



Adsorption of arsenic (V) from aqueous solution using modified saxaul ash: isotherm and thermodynamic study

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Abstract

Recently, arsenic-contaminated water has become a big concern. Therefore, the present study aimed to absorb arsenic from the aqueous solution using modified saxaul tree ash. Arsenic adsorption process was performed in vitro by investigating the effect of various parameters such as pH, contact time, arsenic concentrations, temperature and adsorbent dosage on the adsorption efficiency. Isotherms, kinetics and thermodynamic studies were also conducted to better understand the process of adsorption. Maximum level of arsenic adsorption was obtained at a pH of 7, adsorbent dosage of 1.5 g/L, contact time of 60 min, initial arsenic concentration of 250 µg/l and temperature of 323 K. The amount of adsorbed arsenic was increased with increasing initial concentration of arsenic and temperature. Freundlich adsorption isotherm clearly described the arsenic adsorption by modified saxaul ash. Based on the results obtained, it could be concluded that the modified saxaul ash can efficiently remove arsenic from its aqueous solutions.

Keywords Adsorption · Arsenic (V) · Aqueous solution · Isotherm · Thermodynamic

Introduction

Contamination of underground water caused by heavy metals is one of the most important hazards to water resources (Asgari et al. 2008). Arsenic is the third element of group V of the periodic table with atomic number of 32 and relative atomic mass of 74.92 (Golami et al. 2009). Arsenic concentrations are in the range of 2–5 ppm (Uddin et al. 2006). Arsenic contaminates the surface and underground water resources within the natural processes such as dissolving minerals, chemical decomposition and corruption, and human activities like animal husbandry, medicine, industry, electronics and metallurgy (Golami et al. 2009; Uddin et al. 2006; Zaw and Emett 2002). Human activities are the main cause of arsenic contamination of surface water and groundwater (Jafari-Mansoorian et al. 2016). Arsenic compounds

based on the origin of production are mobile in the environment and could get into the food chain and hydrological cycle by rainfall (Babaakbry Sari et al. 2014). Arsenic is a toxic and accumulative substance and can inhibit SH-group enzymes. Trivalent arsenic (arsenite) is more toxic than arsenic (V) (arsenate) due to its high portability (Tyrovola et al. 2006; Triszcz et al. 2009). Arsenic may cause dysfunction in digestive system, shock leading to death, pulmonary and respiratory failures (Golami et al. 2009; Zaw and Emett 2002; Triszcz et al. 2009). It is also known as a carcinogenic substance and causes testicular, bladder, lung and liver cancers (Golami et al. 2009; Smedley and Kinniburgh. 2002). The resulting complications depend on factors such as duration of exposure, way of entering to body, type and sources of arsenic (Smith et al. 2000).

Numerous arsenic poisoning caused by contaminated drinking water have been reported in Bangladesh, Argentina, Taiwan, America and Malaysia (Ferguson et al. 2007; Smedley et al. 2005). Also in Iran, arsenic level is higher than the standard limit in areas such as Sistan and Baluchestan, Khorasan, East Azerbaijan and Tuyserkhan (Rajaei et al. 2012; Mesdaghinia et al. 2005; Feizi et al. 2008; Olyaie et al. 2012). Lately, the International Agency for Research on Cancer (IARC) has classified inorganic compounds of arsenic in drinking water as a group 1 carcinogenic agent for

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respiratory system (Asgari et al. 2008). Due to the extraordinary toxicity of arsenic, allowable level for arsenic in drinking water has been reported 10 micrograms per liter by the World Health Organization (WHO) and America Environmental Protection Agency (USEPA) (Shih. 2005; Malik et al. 2009; Jiang 2001). According to Iranian standard for drinking water, this level is 0.05 (MCL) milligrams per liter (Mosaferi and Mesdaghinia 2005). In addition, acceptable level recommended by the Food and Agriculture Organization (FAO) is 0.1 mg/l for irrigation water (Golami et al. 2009).

