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Research Article

Adsorption of Arsenite from Aqueous Solutions Using Granola Modified Lemon Peel

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Abstract

The arsenite species is a common form of arsenic in nature and ground waters and is categorized as a major public health group. In the present study, the arsenite ions from contaminated solutions were removed by adsorption on the granola modified lemon peel. The arsenite adsorption on lemon peel was investigated by various concentrations of arsenite with 0.2 g/100 mL of adsorbent at a range of pH 3 - 10 and a constant temperature of 25°C for 0 to 240 minutes using batch experiments. Data of the adsorption experiment were analyzed by the pseudo-first and second- order kinetic equations. The Freundlich and Langmuir isotherm models were used to understand the adsorption relationship between the arsenite ions and functional groups on the lemon peel. pH equal to 5.2 was recorded as pH_{zpc} of this adsorbent in aqueous solution. The optimum condition was obtained at 60 minutes, pH value 8, and 2 mg/L of arsenite, with a removal efficiency of 88%. The maximum adsorption capacity of granola lemon peel was 27 $mg.g^{-1}$ in Langmuir model. Lemon peel adsorbent presented good removal efficiency for arsenite in contaminated aqueous solutions and real water.

Keywords: Arsenite, Lemon Peel, Kinetics, Real Water

1. Introduction

General human exposure to arsenic is mainly through drinking water and food. The most important source of pollutants is food, but in some areas, a significant source of exposure to inorganic arsenic is the little amount of arsenic in the drinking water. Wastewaters and contaminated soils are also the main source of arsenic exposure to humans and animals (1). The world health organization (WHO) categorized arsenic as a major public health group. The Environment Protection Agency (EPA) and international agency for research on cancer (IARC) classified arsenic as group A and Category 1 human carcinogen (2, 3). Arsenic exists as oxyanions in an oxidation environment (4). Generally, 2 oxidation states of arsenic (III) and arsenic (V) are common in the nature and ground waters. Since 2006, the drinking water standard announced that the maximum contaminant level (MCL) for arsenic is 10 μg/L. At concentrations above the MCL, arsenic can cause skin damage, circulatory problems, and risk of cancer (5). Thus, consumption of food containing arsenic causes the following problems: nausea; cancer in kidney; skin thickening; pigmentation; neurological disorders; and damage to bladder, lungs, and skin (6, 7). The intensity of arsenic poisoning causes vomiting, bloody diarrhea, abdominal and esophageal pain (8).

Several chemical methods such as coagulation, adsorption, precipitation, ion exchange, membrane filtration, and biological methods such as biomass and biofiltration have been developed to remove heavy metals from aqueous solutions (9, 10). In the recent years, agricultural wastes as an adsorbent have received much attention due to the functional groups on the surface of these materials (11). Compared to other removal methods, adsorption by agricultural wastes has various advantages such as high metal binding efficiency, selectivity for specific pollutants, no production of secondary toxic compounds, and low cost of sorbent. Further applicability of this method is highly suitable for small scale industries (12).

The literature indicates that various economical materials have been used for the adsorption of arsenic such as iron oxide impregnated carbon, fruit shells, modified coconut coir pith, metal oxide nanoparticles, iron oxide coated sand, modified biomass, residue rice polish, modified cotton cellulose, sawdust, modified orange peel, surfactant modified zeolite, iron oxide, bone char, and coconut fiber (13-15). Most of the agricultural materials were utilized after simple treatment and their performance in the removal of pollutants was encouraging at lower concentrations. Taking into account their effectiveness and performance, these adsorbents, which were economic and simple, were selected to eliminate heavy metals from aqueous solutions.

In this regard, the present research aimed at investigating the performance of modified lemon peel adsorbent for arsenite removal at low concentration levels. An additional objective of study was to determine the kinetic and the isotherm model of the adsorption process. The efficiency in arsenite removal was finally examined using arsenite polluted natural water from laboratory tap.

