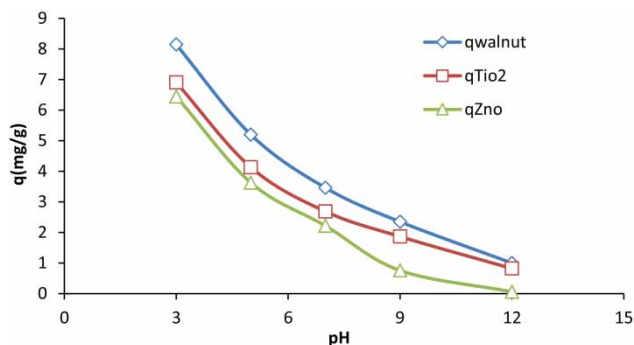
The results indicate that the extent of adsorption varies with pH. According to Figure 3, the adsorption efficiency of humic acid decreases with an increase in pH. It can be observed from the figure that the maximum adsorption capacity of walnut shell occurred at pH = 3 and q = 8.14 mg/g.

Effect of initial concentration of humic acid on adsorption efficiency of the adsorbents

Results of the influence of initial humic acid concentration on the adsorption capacity by the three adsorbents raw walnut shell, walnut shell modified with TiO_2, and walnut shell modified with ZnO are shown in Figures 5–7.

According to Figure 5, adsorption reaches equilibrium in all the used concentrations of humic acid after 15 min. The adsorption capacity reached 0.57, 1.62, 5.1, and 5.32 mg/g after 20 min at concentrations of 10, 15, 20, and 30 mg/L, respectively. Therefore, regarding this figure, the maximum adsorption capacity was 5.32 mg/g after 15 min at a humic acid concentration of 30 mg/L.

As is evident from Figure 5, the maximum adsorption capacity of modified walnut shell with TiO_2 was 12.23 mg/g at a humic acid concentration of 30 mg/L. From Figure 5 it can be seen that the maximum adsorption capacity at concentration 10 mg/L and contact time 30 min was 4.30 mg/g. At a humic acid concentration of 15 mg/L and contact time of 30 min, the maximum adsorption capacity obtained was 7.78 mg/g. Also, the peak of adsorption capacity at 15 min contact time and at a concentration of 20 mg/L was
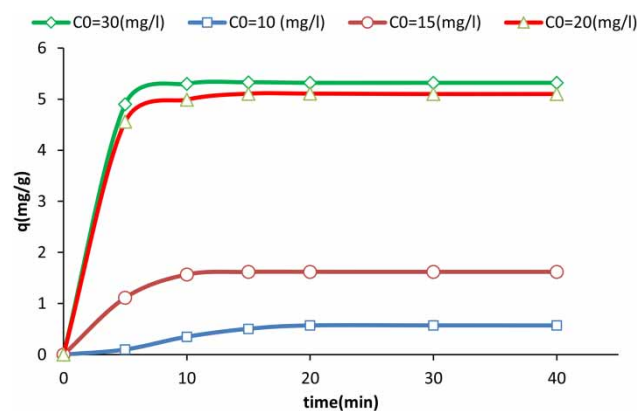

Figure 4 | Effect of pH on the adsorption of humic acid by the three adsorbents raw walnut shell, walnut shell modified with TiO_2, and walnut shell modified with ZnO.

Figure 5 | Effect of initial humic acid concentration on the adsorption capacity of walnut shell with time.
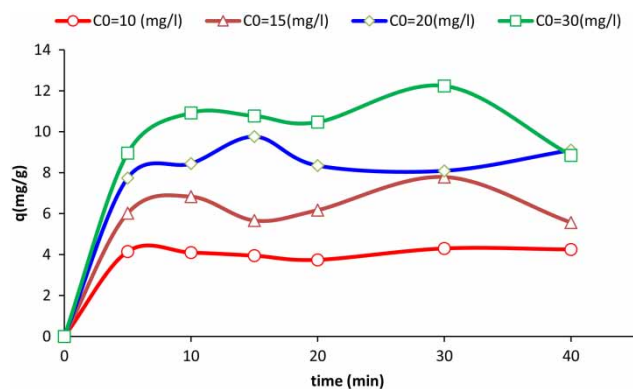
Figure 6 | Effect of initial humic acid concentration on adsorption capacity of walnut shell modified by TiO$_2$ with time.
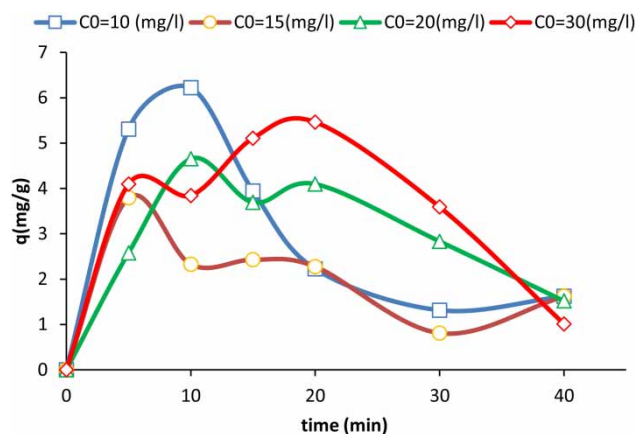