There are different techniques such as coagulation (Kord Mostafapour et al. 2010), chemical oxidation (Gihring et al. 2001), chemical precipitation (Bissen and Frimmel 2003), ion exchange (Kim and Benjamin. 2004), chemical process (Zheng et al. 2011), adsorption and reverse osmosis for reducing concentration of arsenic in aqueous solutions (Sun and Doner 1998). Some of the mentioned techniques require extremely high investment and operation costs and produce high levels of wastes, which in turn makes their treatment and disposal problematic (Junyapoon 2005; Wang et al. 2002). However, the adsorption process has an extensive application due to the ease of exploitation, high efficiency and insensitivity to toxic compounds and availability of a wide range of adsorbents (Bazrafshan and Kord Mostafapour 2012; Rahdar et al. 2016). Nowadays, simple and cost-effective adsorbents such as agricultural residues like rice paddy, sawdust, orange peel, almonds and peanuts peel and wheat bran have been used by different researchers as adsorbents due to proper efficiency of metal adsorption (Mehrasbi 2008). Saxaul tree, *Haloxylon persicum*, is abundance in Iran and native to Iran. That is why it is also known as Iranian haloxylon. This tree distributes in the arid and desert-like areas in Zabol, Tabas and Garmsar (Sanchooli Moghaddam et al. 2016). Therefore, the aim of our research is to investigate saxaul ash ability in arsenic removal from aqueous solutions and assess the effects of some parameters including effective temperature, contact time, initial concentration, pH, adsorption isotherms, reaction kinetics and thermodynamic studies on the adsorption process.

Materials and methods

Collection and preparation of adsorbent

Saxaul trees were provided from Zabol city, Iran. First, the tree branches were washed to remove possible contaminants and cut to approximately one square centimeter pieces. They were rinsed with deionized water and then placed into the oven at 105 °C for 12 h. In order to modify adsorbent, the tree was immersed in sodium hydroxide solution with 30% volume concentration for 24 h. The mass of the plant was considered

relatively twice as sodium hydroxide to investigate the effects of adsorbent modification on the adsorption level. Next, the adsorbent was placed in the oven to dry again at a temperature of 105 °C for 12 h, and then, it was converted to ash in an electric furnace at a temperature of 650 °C for 3 h. The obtained ashes were made cold in desiccator by standard ASTM sieves with 60 and 200 mesh, and finally kept cold in the desiccant cooling system (Vijayaraghavan and Yun 2008).

Preparation and analysis of arsenic (V) solution

All chemicals used in this study were provided from Merck Co (Germany). In this research, arsenate stock solution was prepared by dissolving arsenate ($\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$) in deionized water with 99% of purity, and then, required concentrations were obtained by diluting stock solution. The pH was adjusted by pH meter using 0.1 N sulfuric acid or 0.1 N sodium hydroxide solution. The experiments were performed considering five variables, including initial pH of solution, adsorbent dosage, contact time, initial concentration of arsenic and temperature. Arsenic measurements in the solutions were done by silver diethyl dithiocarbamate method (SDDC) using UV–Vis spectrophotometer (GBC, Cintra 202) at 530 nm.

Batch study

The experiments were performed discontinuously in 100-ml flasks on a shaker with a speed of 120 rpm and were carried out considering five variables, including the initial pH of solution (3, 5, 7, 9, 11 and 13), adsorbent dosage (0.1, 0.5, 1, 1.5, 2, 2.5 and 3 g/L), contact time (5, 10, 30, 60, 90 and 120 min), initial concentration of arsenic (10, 50, 100 and 250 $\mu\text{g/L}$) and temperature (293, 298, 303, 308, 313 and 323 K).

The amount of adsorbed arsenic per unit weight of modified saxaul ash in time t , q_t ($\mu\text{g/g}$) was calculated using the following equation (Ahmadi and Kord Mostafapour 2017a; Balarak et al. 2016a):

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where C_0 and C_t are, respectively, arsenic concentrations at time zero and t ($\mu\text{g/L}$), V is volume of the solution (L) and M is the adsorbent mass (g).

