



Elimination of arsenic contamination from water using chemically modified wheat straw

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ABSTRACT

Presence of arsenic in natural water resource as a common contaminant has always been a great concern for the scientists. The objective of this study was to explore the possibility of wheat straw modified with sodium bicarbonate (NaHCO_3) for removing arsenate from aqueous solution. Adsorption process was accomplished in a laboratory-scale batch with emphasis on the effect of various parameters such as pH, contact time, arsenic concentration, and adsorbent dosage on the adsorption efficiency. In order to understand the adsorption process, sorption kinetics and equilibrium isotherms were also determined. It was found that adsorption of the arsenic is influenced by several parameters such as arsenic initial concentration, adsorbent dosage, and solution pH. Maximum adsorption efficiency was achieved at a pH of 7. The equilibrium adsorbed amount also increased with the initial concentration of the metal ions, as expected. NaHCO_3 was used to modify wheat straw and scanning electron microscopy images showed that all of the adsorbents have been affected and modified by NaHCO_3 solution. Among the models tested, both the Langmuir and Freundlich models represented the experimental data well. According to the Dubinin–Radushkevich isotherm model, mean free energy of adsorption (15.2 kJ mol^{-1}) indicates that adsorption of arsenic by wheat straw might follow a chemisorption mechanism. It was also found that adsorption of arsenic by wheat straw followed pseudo-second-order kinetics. It is concluded that adsorption using modified wheat straw is an efficient and reliable method for arsenate removal from liquid solutions.

Keywords: Adsorption; Wheat straw; Sodium bicarbonate; Adsorption isotherm; SEM

1. Introduction

Presence of arsenic in natural water resource as a common contaminant has always been a great concern for the scientists. Arsenic finds its way into the aquatic environment from both natural and man-made

sources. However, the most common scenario for arsenic to occur in water is through weathering and dissolution of arsenic bearing rocks, minerals, and ores. Typically, both organic and inorganic arsenic compounds exist in water, but the inorganic forms are more prevalent and are considered more toxic [1]. Recently, there has been reports about the presence of arsenic in water from different parts of the world, such as the USA, China, Chile, Bangladesh, Taiwan,

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Mexico, Argentina, Poland, Canada, Hungary, Japan, India, Vietnam, and Nepal [2,3] and more recently from Iran [4,5]. Many chronic and acute health consequences have been associated to arsenic exposures [1]. Among arsenicals, inorganic forms have been classified as group I carcinogens based on human epidemiological data [4].

The water sources of some regions in the western part of Iran are naturally contaminated with arsenic. This has exposed the inhabitants of these regions to arsenic via the consumption of unsafe drinking water for a long period of time [4]. On the other hand, an increasing demand of water and an upcoming water shortage in some regions may soon lead to the necessity to use even raw waters contaminated with arsenic for drinking water production. Therefore, lack of suitable water treatment processes may lead to the drinking water contamination and pose a health risk to those drinking such water.

Reviewing the literature, several methods such as chemical precipitation, ion exchangers, adsorption, biological processes, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultrafiltration, etc. have been used for removing metal ions from aqueous solutions [5–10]. However, almost all of these methods have had serious disadvantages such as less efficiency, relatively high operating cost, regeneration problem, sensitive operating conditions, and high energy requirement [7,11].

Among the suggested methods, adsorption is believed to be a very cost effective one. However, using activated carbon as an adsorbent is not economical [12]. Therefore, the idea of developing cheaper and readily available materials had grown fast in the past few years. According to Bailey et al. [13], “an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry” [14].

To tackle the problems, cheaper and renewable biomass adsorbents have been proposed as promising alternatives to activated carbon. Since 1990s, there has been an inclination among researchers to use low cost renewable organic materials for adsorption of heavy metal ions [13,15–17]. Recent studies have even focused on the biomaterials which are byproducts or the wastes from large-scale industrial operations and agricultural waste materials. Biosorption seems to have some major advantages over conventional treatment methods which can be listed as: lower cost, higher efficiency, minimization of chemical or biological sludge, no need for additional nutrient, regeneration of biosorbents, and possibility of metal recovery [7].

Agricultural cellulose containing materials are one of the adsorbent which have the best potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch containing variety of functional groups that facilitate metal complexation which helps for the sequestering of heavy metals [7,13,18–20]. Because of the fact that using agricultural waste materials is economical and eco-friendly and many other merits, they seem to be a viable option for heavy metal remediation [7]. Wheat straw is the most commonly available crop residue all over the world and is widely available and abundant natural material in Iran. It contains 40–60% natural cellulose and hemicellulose. Therefore, it could provide an economical source of biosorbent for the metal removal and no elaborate preparation is needed while being used [21–23]. However, as Wan Ngah and Hanafiah and Gaballah et al. have stated “the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity and release of color to aqueous solution” [14,24]. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals [23]. The objective of the present study was to investigate the feasibility of the use of wheat straw as a biosorbent for the removal of trace amounts of arsenic from water and modification of wheat straw using sodium bicarbonate (NaHCO_3) to improve the adsorption capacity. In the investigation, we also studied several factors influencing the adsorption efficiency. In order to understand the biosorption process by wheat straw, biosorption kinetics and equilibrium isotherms were also determined.