Figure 7 | Effect of initial humic acid concentration on adsorption capacity of walnut shell modified by ZnO with time.

9.75 mg/L. At a concentration of 30 mg/L and contact time of 30 min, the highest adsorption capacity was about 12.23 mg/g.

According to Figure 7, the maximum adsorption capacity at a contact time of 10 min and concentration of 10 mg/L was 6.21 mg/g. Also, at a concentration of 15 mg/L and contact time of 5 min, the peak adsorption was 3.79 mg/g. Moreover, at a concentration of 20 mg/L and contact time of 10 min, the highest recorded efficiency was 4.65 mg/g. For a concentration of 30 mg/L and contact time of 20 min, the maximum observed efficiency was 5.46 mg/g. From Figure 5, it can be concluded that the adsorption capacity of humic acid increases with the increase in initial concentration of humic acid. Also, from Figure 6 it can be seen that the adsorption capacity of humic acid increases with

time until 30 min. A study by Wang *et al.* (2006) confirmed that the removal efficiency of fulvic acids via modified zeolite increased with an increase in the concentration of fulvic acids and reached equilibrium at a contact time of 120 min. Figure 7 indicates that the ZnO modified adsorbent has significant differences to the other two adsorbents and showed desorption after 15 min. The effects of initial concentration of pollutant and contact time are similar. Mezenner & Bensmaili (2009) studied the kinetics and thermodynamics of phosphate adsorption on iron hydroxide-eggshell and found that adsorption efficiency decreases with an increase in initial concentration of pollutant and contact time.

Effect of adsorbent dose on the adsorption efficiency of three adsorbents

The effect of adsorbent dose on the adsorption efficiency is presented in Figure 8.

As shown in the figure, the maximum adsorption capacity for the above adsorbents was determined to be 0.02 g per mass of adsorbent. Figure 8 shows adsorption capacity of humic acid for the three adsorbents in adsorbent doses of 0.02, 0.03, 0.05, and 0.1 g. At 0.02 g of walnut shell, contact time of 5 min and humic acid concentration of 30 mg/L, the adsorption capacity was 35.27 mg/g. Moreover, 0.02 g of walnut shell modified with TiO$_2$ at contact time of 10 min and humic acid concentration of 30 mg/L showed 40.20 mg/g adsorption capacity. Also, the adsorption capacity for 0.02 g of walnut shell modified with ZnO, contact time 30 min, and humic acid concentration 30 mg/L was 37.93 mg/g. From the above discussion, it can be concluded that the adsorption capacity decreases as the adsorbent dose increases. Other studies also show that the humic acid adsorption decreases as the adsorbent dose increases, which indicates the binding sites on the adsorbents are not fully used (Naghizadeh *et al.* 2013). The removal percentage of humic acid increased with increasing adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more binding sites resulting from the increasing adsorbent dosage. However, although humic acid adsorption capacity increases with increasing adsorbent dosage, generally it decreases per adsorbent mass because of remaining unsaturated adsorption sites on the adsorbent (Sulak *et al.* 2007).
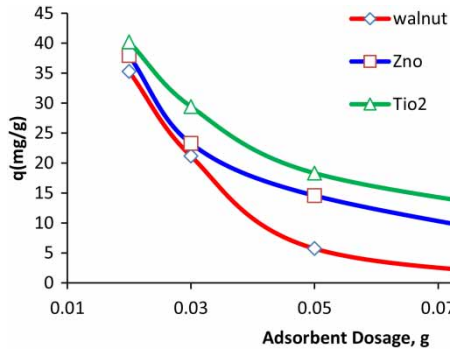
Figure 8 | Effect of adsorbent dose on the adsorption capacity of the three adsorbents (Walnut shell adsorbent at concentration of 30 mg/L of humic acid and contact time 10 min, walnut shell modified with TiO$_2$ at concentration of 30 mg/L of humic acid and contact time 30 min, and walnut shell modified with ZnO at concentration of 10 mg/L of humic acid and contact time 10 min).