2. Materials and Methods

2.1. Reagents and Equipment

All used chemicals were of analytical grade. A suitable amount of sodium arsenite was dissolved in deionized water to prepare 100 ppm stock solution. Fresh working solutions of desired concentrations were prepared from stock solution. Different buffers such as acetate and ammonium were used to adjust the pH of the sample solutions. The sodiumborohydride 0.02% w/v was added to sodium hydroxide 0.05% w/v to reduce the agent for arsenic (V); pH meter model Sension 3 (Huch, USA) (for measuring the pH values), orbital shaker model GLF 137 (Germany) (for agitating suspension), and atomic absorption spectrometer (AAS) equipment with furnace (20AA, Perkin Elmer, Singapore) were used to determine As during adsorption experiments. Chemical oxygen demand (COD) of the effluent of adsorbent material was measured by COD reactor and DR 2000 (Huch, USA).

2.2. Collection and Preparation of the Adsorbent

The lemon peel adsorbent material was obtained from a fresh juice store in Yazd. The peels were simply washed with tap water and deionized water to make them clean from unwanted material. The collected peels contained dye and other volatile compounds, so they were washed with HNO_3 5% and dried in an incubator at 75°C for a day. Initially, COD of the suspension containing peels was greater than the permissible limit. Thus, to maintain the COD of suspension, lemon peel was washed several times with 5% HNO_3 solution and with deionized water till the value of COD was achieved to the permissible level. Finally, the washed adsorbent material was dried at the 65°C for 24 hours. Dried material was grounded by an electrical mill and sized at mesh 60 - 100 (149 - 155 μ) by standard sieves.

2.3. Equilibrium Adsorption

Arsenite adsorption on lemon peel was investigated using batch experiments. For this purpose, the 50 mL solution containing 5 to 20 mg/L of As (III) with 0.2 g/100 mL of adsorbent was fixed at pH 3 - 10. Suspension was agitated in 150 RPM at 25°C. Then, suspension was filtrated by Wathman paper. The concentration of arsenite ions in the filtrate solution was measured by AAS at 197.2 nm wavelength. The equations 1 and 2 were employed to calculate removal efficiency (%) and adsorption capacity, respectively.

$$RE\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

$$q = \frac{C_{0-C}}{m} \times V \tag{2}$$

Where RE is removal efficiency (%), q is adsorption capacity (mg/g), C_0 and C are arsenite ions concentration (mg/L) of the solution before and after adsorption, m is the adsorbate amount (g) and, v is solution volume (L).

To investigate the kinetic of the adsorption process, the adsorption experiments were done in the initial pH solution with 2 mg/L of arsenite at various contact times. The contact time was varied from 0 minutes to 240 minutes, the time when the adsorbent is added to the arsenite solution and immediately filtered without shaking the mixture is termed as t time. Flasks were shaken on the orbital shaker at different desired times in constant of adsorbent amount, solution volume, and pH. Then, it was taken out and the suspension was filtrated to analyze the residual arsenic concentrations.

2.4. Determination of pHzpc

Zero point charge of adsorbent was determined by the salt addition method (16). In this method, the 0.2 g sample and 40 mL of 0.005 M $NaNO_3$ were mixed in 6 reaction vessels at 298 K. The pH of the suspension was then adjusted to an initial pH value of 2, 4, 6, 8, 10, or 12 by either 0.1 and 1 M HNO_3, or 0.1 and 1 M NaOH solution using a pH-meter. Each flask was then vigorously agitated in an orbital shaker for 24 hours. Next, the final pH of each suspension was measured very carefully. The final pH (the measured pH) values were then plotted against the initial pH values. The intersection of final pH with initial pH was taken to be the pH_{zpc}.

2.5. Adsorption Kinetics

The pseudo-first and pseudo-second order equations were used to further understand the adsorption kinetics. The linear form of pseudo- first and second- order rate equation is given as follows (17):

$$\ln\left(q_e - q_t\right) = lnq_e - k_1 \times t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Where k_1 (min^{-1}) and k_2 (g/mg.min) are rate constants, q_e and q_t are the amount of metal ion on the surface of adsorbent (mg/g) at equilibrium and specified time, respectively.