2. Materials and methods

2.1. Chemicals

As(V) standard reference (arsenic oxide, concentration $1,000 \text{ mg l}^{-1}$) was purchased from Merck. Deionized water ($\text{EC} \approx 1 \Omega$) was used for preparing all samples. Stock solutions of As(V) were prepared by dissolving accurately weighed amount of analytical grade Na_2HAsO_4 in 1 l deionized water. The test solutions were prepared by diluting 1 g l^{-1} of stock solution of As(V) to the desired concentrations. The range of concentrations of As(V) solutions prepared was $500\text{--}2,000 \mu\text{g l}^{-1}$. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value using diluted and concentrated H_2SO_4 and NaOH solutions, respectively. Other agents used were all of analytical grade.

2.2. Preparation of raw and modified adsorbent

Wheat straw collected from a local farm in Kurdistan Province, Iran was used as a biosorbent. Wheat straw was subjected to repeatedly washing with water to remove dust and soluble impurities. Then we crushed and sieved them to retain the 20–40 mesh fractions. Later, the crushed and shredded straw was washed again with distilled water and was dried overnight at 80°C until constant weight. The dried straw was then stored in a glass container and designated as raw (unmodified) wheat straw (UWS).

The chemically modified wheat straw was prepared by soaking a known amount of UWS in 1 l of 0.1, 0.4, 0.7, and 1 mol NaHCO₃ solutions at the ratio of 1:20 (straw: NaHCO₃, w/v). The suspension was shaken using a rotary shaker at a speed of 170 rpm at room temperature (25°C) for 4 h. The modified wheat straw was then separated from the liquid and washed with distilled water several times to remove superficially retained NaHCO₃. Finally, the modified wheat straw was dried in an oven at 80°C overnight and stored in a glass container and labeled as NaHCO₃ modified wheat straw (SBMWS).

2.3. Analytical determinations

The determination of As(V) was performed by hydride generation atomic absorption spectrometry (PG-990, England), according to Water and Wastewater Standard Methods 206.3 [25]. The morphological properties of sorbent were analyzed using scanning electron microscopy (SEM, JEOL, JSM 5800) coupled with energy dispersive X-ray analysis (EDAX) with 20 kV at 2,500 times magnification for comparison of the effect of pretreatment. The Fourier transform infrared spectroscopy (FTIR) spectra of UWS and SBMWS samples were taken in KBr pellets using a Tensor 27 spectrophotometer (Bruker Optik GmbH, Germany). Each analysis for arsenic concentration was carried out in duplicates and the average value was used for further calculations.

2.4. Adsorption studies

Sorption studies were conducted in a routine manner by the batch technique. The effects of experimental parameters for the kinetic studies such as initial arsenic concentration (500–2,000 µg l⁻¹), pH (4–10), and adsorbent dosage (1–1.5 g l⁻¹) were studied for a contact time of 360 min. The studies were performed at a constant temperature of 25°C to be representative of environmentally relevant condition. As(V) solution (100 ml) of known concentration and initial pH was taken in

250 ml stoppered Erlenmeyer Pyrex glass with a required amount of adsorbent (UWS and SBMWS) and was agitated at 150 rpm constant shaking rate for 6 h to ensure that equilibrium was reached. Solution samples were taken at preset time intervals. The solutions were separated from the adsorbent materials and the amount of As(V) adsorbed was determined by difference between the initial and final concentrations of As(V) aqueous solution.

In order to evaluate the adsorption capacity of UWS and SBMWS, the experimental data were fitted to the Langmuir and Freundlich isotherm models, which are commonly used in describing adsorption. Microsoft Excel was used for a quick linear regression curve fitting. In linear regression using the least-square method, the coefficient of determination, r^2 , was used to evaluate the goodness of fit of the data to the model. In order to evaluate the effect of the solution pH on the sorption, experiments were conducted at different pH values between 4 and 10. The initial metal concentration of 1 mg l⁻¹ was used in experiment with varied pH values.

Each experiment was repeated three times, the average results are presented. A control experiment was also carried out using the same solution and equipment in the absence of sorbents. There was no change in the metal concentration with the run time for the control experiment.

3. Results and discussion

3.1. Effect of pH

Solution pH is important factor affecting biosorption of metal ions on different biosorbents because pH has a direct influence on the physical and chemical characteristic of both the adsorbent and the adsorbate. According to Lodeiro et al. the acidity or alkalinity of the medium affects the competition ability of hydrogen ions or hydroxyl ions with metal ions to active sites on the biosorbent surface [26]. Therefore, the effects of initial pH on biosorption capacity of As(V) ions using UWS and SBMWS were evaluated within the pH range of 4–10 and the removal percentage is shown in Fig. 1.

For SBMWS, adsorption increased with increasing pH and a sharp increase in adsorption at pH 7 was observed. At pH 7–10, the adsorption still shows a decreasing trend. For UWS, the adsorption still shows a similar trend but will not change significantly. Thus, the maximum biosorption occurred when pH was set between 6 and 7.