Adsorption isotherms

The results of two types of most commonly used isotherms, Freundlich and Langmuir, are summarized in Table 1.

Considering the results obtained from the Langmuir and Freundlich models and also results of maximum correlation coefficients, it can be ascertained that both walnut shell and walnut shell modified with TiO$_2$ fitted well with the Langmuir isotherm equation. This result is consistent with the results reported by Hashemi et al. (2014), who studied the performance of walnut green hull adsorbent in removal of phenol from aqueous solutions. In another work, Asgari et al. (2009) studied the removal of humic acid by modified pumice with hexadecyltrimethyl ammonium bromide and reported that adsorption data fitted well with the Langmuir isotherm and second-order kinetic which is similar to the results obtained in the present study. Derakhshani & Naghizadeh (2014) studied ultrasound regeneration of multi-wall carbon nanotubes saturated by humic acid and reported the adsorption isotherms fitted with the Freundlich isotherm model.

Effect of temperature on adsorption process and determination of thermodynamic parameters

Figure 9 and also Table 2 show the effect of temperature on adsorption of humic acid by walnut shell, walnut shell modified with TiO$_2$, and walnut shell modified with ZnO.

Table 1 | Results of isotherms (Langmuir and Freundlich)

Adsorbents	Langmuir			Freundlich		
	k$_l$ (mg/L)	q$_m$ (mg/g)	R^2	k$_f$	n	R^2
Walnut shell	0.01	51.49	0.94	0.47	1.00	0.92
Walnut shell modified with TiO$_2$	0.04	34.42	0.95	2.22	1.49	0.94
Walnut shell modified with ZnO	0.11	18.59	0.65	2.66	1.80	0.79

According to the results given in Table 2, the adsorption process of humic acid is endothermic in nature for walnut shell and walnut shell modified with TiO$_2$ (positive sign of $\Delta H°$). However, for walnut shell modified with ZnO, it is exothermic (negative sign of $\Delta H°$). Thermodynamic parameters include change in the enthalpy ($\Delta H°$), entropy ($\Delta S°$), and free energy ($\Delta G°$). These parameters confirm whether the adsorption process is spontaneous in nature or not. When the value of $\Delta G°$ is negative, the adsorption reaction is spontaneous in nature (Irani et al. 2013). In the present study, thermodynamic parameters are conducted at different temperatures (293, 303, and 313 K). All of these parameters were determined by using the following equations:

$$K_c = \frac{C_{Ad}}{C_e}$$

$$\Delta G° = -RTLnK_c$$

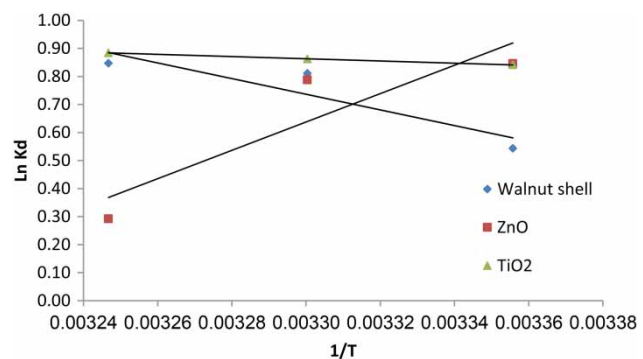$$LnK_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

Figure 9 | Effect of temperature on adsorption of humic acid by walnut shell, walnut shell modified with TiO$_2$, and walnut shell modified with ZnO.

Table 2 | Effect of temperature on adsorption of humic acid by walnut shell, walnut shell modified with TiO$_2$, and walnut shell modified with ZnO

Adsorbent	Temperature (K)	$\Delta G°$ (KJ mol^{-1})	$\Delta S°$ (J mol^{-1} k^{-1})	$\Delta H°$ (KJ mol^{-1})	R^2
Walnut shell	293	−1.35	82.8	32,227.8	0.84
	303	−2.04			
	313	−2.17			
Walnut shell modified with TiO$_2$	293	−2.08	18.0	3,279.2	0.99
	303	−2.17			
	313	−2.26			
Walnut shell modified with ZnO	293	−2.10	− 133.5	− 42,068.8	0.99
	303	−1.99			
	313	−0.75			

The negative value of $\Delta G°$ at all temperatures indicates that the humic acid adsorption reaction by walnut shell and walnut shell modified with TiO$_2$ was spontaneous in nature and it was also observed that its value decreases as the temperature increases. Thus, it can be inferred that the adsorption process is endothermic. The value of $\Delta G°$ increases for walnut shell modified with ZnO, indicating that the humic acid adsorption reaction was spontaneous. $\Delta S°$ value was also positive for walnut shell and walnut shell modified with TiO$_2$ which indicates that the removal percentage increases with any increase in temperature (Kakavandi *et al.* 2013).