Distribution coefficient (K_d), which describes the binding ability of the adsorbate on the adsorbent surface, could be calculated using the following equation (Rahdar and Ahmadi 2017):

$$K_d = \frac{(C_0 - C_e)V}{C_e m} \quad (2)$$

where C_0 and C_t are, respectively, the initial arsenic concentration and arsenic concentrations in equilibrium ($\mu\text{g/L}$), V is volume of the solution (L) and M is the adsorbent mass (g).

Results and discussion

Effect of pH

As mentioned in Introduction, in this review one of our aims is to understand effect of pH in removal arsenic and on the adsorption capacities of modified saxaul ash. Experiments were carried out using initial pH_s varying from 3 to 13, at constant initial arsenic concentration of $100 \mu\text{g L}^{-1}$, adsorbent dose of 1 g L^{-1} and contact time of 60 min and ambient temperature. The effect of pH on the arsenic removal efficiency and adsorption capacity (q_e) is presented in Fig. 1. The adsorption efficiency increased from 50% to 86% as the pH increased from 3 to 7. The rate of arsenic removal was maximum at pH of 7. As shown in Fig. 1, the maximum absorption capacity, $8.6 \mu\text{g/g}$, was obtained at the $\text{pH} = 7$ in which the arsenic removal efficiency was 86% but the removal efficiency was only 62%, and absorption capacity was $6.2 \mu\text{g/g}$ at $\text{pH} = 13$. The results obtained from the present study demonstrated that the arsenic removal efficiency is decreased by increasing pH value that is effective on the contaminant structure and surface charge of adsorbent. In addition, binding of metal ions by surface groups depends on the pH level (Rahmani and Amini 2015). The removal efficiency at $\text{pH} = 7$ reaches the maximum level, and then, removal amount decreases in higher pH levels. In the study of Thirunavukkarasu et al. (2003), optimum pH for arsenic removal was determined 7.6 using GFH. The results of the present study are in line with the findings of Askari et al. (2008).

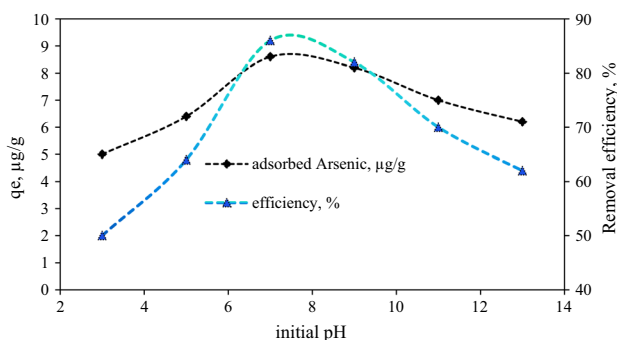


Fig. 1 Effect of initial pH of solution on arsenic removal using modified saxaul ash (initial arsenic concentration of $100 \mu\text{g/L}$, adsorbent dosage of 1 g/L , contact time of 60 min and temperature of 298 K)

Effect of adsorbent dosage

The effect of adsorbent dose on the removal of arsenic and adsorption capacity (q_e) was studied (Fig. 2). The effect of arsenic dosage ($0.1\text{--}3 \text{ g/L}$) on the removal efficiency of arsenic was investigated at the reaction time of 60 min, temperature 298 K and optimum pH of 7. As shown in Fig. 2, the amount of absorbed arsenic per adsorbent mass (q_e) is rapidly decreased by increasing the adsorbent dosage from 0.1 to 1.5 g/L , but is dropped with lower slope from adsorbent dosages of $1.5\text{--}3 \text{ g/L}$. Maximum capacity of arsenic adsorption using ash ($14.833 \mu\text{g/g}$) was observed at the dosage of 0.1 g/L adsorbent. However, the highest efficiency was reported as 89% at a dosage of 1.5 g/L of adsorbent. The distribution coefficient for arsenic adsorption on saxaul ash is also given in Fig. 2 showing decreased distribution coefficient by increasing adsorbent dosage. Removal rate is improved by increasing adsorbent dosage, its optimum dosage was 1.5 g/L , and the number of active adsorption sites on the adsorbent surface, available for arsenic ions, is increased in high dosages of adsorbent (Abbad et al. 2012). Due to the increasing adsorption sites during the adsorption process, the number of active sites of adsorbent remains unsaturated (Rahmani and Amini 2015). These findings are consistent with the findings of Rahmani and colleagues (Rahmani et al. 2010; Lackovic 2000; Rahmini et al. 2009).