A possible explanation for this observation concerns to surface charge. At pH 2, the predominant

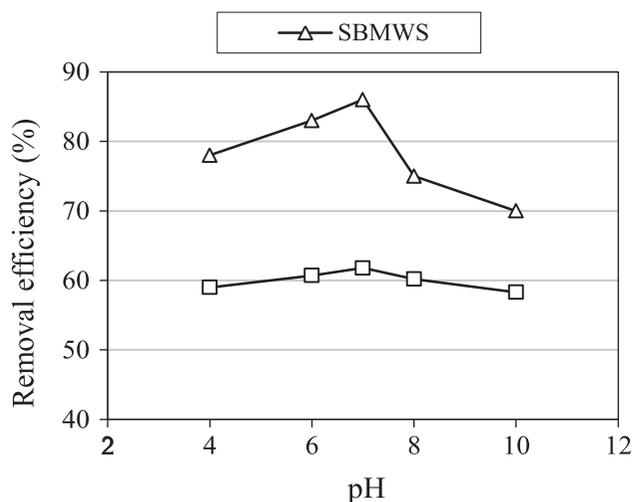


Fig. 1. Effect of pH on adsorption of arsenic by RWS and SBMWS.

arsenate species present in aqueous medium is uncharged H_3AsO_4 , which cannot undergo electrostatic interaction with the adsorbent [27].

According to a speciation diagram for As(V), as declared by Dambies et al. the predominant arsenate species is H_2AsO_4^- between pH 3 and 4 and it mainly exists as H_3AsO_4 and H_2AsO_4^- at pH of 4 [28]. For pH values between pH 4 and 10, Reed et al. reported that arsenate speciation in an aqueous medium is controlled by $\text{H}_2\text{AsO}_4^- \leftrightarrow \text{HAsO}_4^{2-} + \text{H}^+$ at $\text{p}K_a$ of 7 [29]. Based on the experimental results, the pH_{zpc} of UWS and SBMWS is around 7.5, which suggests that the surface charge of both the sorbent is negative at pH higher than 7.5 and it will change to positive charge at pH lower than 7.5. Arsenate is an anion with negative charge upon dissolution in aqueous solution, thus, its adsorption will be reduced after pH 7.5 due to electrostatic repelling. Moreover, at higher pH values, sorption was unfavorable because the OH^- ion is competing with arsenic ions for sorption sites on the UWS and SBMWS.

A similar trend was also observed by Pokhrel and Viraraghavan during their investigation on arsenic adsorption from aqueous solution using modified fungal biomass as adsorbent [30].

3.2. Cause and effect of modification process

Agricultural wastes generally contain cellulose and lignin as main constituents, and in this regard, wheat straw is one of the lignocellulosic compounds containing 35–40% cellulose, 20–25% hemicelluloses, and 8–15% lignin [31,32]. Since compounds above mentioned have different ability in adsorbing organic

and mineral materials, application of wheat straw in removal of aqueous pollutants including metals has been considered by researchers [14]. Removal of heavy metals using wheat straw has been reported by other researchers. In this regard, Doan et al. used wheat straw for removal of cadmium and copper [22]. Their studies revealed that this adsorbent has high capacity in adsorbing copper rather than cadmium so that based on Langmuir model, Q_L index for cadmium and copper was 0.18 and 0.12 mg g^{-1} , respectively, indicating about 38% of this capacity was more for copper compared to cadmium [22]. However, the adsorbing capacity of wheat straw is less than what Doan et al. has reported for adsorbing copper [22]. It can be attributed to the difference in cell wall structure of the adsorbent and groups and sites of adsorbent on the adsorbent surface, especially after activation. Moreover, it may be due to the initial concentration of the metal discussed later. However, it should be noted that metal removal efficiency using agricultural wastes depends upon its capacity, physical, and chemical nature [7]. Although cellulose has suitable adsorbing ability, it has been indicated that it has low capacity in adsorbing heavy metals. Therefore, it has been considered to modify and alter its structure in order to access a durable structure having high adsorbing capacity for heavy metals. In fact, this modification is carried out to change particular properties of cellulose, for example, hydrophobic and hydrophilic characteristics, elasticity, soaking, adsorbing capacity, ion exchange, and heat resistance [33].

Thus, in the present study, NaHCO_3 has been used to modify wheat straw. Since concentration of NaHCO_3 could be effective in modification process, wheat straw was exposed with different concentrations of NaHCO_3 and in each case; surface properties of the adsorbent modified was assessed using SEM and EDAX software to evaluate the ability in adsorbing arsenic.

SEM images (Fig. 2) show that all adsorbents have been affected and modified by NaHCO_3 solution. In addition, the modification was resulted from addition of NaHCO_3 solution and the change and destruction of adsorbents has been more and visible as concentration of NaHCO_3 increased.

Among the adsorbents named as SBMWS1, SBMWS2, SBMWS3, and SBMWS4 based on the NaHCO_3 concentrations of 0.1, 0.4, 0.7, and 1.0 mol, respectively, excluding unmodified adsorbent named UWS, SBMWS1 had the least destruction and SBMWS4 had the most destruction. In spite of destruction at the adsorbents surface, number of voids and their morphology on their surface were different depending upon the concentration of NaHCO_3 . It