2.6. Adsorption Isotherms

The Langmuir adsorption isotherm assumed formation of monolayer of metal ions on the surface of the adsorbent. K_L and q_m are the 2 main parameters of Langmuir model (18). The Langmuir linear equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{5}$$

Where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the same as above, Q_m is the maximum amount of metal ions adsorbed on the adsorbent, and the K_L is the binding energy of solute (L/mg). Dimensionless constant separation factor R_L is an essential characteristic of Langmuir isotherm, which is calculated by the following equation. (19).

$$R_L = \frac{1}{1 + C_0 \times K_L} \tag{6}$$

Like Langmuir equation, Freundlich equation is commonly used in the isotherm study of adsorption. The linear form of the Freundlich equation can be represented as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Where K_F is adsorption capacity (L/g), 1/n adsorption intensity; q_e and C_e are the same in the Langmuir isotherm equation.

2.7. Treatment of Arsenite Contaminated Water Sample

The actual efficiency of modified adsorbent can be evaluated by testing real water samples. The sample water was collected in plastic bottles from the tap of the laboratory. The real samples were filtered and their initial arsenic concentrations were analyzed by AAS. A suitable amount of water sample was spiked with a constant volume of standard arsenite solution and the adsorption experiment was performed under optimum conditions. The removal efficiency of the adsorbent was obtained on contaminated real water samples.

3. Results and Discussion

3.1. pH of Zero Point Charge

The results for determining pH_{ZPC} are demonstrated in Figure 1. The point of intersection of the curves of pH_{final} vs. $pH_{initial}$ was recorded as pH_{zpc}, which was set equal to 5.2 according to the Figure 1.

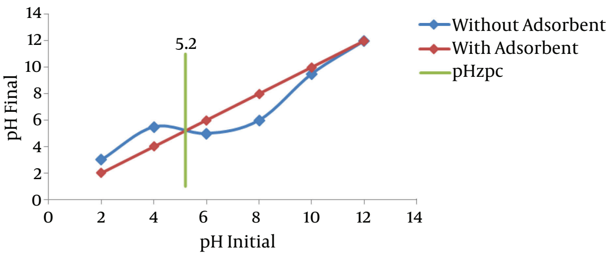

Figure 1. The Change of pH_{final} via $pH_{initial}$ for Modified Lemon Peel (m = 0.2 g, V = 100 mL, and RPM = 150)

The pH of zero point charge is the pH, and the net charge on the surface of a solid in the solution is zero.This pH indicates that the surface of adsorbent has a positive charge in the pHs lower than 5.2 and has a negative charge in pHs higher than 5.2. Then, the granola of lemon peel is suitable for adsorption of cations and neutral molecules such as arsenite in pHs higher than pH value 5.2.

3.2. Effect of pH

Lemon peel adsorbent performance for arsenic removal at different pH is shown in Figure 2. An increase in pH from 3 to 8 causes an increase in removal efficiency from 33.1% to 79.8%, but the removal efficiency decreases to 47.2%, with a more increase in pH until 10. The maximum removal was obtained 79.8% at pH 8, and then this pH was selected as optimum pH for the adsorption of arsenite by lemon peel.

pH has an important role in adsorption process that can change the charge of species and also the electrical charge on the surface of granola adsorbent in the solution, so it controls the adsorption progress. According to Figure 2, in medium acidic, neutral, and low basic pHs, the high adsorption was registered. However, the adsorption revealed a decreased trend in pH value lower than 5 and upper than pH 9. The same trend was noticed in the case of arsenic adsorption on rice polish in the study of Ranjan et al. (20). In the present study, the optimum removal was obtained in the pH, ranging from 6 to 8, which is the suitable pH for drinking water and wastewaters. Thus, this adsorbent can show a good performance for arsenite removal in the polluted waters.