Effect of contact time and initial concentration of arsenic

The effect of contact time and initial concentration on arsenic removal using saxaul ash was investigated in the range of $5\text{--}120 \text{ min}$ and $10\text{--}250 \mu\text{g/L}$, respectively. As shown in Fig. 3, the arsenic removal is enhanced with increasing contact time in all initial concentrations of arsenic. In the beginning until 30 min, absorption occurred sharply and

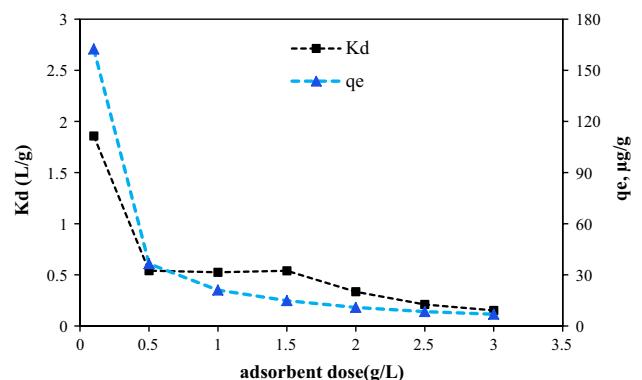


Fig. 2 Effect of adsorbent dosage on arsenic removal using modified saxaul ash (initial arsenic concentration of $100 \mu\text{g/L}$, optimum pH of 7, contact time of 60 min and temperature of 298 K)

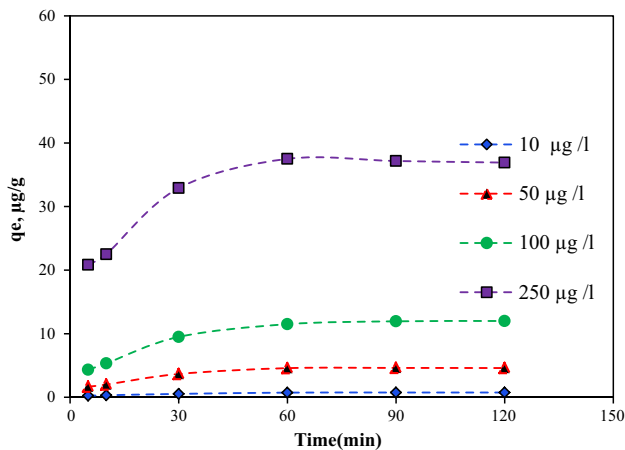


Fig. 3 Effect of contact time and initial concentration on capacity of arsenic adsorption by modified saxaul ash (initial arsenic concentration of 100 µg/L, optimum pH of 7, optimum adsorbent dosage of 1.5 g/L and temperature of 298 K)

the amount of arsenic absorbed per unit mass of adsorbent reached 0.25 µg/g and 36.91 µg/g, respectively, for initial concentrations of arsenic of 10 and 250 µg/L. Then, the elevation in q_e goes ahead at a slower rate with increasing contact time and finally reaches equilibrium within contact time of 60 min. Absorption rate was fast in the first 30 min and reached equilibrium in 60 min, and no changes were observed in the time needed for equilibrium by changing the initial arsenic concentration. The monolayer and rapid absorption was due to physically passive absorption or ion exchange at the surface of adsorbent. Since there are a specified number of adsorption sites on the adsorbent surface, the metal absorption on the adsorbent is firstly fast, but over time the number of available active sites reduces and competition of remaining metal ions decreases absorption rate because of reduced binding sites (Abdel-Ghani et al. 2007). The findings of the present study are in agreement with the results of Mosafiri and Mesdaghinia (2005) and Nourozi and Azizian (2014).