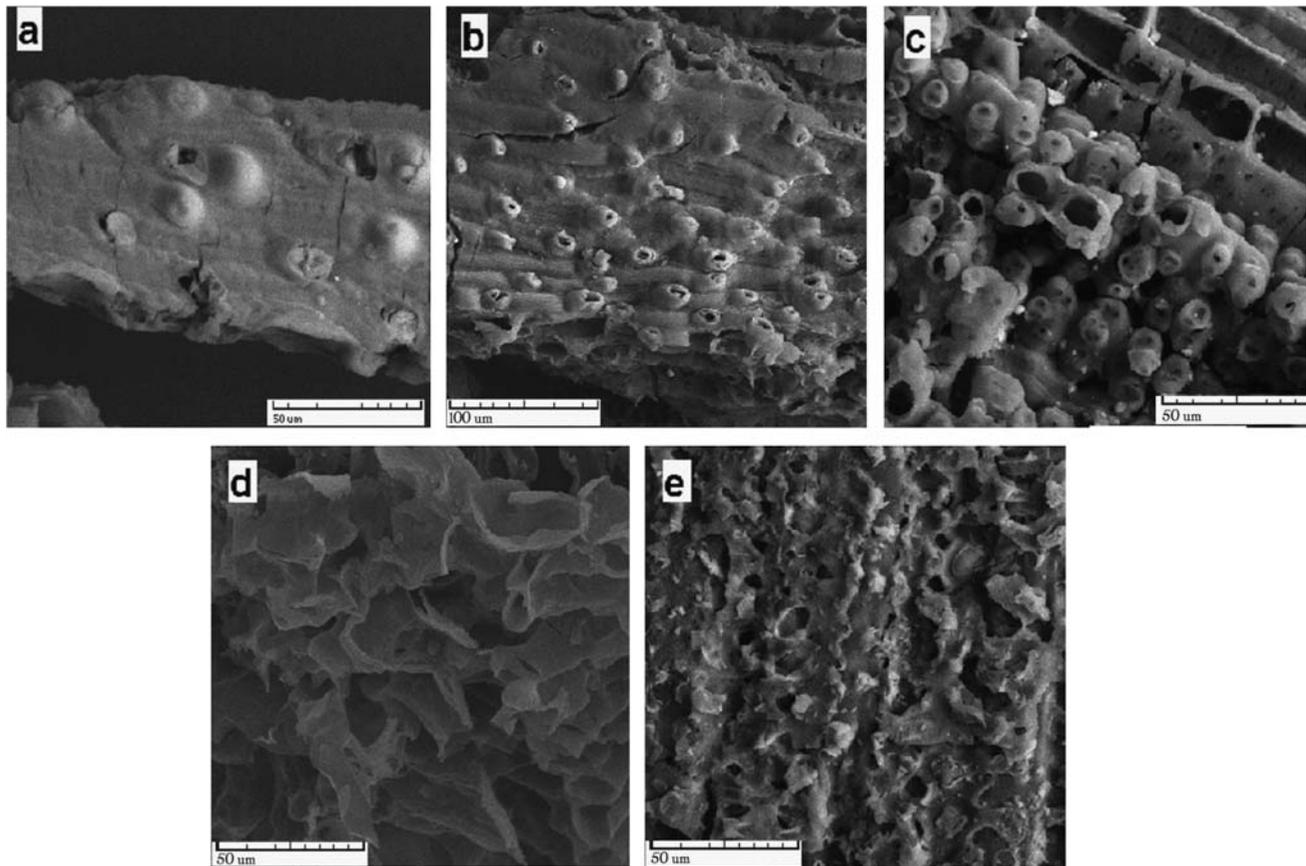


Fig. 2. SEM images of wheat straw samples (a) untreated; (b) treated by 0.1 mol NaHCO_3 ; (c) treated by 0.4 mol NaHCO_3 ; (d) treated by 0.7 mol NaHCO_3 ; and (e) treated by 1 mol NaHCO_3 .

seems that number of voids has decreased with increasing NaHCO_3 concentration because destruction of the adsorbent surface at higher concentration of the solution modified has been manifested as increased voids diameters. As a result, number of voids is decreased, which can result in decreasing adsorbent efficiency in adsorbing arsenic due to decreasing active surface and sites involved in adsorbing arsenic. This trend could be deduced from comparing arsenic adsorbing efficiencies using adsorbents modified (Fig. 3).

Moreover, assessing situation of adsorbents surface based on SEM images indicates that the adsorbents surface, especially in SBMWS3 is almost irregular. This structure makes the adsorbent to absorb the arsenic ions in different parts. EDAX spectra of adsorbents before adsorbing (Fig. 3(a)) show that the adsorbents mainly include carbon, oxygen, and small amount of silica and calcium and there is no trace of arsenic. Sodium peak could be observed at spectra of Fig. 3(b), which belong to NaHCO_3 , and as it is

observed from the spectra that sodium peak becomes bigger with increasing NaHCO_3 concentration. After adsorption, arsenic peak is detectable in spectra, varying depending upon the type of adsorbent (Fig. 3(c)). Therefore, as Fig. 4 indicates, adsorbing arsenic increases with increasing NaHCO_3 concentration and it increases from 69.4% for SBMWS1 to 83.6% for SBMWS3. In addition, EDAX spectra represents a sharp and characteristic peak for this adsorbent, however, adsorbing arsenic has again reduced with increasing NaHCO_3 concentration so that the removal efficiency of arsenic has decreased to 76% using SBMWS4. This decreasing tendency in adsorbing arsenic has resulted in creating smaller peaks in EDAX spectra. Fig. 5 shows the characteristic FTIR spectra of UWS (a) and SBMWS (b) wheat straw after eliminating O–H and C=O=C bonds at approximately 4,000–3,800 and 2,360 cm^{-1} , respectively. The purpose of elimination of these bonds was to highlight other peaks, which could not be easily indicated in the presence of the above mentioned bonds. Comparing