Adsorption kinetics

Table 2 present the results of adsorption kinetic for humic acid adsorption onto walnut shell, walnut shell modified with TiO$_2$, and walnut shell modified with ZnO.

Results show that the kinetics of humic acid adsorption onto walnut shell, walnut shell modified with TiO$_2$, and walnut shell modified with ZnO can be described better by pseudo-second-order equation. Additionally, correlation coefficients (R^2) for pseudo-second-order equations are more than those of pseudo second order. Kinetic studies are important in adsorption processes when considering the effects of contact time with adsorption capacity (Esfehani & Shamohammadi 2011). Kinetic studies predict the rate of adsorption that can be used for design and modeling. Considering the adsorption kinetics of walnut shell and walnut shell modified with TiO$_2$ and ZnO at humic acid concentrations of 10 mg/L, 15 mg/L, 20 mg/L, and 30 mg/L (Table 3), the second-order equation model was well fitted

for all working concentrations in all these adsorbents. According to results of the present work, equilibrium adsorption capacity increases with an increase in pollutant concentration, i.e., higher removal efficiency is obtained in higher concentrations. In their work, Asgari *et al.* (2009) studied the removal of humic acid by modified pumice with hexadecyltrimethyl ammonium bromide and reported that adsorption data fitted well with the Langmuir isotherm and second-order kinetic model, which is similar to the results obtained in the present study. Tao *et al.* (2010) used first- and second-order equations for humic acid adsorption and found that the adsorption process obeys the pseudo-second-order equation, which is also consistent with the results of the present study. Walnut shell, due to its availability, cost-effectiveness, and also its high adsorption efficiency, can be proposed as a good natural adsorbent in the removal of humic acid from aqueous solutions.

CONCLUSION

In this study, application of raw walnut shell, modified walnut shell with TiO$_2$ and ZnO for the removal of humic acid from aqueous solution was investigated. The results showed that these adsorbents have high efficiency in the removal of humic acid from aqueous solutions. Walnut shell is a cheap and sustainable agricultural by-product and its shell is commonly discarded as waste. If this material is released into the environment, it can create a potential risk to human health and the surrounding environment. We used this material as an efficient adsorbent for the removal of important precursors which commonly form

Table 3 | Pseudo-first- and second-order equations for humic acid adsorption by walnut shell, walnut shell modified with TiO_2 and ZnO

Adsorbent	C_0 (mg/L)	Pseudo-first-order			Pseudo-second-order			q_e, exp (mg/g)
		K_1 (min^{-1})	q_e, cal (mg/g)	R^2	K_2 (g/mg min)	q_e, cal (mg/g)	R^2	
Walnut shell	10	0.08	0.78	0.78	0.10	0.80	0.63	0.67
	15	0.08	0.63	0.60	0.72	1.66	1.00	1.72
	20	0.08	0.69	0.62	0.82	5.14	1.00	5.21
	30	0.07	0.56	0.53	1.33	5.34	1.00	5.43
Walnut shell modified with TiO_2	10	0.04	0.67	0.47	0.38	4.26	0.99	4.40
	15	0.02	1.41	0.04	0.33	6.06	0.95	7.89
	20	0.00	0.99	0.00	0.36	8.81	0.99	9.86
	30	0.01	1.61	0.03	0.10	9.62	0.96	12.34
Walnut shell modified with ZnO	10	0.06	0.46	0.40	0.16	1.40	0.92	6.32
	15	0.05	0.49	0.37	0.26	1.18	0.74	3.89
	20	0.03	0.55	0.18	0.12	1.69	0.84	4.75
	30	0.03	0.65	0.08	0.12	1.21	0.69	5.56

carcinogenic disinfection by-products in the chlorination chambers of water treatment plants. Therefore, the use of walnut shell is economically reasonable.

ACKNOWLEDGEMENT

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