Initial absorbed arsenic per unit mass of adsorbent improves by increasing initial concentration of arsenic. Therefore, capacity of arsenic adsorption by modified saxaul ash strongly depends on initial concentration of arsenic.

Effect of temperature

The effect of temperature on arsenic adsorption was investigated at the temperature range of 293–323 K. As shown in Fig. 4, arsenic removal efficiency is increased for all of initial concentrations increasing temperature from 293 to 323 K. For example, removal efficiency in initial arsenic concentration of 100 µg/L was reached from 71% to 87.24% by increasing the temperature from 293 to 323 K. Absorption capacity of

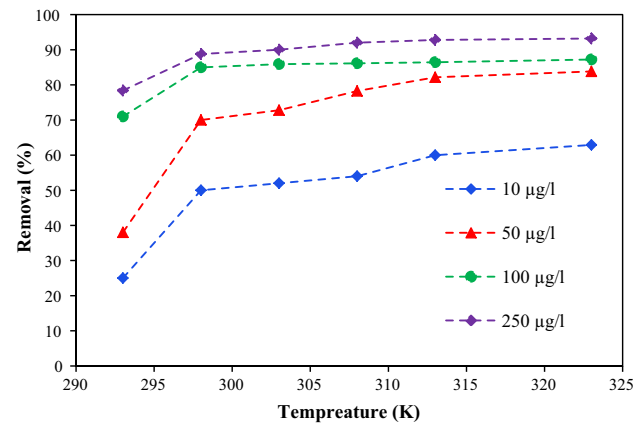


Fig. 4 Effect of temperature and initial concentration on arsenic removal by modified saxaul ash (optimum adsorbent dosage of 1.5 g/L, optimum pH of 7 and optimum contact time of 60 min)

adsorbent was elevated for modified saxaul ash by increasing temperature. (Respective data are not given.) Regarding the effect of temperature on the arsenic adsorption (using modified saxaul ash), when the temperature increases from 293 to 323 K, arsenic removal efficiency is increased for all initial concentrations. The viscosity in aqueous solutions is decreased by increasing temperature. In addition, the release of adsorbent molecules is increased across the external boundary layer and in the pores of adsorbent particles, hereby resulting in increased removal efficiency. Moreover, the changes in temperature also increased the adsorption capacity of adsorbent (Ananta et al. 2015; Al-Qodah and Lafi 2003).

Isotherm study

Adsorption isotherms show the models on distribution status of adsorbate molecules in the liquid and solid phases in equilibrium. The most important adsorption models include linear Langmuir, Freundlich and the Temkin adsorption isotherm models.

Langmuir isotherm model is based on scientific assumptions; the most important of these assumptions is that the adsorbates (atoms, molecules or ions) are bound to certain and identical sites on the surface of adsorbent as monolayer adsorption (Bazrafshan et al. 2015a; Ahmadi and Igwegbe 2018), which can be presented by the following equation (Bazrafshan et al. 2015b; Nur-E-Alam et al. 2018):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (3)$$

where q_e (µg/g) is the amount of fluoride adsorbed per specific amount of adsorbent, C_e is equilibrium concentration of the arsenic solution (µg/L), K_L (L/µg) is Langmuir constant and q_m (µg/g) is the maximum amount of arsenic required

to form a monolayer. The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining K_L and q_m with drawing the curve $1/q_e$ versus $1/C_e$ (Ahmadi and Kord Mostafapour 2017b; Azarpira et al.2016):

$$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot \frac{1}{k_L} + \frac{C_e}{q_m} \tag{4}$$

Freundlich is merely an empirical equation representing heterogeneous and multilayer adsorption on the surface of adsorbent. The Freundlich model is an empirical relation between q_e and C_e . It is obtained by assuming a heterogeneous surface with nonuniform distribution of the adsorption sites on the adsorbent surface and can be expressed by the following equation (Fu et al. 2011):