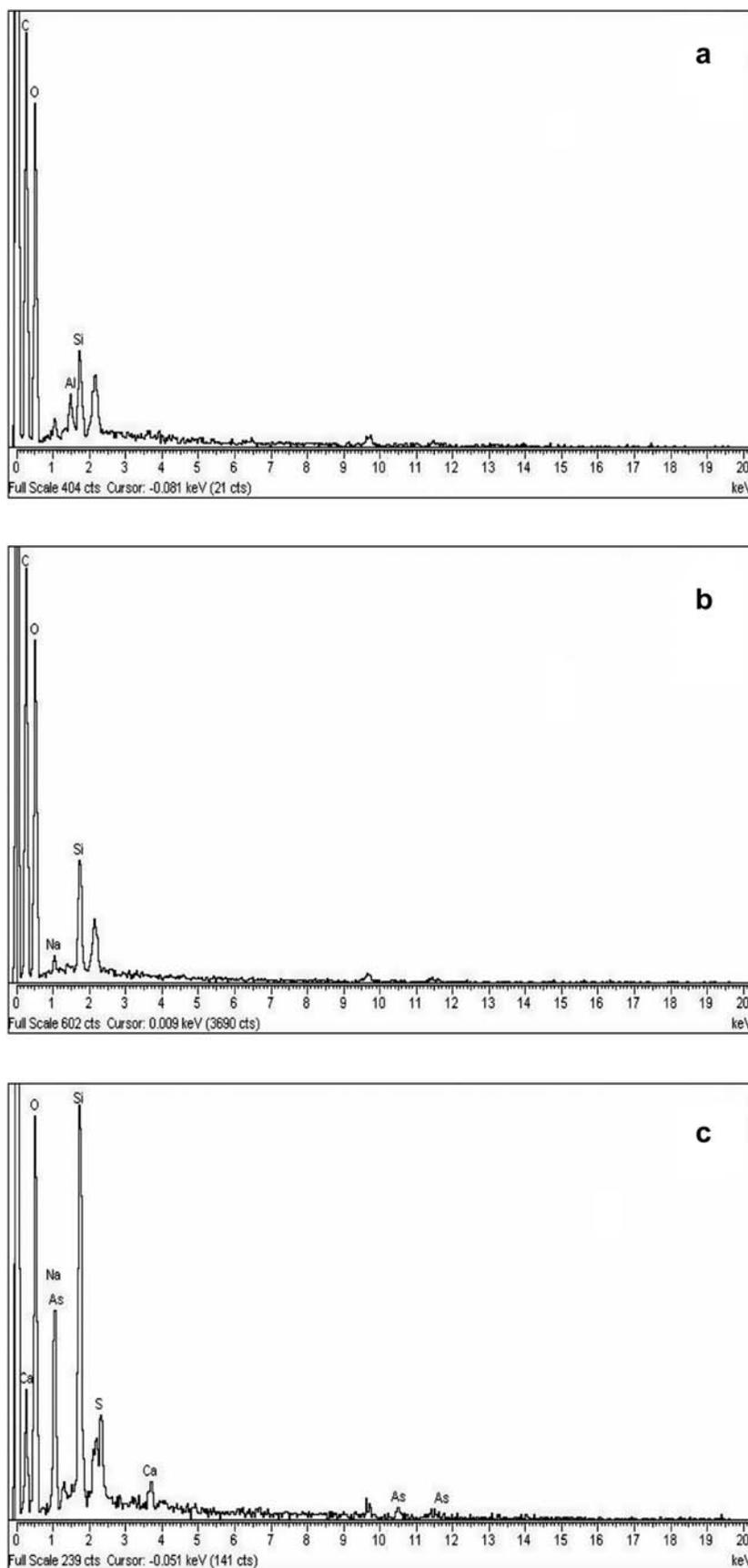


Fig. 3. EDAX spectra of wheat straw (a) untreated; (b) treated before adsorption; and (c) treated after adsorption.

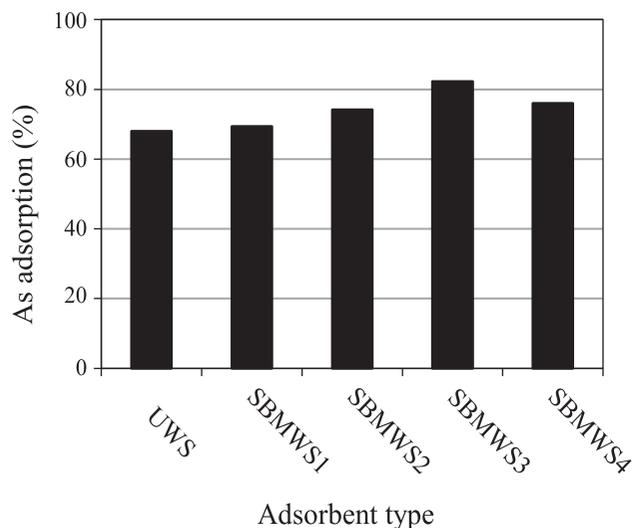


Fig. 4. Effect of adsorbent type on adsorption of arsenic.

FTIR plots of UWS and SBMWS revealed appearance of no new peaks. However, the intensity of the bonds has been significantly increased after treatment.