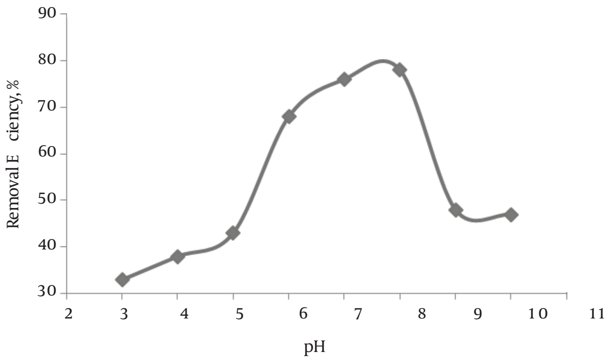

Figure 2. Effect of pH on Removal of Arsenite by Lemon Peel (C_0 = 20 mg/L, m = 0.2 g/100 mL, and Time = 90 min)

3.3. Effect of Contact Time

Figure 3 represents the effect of contact time on the adsorption of arsenite by granola lemon peel. This revealed the adsorption of arsenite increase to 70% when the time reached in 60 minutes. After this time, the removal efficiency was increased slowly. Hence, the optimum contact time for arsenite adsorption by granola lemon peel was 60 minutes.

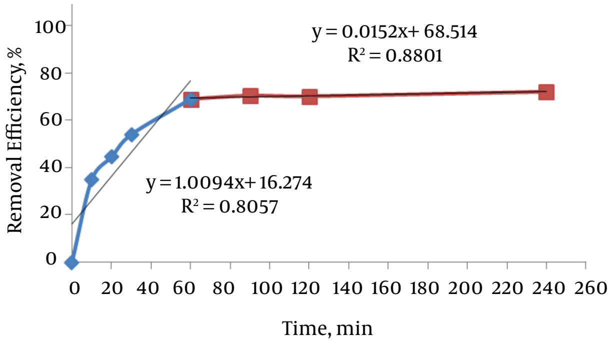

Figure 3. Effect of Contact Time on the Adsorption of Arsenite by Lemon Peel (C_0 = 20 mg/L, m = 0.2 g/100 mL, and pH = 8)

Equilibrium study has an important role in determining the efficiency of the adsorbent and adsorption process. Based on Figure 3, adsorption was found to be very fast in the first 60 minutes, and it was slowly increased up to 240 minutes, so the value did not significantly change with the contact time. This phenomenon can be attributed to the surface of the adsorbent, which is free in the initial stage and adsorption was fast. According to Figure 3, the adsorption process consists of 2 stages (first stage up to 60 minutes and the second stage up to 240 minutes). It suggests that intraparticle diffusion is not the only rate- limiting step for the whole sorption process (21). The high value of correlation coefficient (0.805) up to 60 minutes indicates that the diffusion process occurs on the arsenite anions from bulk solution into the adsorbent up to 60 minutes. The linear part of the curve, which is not passing through the origin, reveals that the sorption mechanism was complex and both the surface adsorption as well as intraparticle diffusion occurred in the process. A similar mechanism was observed in the study of arsenic (V) adsorption on bone char from aqueous solution (22).

To investigate the detail kinetic of sorption, the experimental data were fitted by pseudo- first and second- order kinetic models. The constants of 2 kinetic equations were determined from the linear equations that are presented in Table 1.

According to Table 1, the high value of correlation coefficient for 2 models ($R^2 > 0.97$) indicated that experimental data were well fitted to 2 kinetic models, specifying that the rate of adsorption depended on the both arsenite ions and the functional groups in the active sites of lemon peel.

3.4. Effect of Initial Concentration

The effect of initial concentration on the Lemon peel efficiency was examined in the range of 2 - 50 mg/L^{-1} of arsenite. The results are presented in Figure 4. The figure demonstrates that the maximum removal occurred (78.1%) in the concentration of 2 mg/L arsenite. With an increase in initial concentration to 50 mg/L, the removal efficiency was decreased to 40.5%.