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich constants can be obtained by drawing the Log q_e versus Log C_e based on experimental data in light to linear equation (Khoshnamvand et al. 2017; Akbari et al.2018):

$$\text{Log } q_e = \frac{1}{n} \text{log } C_e + \text{log } K_f \tag{6}$$

Temkin model corrects the adsorption theory by considering adsorbate–adsorbate and adsorbate–adsorbent interactions. The adsorption heat of all molecules in absorption layer is decreased linearly with the amount of coverage. In Temkin model, the surface absorption theory was corrected considering possible reactions between adsorbent–adsorbent and adsorbent–adsorbate. This model can be expressed by the following equation (Ahmadi et al. 2017):

$$q_e = B \ln A + B \ln C_e \tag{7}$$

A (l/g) plot of q_e versus $\ln C_e$ ($\mu\text{g/l}$) enables the determination of the constants A and B (J/mol). B is corresponding to the heat of sorption, and A is the equilibrium binding constant.

The constants and correlation coefficients of three adsorption isotherms of Langmuir, Freundlich and Temkin are calculated and presented in Table 1. According to this table, the correlation coefficient for Freundlich ($R^2 = 0.99$) model is higher than the other models; this demonstrates that Freundlich model is more appropriate to describe the equilibrium adsorption of arsenic on modified saxaul ash. In the Langmuir isotherm model, monolayer of dissolved molecules is absorbed on adsorbent, the energy level of absorption is the same in whole surface of adsorbent, and absorbed links are assumed to be reversible. In Freundlich model, adsorbent surface areas are not uniform and have different absorption force (Gulnaz et al. 2011). The correlation coefficient of Freundlich model was higher than the other models. This shows that Freundlich model is more suitable to describe the adsorption equilibrium of arsenic on modified saxaul ash. Also, the intensity of adsorption, n (2.1–2.27), lies within the range of 1–10 ($1 < n < 10$) which suggests that the adsorption of arsenic on modified saxaul ash is favorable.

Kinetic study

Adsorption kinetics are used to determine the mechanisms of controlling adsorption processes and for describing the behavior of transfer of adsorbate molecules per unit of time or for investigating the variables affecting the reaction rate (Mohammadnia and Naghizadeh 2016).

The pseudo-second-order, pseudo-first-order and intra-particle diffusion models were applied in this study to examine the mechanism behind the adsorption of arsenic on modified saxaul ash at pH 7, modified saxaul ash dosage of 1.5 g/L and arsenic concentration of 10-250 $\mu\text{g/L}$

Table 1 Isothermal parameters for arsenic adsorption on modified Saxaul ash at different temperatures

	293 K	298 K	303 K	308 K	313 K	323 K
<i>Langmuir isotherm</i>						
q_m ($\mu\text{g/g}$)	2.604	3.661	3.641	3.231	3.916	4.203
k_L (L/ μg)	0.018	0.038	0.041	0.049	0.053	0.056
R^2	0.98	0.97	0.966	0.958	0.953	0.949
<i>Freundlich isotherm</i>						
k_f ($\mu\text{g/g}$) (L/g) ^{1/n}	0.002	0.010	0.006	0.007	0.015	0.021
n	2.1	2.2	2.27	2.59	2.38	2.27
R^2	0.887	0.949	0.960	0.995	0.992	0.990
<i>Temkin isotherm</i>						
A (L/ μg)	0.100	0.161	0.169	0.180	0.210	0.228
B (J/mol)	5.297	7.541	7.97	8.953	8.56	8.531
R^2	0.578	0.712	0.717	0.719	0.716	0.728

at temperature of 323 K. In first-order kinetic model, it is assumed that the rate of changes in withdrawal of the solute over time is directly proportional to variations in the saturation concentration and the amount of adsorbent withdrawal with time. The pseudo-first-order rate equation is defined as Eq. (8) (Agarwal et al. 2016; Rahdar et al. 2018):

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{k_1}{2.303}t \tag{8}$$

where q_t and q_e are the amounts of arsenic adsorbed at time t and at equilibrium ($\mu\text{g/g}$) and k_1 is the pseudo-first-order rate constant for the adsorption process ($\text{g}/\mu\text{g}/\text{min}$).