3.3. Effect of adsorbent dosage

The amount of adsorbent is an important factor because this parameter determines the capacity of an adsorbent for an apparent concentration of the

adsorbate. Therefore, adsorbent dosage on the efficiency of adsorption was also investigated. The results showed that for the initial concentration of $1,000 \mu\text{g l}^{-1}$, the percentage adsorption increased from 46 to 61% for UWS and from 83.6 to 98% for SBMWS when adsorbents doses were increased from 1 to 1.5 g L^{-1} for both adsorbents, but at the same time the amount of the adsorbed per unit mass of the adsorbent (adsorption capacity) decreased from 0.046 to 0.04 mg g^{-1} for UWS and from 0.084 to 0.065 mg g^{-1} for SBMWS. The decrease in amount of As(V) adsorbed with increasing dose of adsorbent was basically due to adsorption sites remaining unsaturated during the adsorption reaction. This was due to the fact that as the adsorbent mass was increased, there was less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent [13]. This implied that the number of active sites increased on the adsorbent surface as parallel to increasing adsorbent dosage.

3.4. Effect of initial arsenic concentration

The initial concentration of adsorbate is another important factor in the biosorption process because it provides an important driving force to overcome all mass transfer resistance of adsorbate between the aqueous and solid phases, hence, the effects of the

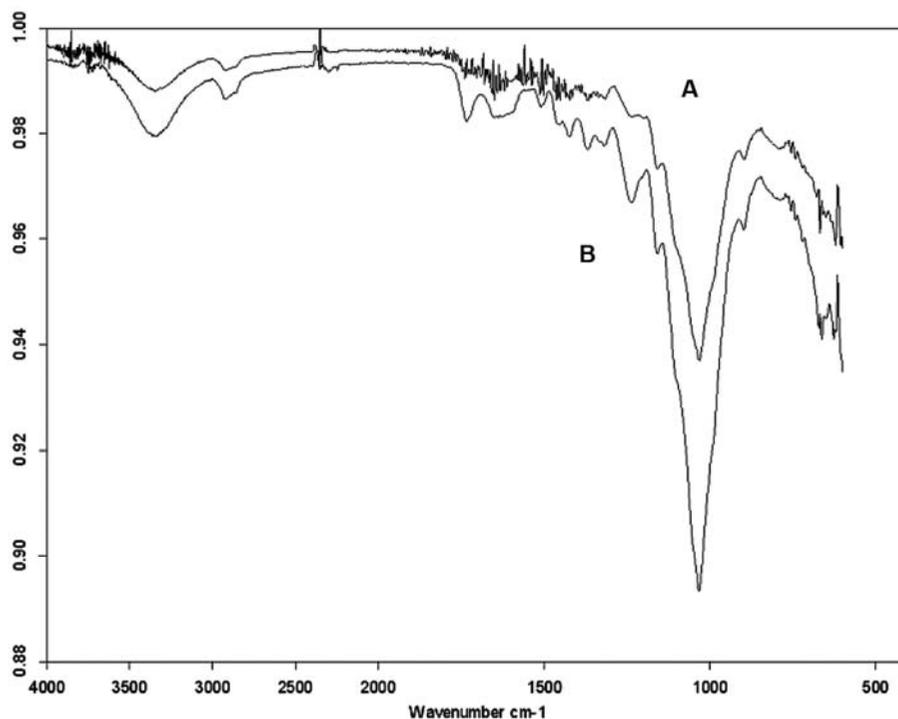


Fig. 5. FTIR spectra of wheat straw (A) untreated; (B) treated.

initial arsenic concentration on the adsorption capacities of the adsorbents were evaluated within the concentration levels ranging from 500 to 2,000 $\mu\text{g l}^{-1}$ and the results are shown in Fig. 6. As expected, the sorption capacities of the sorbents increased with increasing arsenic concentration while the adsorption yields of arsenic showed the opposite trend. When the initial arsenic concentration was increased from 500 to 2,000 $\mu\text{g l}^{-1}$, the loading capacity increased from 0.048 to 0.108 mg g^{-1} of SBMWS3 and from 0.028 to 0.054 mg g^{-1} of UWS (result not showed). As seen from results, the uptake capacity increased rapidly at 30 min, and then kept on increasing gradually until equilibrium is reached constantly that the equilibrium time is found as 120 min. As it is known from the literature [34], at lower concentrations, all metal ions present in solution could interact with the adsorption sites and thus the percentage sorptions were higher than those at higher initial metal ion concentrations. In fact, at higher concentrations, the available sites of biosorption become fewer and subsequently, the removal of metals depends on the initial concentration. At lower concentrations, however, the ratio of initial number of metal ions to the available sorption sites is low and subsequently, the fractional biosorption becomes independent of initial concentration. It is also clear that the arsenic uptake capacity of SBMWS is significantly larger than RWS because of the greater specific surface area and the microporous structure of SBMWS compared with RWS.

3.5. Adsorption isotherm models

Adsorption isotherms are important for the description of how adsorbate will interact with an

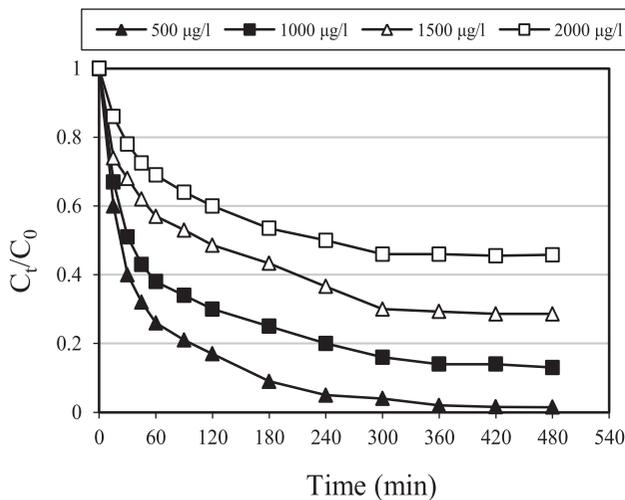


Fig. 6. Effect of initial concentration on adsorption of arsenic by SBMWS in various contact time.

adsorbent and are critical in developing an equation that can be used for design of the most appropriate adsorption system. Several isotherm equations have been used for the equilibrium modeling of adsorption systems [22]. In the present study, in order to investigate the adsorption equilibrium, three adsorption models, namely Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were applied.