Also, 2 general Freundlich and Langmuir isotherm models were used to understand the mechanism of adsorption. The obtained data were fitted to linear equations and the constants of the 2 models were obtained for the arsenite adsorption ions onto lemon peel, which are presented in Table 2.

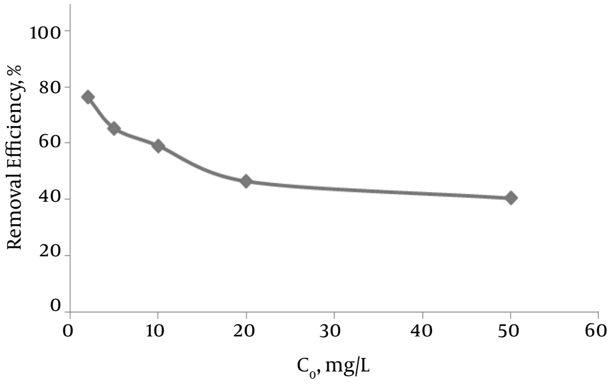

Figure 4. Effect of Initial Concentration on the Adsorption of Arsenite by Lemon Peel (m = 0.2 g/100 mL, Time = 60 min, and pH = 8)

Table 1. Pseudo - First Order and Pseudo- Second Order Constants for the Adsorption of Arsenite Ions Onto Lemon Peel

Variables	Pseudo- First Order			Pseudo- Second Order		
Adsorbent	q_e	K_1	R^2	q_e	K_2	R^2
Arsenite	17.2	1.133	0.985	13.7	0.384	0.976

Table 2. Freundlich and Langmuir Constants for the Adsorption of Arsenite Ions Onto Lemon Peel

Variables	Isotherm					
	Langmuir			Freundlich		
Adsorbent	Q_m	K_L	R^2	n	K_F	R^2
Arsenite	27.0	0.079	0.864	1.64	2.43	0.995

According to Table 2, the adsorption process is better fitted to the Freundlich than the Langmuir isotherm model based on the correlation coefficient. Also, the values of n that are greater than 1 indicate that the adsorption arsenite on the lemon peel under the studied condition was favorable. Chio reported the 0.38 value of n for the adsorption of arsenite on shermil shell (23). It can be concluded that the modified lemon peel may be due to the complex nature of the sorbent containing various active sites for the sorption and has a good tendency toward arsenite ions. This revealed that reaction between lemon peel adsorbent and arsenite ions is physisorption and chemisorption (24). Thus, in addition to physical attractive forces such as Van Der Wals, the formation of chemical bond is involved between arsenite ions and lemon peel adsorbent. Similar observation was seen in the study of As (III) adsorption on sawdust and bone char (25).

The maximum adsorption capacity (Qm) value of 27.0 $mg.g^{-1}$ was obtained from Langmuir model for the lemon peel in the arsenite adsorption. The R_L was calculated as 0.63 for the adsorption process. According to the R_L value, if R_L is greater than 1, equal to 1, equal to 0, and between 0 and 1, it indicates that the adsorption process is unfavorable, linear, irreversible, and favorable, respectively. This revealed that the adsorption of arsenite on the lemon peel was favorable in 298 K.

3.5. Application for Real Contaminated Water

The proposed lemon peel adsorbent was successfully applied to the arsenic contaminated real water sample. It was observed that the lemon peel showed 80% removal efficiency and proved to be an effective adsorbent for the treatment of arsenite contaminated water samples up to the safe limit recommended by WHO.

4. Conclusion

Lemon peel adsorbent presented good removal efficiency for arsenite in aqueous solutions. The removal efficiency was depended on pH solution, and maximum removal of arsenite was obtained at pH 8. The adsorption process kinetically followed 2 stages and fitted with pseudo- second order equations. According to Langmuir isotherm, maximum arsenic uptake was 27 mg/g by this adsorbent under the optimum condition. Being inexpensive, simple, and eco-friendly, this adsorbent is attractive for arsenite removal from contaminated water.

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