In second-order kinetic model, it is assumed that adsorption process can be controlled by chemical adsorption (Bayramoglu et al. 2009; Ruixia et al. 2002). The pseudo-second-order model can be represented as Eq. (9) (Ahmadi and Kord Mostafapour 2017c):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where K_2 is the pseudo-second-order rate constant ($\text{g}/\mu\text{g}/\text{min}$) and q_e and q_t are the amounts of arsenic adsorbed on the modified saxaul ash ($\mu\text{g g/g}$) at equilibrium and at time t , respectively.

The intraparticle diffusion plot is generally used to identify the mechanism involved in an adsorption process (Bazarafshan and Ahmadi 2017). The intraparticle diffusion model according to Weber Morris is given by Eq. (10) (Ahmadi et al. 2018; Rahdar et al. 2019):

$$q_t = k_{pi}t^{0.5} + c \tag{10}$$

where c is a constant that provides the information about the thickness of the boundary layer, k_{pi} is the intraparticle diffusion rate constant ($\mu\text{g/g min}^{0.5}$) and q_t is the amount of arsenic adsorbed ($\mu\text{g g/g}$) at time t (min.).

Parameters of the three models are listed in Table 2. The goodness of fit of the models was expressed by the coefficients of determination (R^2), and a relatively high R^2 value indicated that the model successfully described the kinetics of arsenic sorption by modified saxaul ash. It was not appropriate to use the pseudo-first-order model to predict the sorption kinetics of arsenic onto modified saxaul ash for the entire arsenic concentration range. The results showed

the intraparticle diffusion model could not fit well with the kinetic data due to the lower R^2 values (0.817–0.907) (Table 2), suggesting that the intraparticle diffusion was not the rate-controlling step for the sorption of arsenic onto modified saxaul ash. Finally, pseudo-second-order model has the best fit for adsorption kinetics of various initial concentrations of arsenic, indicating that the adsorption of arsenic onto modified saxaul ash was a chemical adsorption process. Figure 5 shows the linear fitting lines of pseudo-second-order model.

Comparison with other adsorbents for arsenic removal

Table 3 shows the adsorption capacities obtained for the removal of arsenic on various adsorbents. From the table, it can be seen that the modified saxaul ash can be used efficiently for the removal of arsenic from aqueous environments.

Thermodynamic assessments

Thermodynamic results determine the possibility and spontaneous process, endothermic or exothermic reaction, and the entropy changes during adsorption or changes in Gibbs free energy (ΔG°) and basic excitation criteria. If the ΔG° is minus, absorption process will be spontaneous.

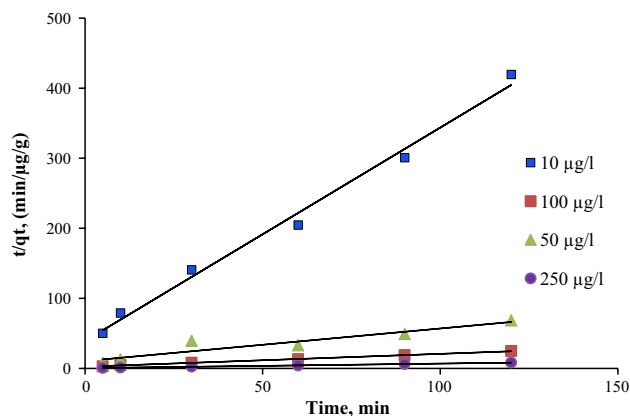


Fig. 5 Pseudo-second-order kinetic plots for arsenic adsorption onto modified saxaul ash

Table 2 Pseudo-second-order adsorption rate constants and q_e values for different initial arsenic concentrations at pH 7