The Langmuir and Freundlich equations have been described in our earlier study [35]. The linear Langmuir and Freundlich isotherms of As(V) using SBMWS are shown in Figs. 7 and 8 and also the values of the theoretical parameters of both models along with the regression coefficient (R^2) are presented in Table 1.

High regression correlation coefficients were found (>0.97) for the modified adsorbent, indicating that both adsorption models fit the experimental data well.

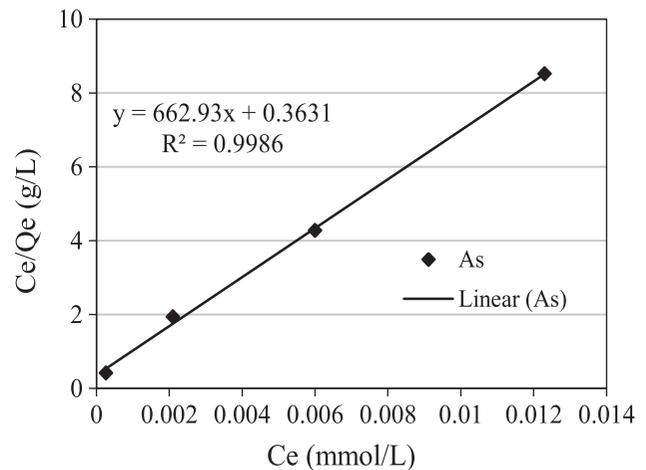


Fig. 7. Linear form of the Langmuir isotherms for the adsorption of arsenic on SBMWS.

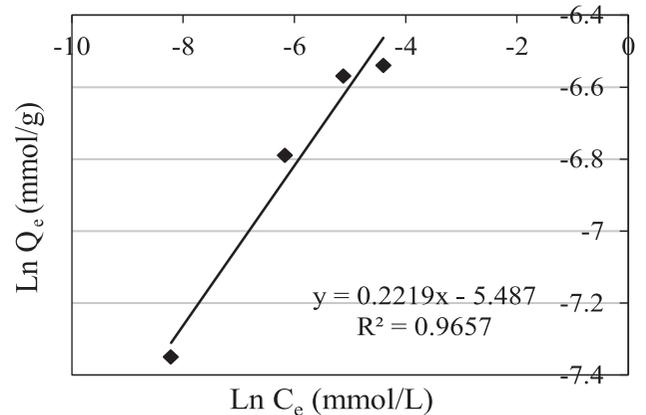


Fig. 8. Linear form of the Freundlich isotherms for the adsorption of arsenic on SBMWS.

Table 1
Parameters of the Langmuir and Freundlich isotherms for adsorption of As(V) on SBMWS

Freundlich model			Langmuir model		
K_F (mmol g ⁻¹)	b_F (L g ⁻¹)	R^2	K_L (L mmol ⁻¹)	Q_L (mmol g ⁻¹)	R^2
0.0042	0.2219	0.97	1,826	0.0015	0.99

This observation suggests that monolayer adsorption, as well as heterogeneous surface conditions may coexist under the applied experimental conditions. Hence, the overall adsorption of As(V) on the SBMWS is complex, involving more than one mechanisms, such as ion exchange, surface complexation, and electrostatic attraction [36].

Another equation can be used to evaluate the adsorption process as separation factor (R_L) that is related to energy of adsorption and shows the adsorption is favorable and defined as [22]:

$$R_L = \frac{1}{1 + K_L C_{\max}}$$

where C_{\max} is the highest (initial) metal concentration in solution (mg L⁻¹) and K_L is the Langmuir constant (L mg⁻¹). Therefore, if the value of R_L is less than 1, the adsorption is considered to be favorable and it is unfavorable when R_L is greater than 1. According to the experimental data for C_{\max} from 0.5 to 2 mg L⁻¹ used in this study, the values of R_L range from 0.02 to 0.08. Therefore, adsorption of As(V) on the SBMWS can thus be considered favorable. In other words, SBMWS is a suitable adsorbent for arsenic.

The equilibrium data were also tested using the D-R isotherm model to determine the nature of adsorption processes as physical or chemical. This model does not assume a homogeneous surface or a constant adsorption potential as the Langmuir model. The D-R isotherm is as follows [22,37]:

$$Q_e = Q_m e^{-\beta \varepsilon^2}$$

where b is a coefficient related to the mean free energy of adsorption (mol² J⁻²), Q_m is the maximum adsorption capacity, and ε (epsilon) is the Polanyi potential (J mol⁻¹) that is as follows [22]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

A plot of $\ln(Q_e)$ vs. ε^2 is shown in Fig. 9 along with the equations of the linear trends through the data

points. As can be seen in Fig. 9, this model well fitted the equilibrium data since the R^2 value was found to be 0.97 for As(V) adsorption.

From the slopes of the linearly regressed lines, which are the coefficients shown in the right-hand side of the correlations in Fig. 9, the coefficient β can be determined, and the mean free energy of adsorption, E , can be estimated using the following equation [22,38]:

$$E = \frac{1}{\sqrt{-2 \cdot \beta}}$$

The value of E was found to be 15.2 kJ mol⁻¹. If E value is between 8 and 16 kJ mol⁻¹, the adsorption process follows chemical ion exchange and if E value is less than 8 kJ mol⁻¹, the adsorption process is known to follow physical adsorption [22,38]. Therefore, the adsorption of As(V) by SBMWS in this study can be carried out by chemical ion-exchange mechanism.

3.6. Adsorption kinetics

For understanding the dynamics of adsorption of As(V) onto SBMWS the adsorption kinetic was studied. This information can be used for obtaining

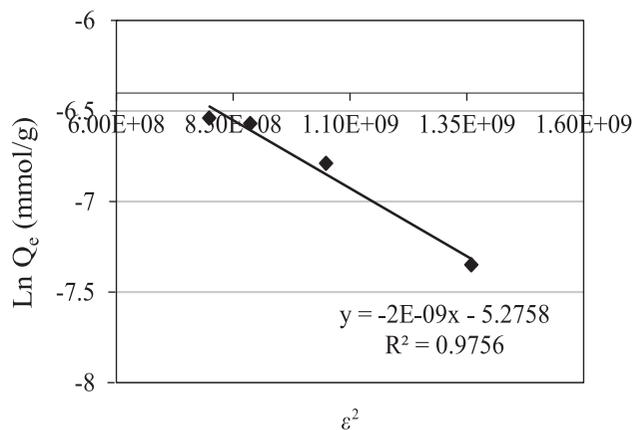


Fig. 9. Adsorption isotherm of arsenic based on the D-R model.

Table 2

Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption of As(V) on SBMWS at different initial concentrations

Initial concentration (mg l ⁻¹)	Expt. Q_e (mg g ⁻¹)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
		Cal. Q_e (mg ⁻¹)	K_I (min ⁻¹)	R^2	Cal. Q_e (mg ⁻¹)	K_{II} (g mg ⁻¹ min ⁻¹)	R^2
0.5	0.048	0.033	0.0161	0.96	0.052	0.77	0.99
1	0.084	0.048	0.0101	0.97	0.092	0.34	0.99
1.5	0.105	0.071	0.0078	0.98	0.119	0.16	0.99
2	0.108	0.088	0.0099	0.99	0.120	0.14	0.99

Note: Expt.: experimental data; Cal.: calculated or estimated from the model.

models that allow estimations of the amount adsorbed with the adsorption time. Therefore, the experimental data were analyzed using pseudo-first and second-order kinetics models. The linearized form of the pseudo-first-order rate equation is generally expressed as follows [22]:

$$\ln(Q_e - Q_t) = -K_I t + \ln Q_e$$

where Q_t and Q_e are the amounts of metal ions adsorbed on the adsorbent at a given time t and at equilibrium, respectively, K_I is the adsorption rate constant. The plot of $\ln(Q_e - Q_t)$ vs. t should give a linear relationship from which K_I and Q_e can be determined from the slope and intercept of the plot, respectively. The model prediction of Q_e and K_I , the values of the adsorption rate constant, along with the experimental Q_e are listed in Table 2.

As seen in Table 2, although linear regression that fits the experimental data reasonably well with the coefficients of determination for this model is high ($R^2=0.96-0.99$), the calculated Q_e is not close to the experimental value, hence it failed to predict Q_e accurately. Therefore, experimental data were also analyzed by the linearized pseudo-second-order kinetic model which is presented in the following form [22]:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_{II}Q_e^2}$$

where K_{II} is the rate constant of pseudo-second-order adsorption. Values of K_{II} and Q_e were calculated from intercept and the slope of the linear plots of t/Q_t vs. t and the results obtained are given in Table 2.

The rate constants (K_{II}), the R^2 and the Q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (0.99). These results indicated that the Q_e value predicted from the

second-order model is much more comparable to the experimental Q_e value than that from the first-order model. Therefore, the adsorption of As(V) ions onto modified wheat straw follows well the pseudo-second-order kinetic model.

4. Conclusion

The adsorption properties of As(V) on SBMWS from aqueous solution were studied under equilibrium conditions. The operating parameters, adsorbent dosage, pH of solution, contact time, adsorbate concentration, and modifier concentration, were effective on the adsorption efficiency of As(V). Based on the results, it can be concluded that the adsorption was highly dependent on operating parameters. For SBMWS, adsorption will increase with increasing pH and there is a sharp increase in adsorption at pH 7. The results showed that the percentage adsorption increased both adsorbents when their doses were increased, but at the same time the amount adsorbed per unit mass of the adsorbent (adsorption capacity) decreased. It can be also concluded that the sorption capacities of the sorbents increased with increasing arsenic concentration while the adsorption yields of arsenic showed the opposite trend. SEM images show that all adsorbents have been affected and modified by NaHCO₃ solution. In addition, the modifications resulted from the concentration of NaHCO₃ solution and the change and destruction of adsorbents has been more and visible as concentration of NaHCO₃ increased. The Langmuir and Freundlich isotherms models were capable of representing the experimental data. From the D-R model, it can be also concluded that the adsorption of As(V) using SBMWS was taken place by chemical ion-exchange mechanism. The adsorption kinetic studies showed that the equilibrium data could better be described by the pseudo-second-order model ($R^2 > 0.99$) than pseudo-first-order model.

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