Concentration arsenic ($\mu\text{g/L}$)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	K_1	q_e	R^2	K_2	q_e ($\mu\text{g/g}$)	R^2	K	C	R^2
10	0.0003	5.468	0.764	39.21	3.044	0.991	0.0239	0.064	0.887
50	0.0247	1.531	0.964	10.44	0.464	0.883	0.152	0.286	0.817
100	0.0526	3.919	0.9933	2.308	0.184	0.998	0.38	1.178	0.907
250	0.0312	6.20	0.8399	0.320	0.064	0.998	0.800	7.29	0.835

Table 3 Adsorption capacities of different adsorbents for arsenic removal

Adsorbent	Maximum adsorption capacity, q_m (mg/g) (maximum% removal)	Conditions	References
Raw and incinerated pine barks	95.86%	$T = 60$ min, $pH = 7$, dose = 1 g/l, $C_0 = 1000$ µg/l	Narooie et al. (2017)
Activated carbon	95% (17.86 mg/g)	$C_0 = 10$ mg/L, dosage = 5 = g/L, $pH = 6$, $t = 60$ min	Yao et al. (2014)
Fly ash	65.4%	Dosage = 2.5 g/25 mL, $C_0 = 100$ mg/L, $pH = 10$, $t = 60$ min, temperature of 353 K	Ayanda et al. (2017)
Modified saxaul ash	94.62% (4.203 mg/g)	$pH = 7$, $C_0 = 250$ µg/l, temperatures of 323 K, dosage = 1.5 g/l.	This study

Table 4 Thermodynamic parameters for arsenic adsorption on modified saxaul ash

Temperature (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (kJ mol K ⁻¹)
298	7.96	14.05	20.6
303	7.91		
308	7.59		
313	7.52		
323	7.50		

Thermodynamic parameters including ΔG^0 , changes in enthalpy (ΔH^0) and changes in entropy (ΔS^0) for the adsorption processes are calculated using the following equations (Balarak et al. 2016b):

$$\Delta G^0 = -RT \ln K_a \tag{11}$$

where R is universal gas constant (314.8 J/mol/k), T is the temperature in degrees Kelvin and K_a is the thermodynamic equilibrium constant.

The enthalpy and entropy changes of the process adsorption can be determined from the slope and intercept of line obtained by plotting K_L vs $1/T$ (Bazrafshan et al. 2015a, b; Dursun 2006; Pimentel et al. 2008). ΔH^0 is 14.05 kJ/mol and ΔS^0 is 20.6 kJ/mol K⁻¹ (2).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

The results of thermodynamic assessment for arsenic adsorption on modified saxaul ash are given in Table 4. Positive value of ΔG^0 for the arsenic represents an increase in randomness of the adsorption process. Table 4 clearly shows that the value of change of the standard enthalpy (ΔH^0) is positive for the adsorption of arsenic by modified saxaul ash considered as adsorbents are endothermic and the removal efficiency of arsenic increases with the increase in temperature T (Bazrafshan et al. 2015b; Twarakavi and Jagath 2006).

Conclusion

Absorption capacity and efficiency of modified saxaul ash were studied in the removal of arsenic from aquatic solutions. The results showed that the efficiency of the process depends on various factors such as contact time, temperature, arsenic concentrations, initial concentration of adsorbent and pH of the solution. The highest absorption was obtained at $pH = 7$. Increasing initial concentration of arsenic, adsorption capacity of adsorbent was increased due to elevated mass transfer force, and high removal rate was observed with increasing temperature for all concentrations. The maximum arsenic removal (94.62%) was obtained at the concentration of 250 µg/l, temperatures of 323 K, pH of 7 and adsorbent dosage of 1.5 g/l. Laboratory data of arsenic absorption are in accordance with the Freundlich model. Because of the saxaul ash benefits such as high absorption capacity, effective removal efficiency, cost-effectiveness and availability, the use of this natural adsorbent can be considered for the removal of arsenic from the aqueous solution.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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