Journal of Environmental Health and Sustainable Development

Using Generation 3 Polyamidoamine Dendrimer as Adsorbent for the Removal of Pentavalent Arsenic from Aqueous Solutions

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ARTICLE INFO

ORIGINAL ARTICLE

Article History:
Received: 15 Dec 2016
Accepted: 14 Mar 2016

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Keywords:
Arsenic,
Dendrimers,
Adsorption,
Aqueous Solution

ABSTRACT

Introduction: Arsenic is known as a carcinogenic compound in drinking water. It can cause acute and chronic effects on human health. In this study, the effect of polyamidoamine dendrimer generation 3 (PAMAM G3) as adsorbents for removal of arsenic (V) from aqueous solutions was evaluated.

Materials and Methods: Adsorption experiment was studied in batch system and the effect of different variables such as pH, contact time, concentrations of arsenic and adsorbent dosage on adsorption was studied. Therefore, absorption kinetics and equilibrium isotherms were determined.

Results: The results showed that adsorption process is affected by some parameters such as initial concentration, adsorbent dose and contact time. The three models of isotherm including Langmuir, Freundlich and Dubinin-Radeshkuvich were studied while Freundlich and Langmuir isotherms were more compliant with results.

Conclusion: According to the results, it can be concluded that adsorption with dendrimer is an appropriate method with high efficiency for arsenic removal from aqueous solutions.

Citation: Yavari Z, Amin MM, Izanloo H, et al. **Using Generation 3 Polyamidoamine Dendrimer as Adsorbent for the Removal of Pentavalent Arsenic from Aqueous Solutions.** J Environ Health Sustain Dev. 2016; 1(1): 28-36.

Introduction

Arsenic is a natural element of the earth's crust. It is used in industrial and agricultural sectors. This element is a byproduct of copper smelting, mining and coal burning to [1-3]. Arsenic can enter the water supplies from natural deposits on the earth or from industrial and agricultural pollution. It is widely believed that naturally occurring arsenic dissolves out of certain rock formations when groundwater levels drop significantly [1]. Arsenic has been linked to a number of cancers. These include cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. EPA set the arsenic standard for drinking water at 10 ppb (or 0.010 ppm). According to WHO, maximum concentration level for arsenic in drinking water is less than 0.01 mg/L

[2]. This quantity protects consumers from the long-term effects and chronic exposure to arsenic. Encounter of high concentration of arsenic in drinking water may lead to skin lesions, nausea, diarrhea, anemia, arrhythmia, insentience and skin cancer [1- 4]. The International Agency for Research on Cancer (IARC) has classified arsenic as a carcinogenic agent in humans [1- 2]. Arsenic can be found in water resources in two forms of organic and inorganic [4- 5]. Biotransformation of different forms of arsenic takes place constantly in the environment and the human body.

From the perspective of toxicology, mineral compounds are usually more harmful and dangerous than the other organic ones [4]. Most common methods for arsenic removal from water resources include precipitation, membrane processes, ion exchange, and adsorption. Each method has some advantages and disadvantages such as complicated technology, sludge production and low removal capacity [1- 6]. Nanotechnology provided an opportunity in environmental sciences especially for water and wastewater treatment. Absorbents are widely used in water treatment to remove organic and inorganic pollutants from contaminated water [7]. Currently, to develop high capacity adsorbent for metal ions and other compounds, many researches are done with nanoparticles [8]. Nanoparticles have unique properties such as high surface area and various chemical functional groups [9]. Ultrafiltration process by enhanced dendrimer polymers is developed for the recovery of metal ions from aqueous solution [10]. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology [11]. The properties of dendrimers are dominated by the functional groups on the molecular surface [12]. These branches trap various molecules and protect them against external factors [13-14]. Diallo et al. studied the feasibility of enhanced dendrimer polymers and polyamidoamine dendrimer polymers of ethylene diamine core for Cu^{2+} recovery from aqueous solutions [10, 15]. Lee et al. investigated the adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} on multi-walled carbon nanotubes (MWCNTs). They reported that the maximum adsorption capacity of Pb^{2+}, Cu^{2+} and Cd^{2+} at ambient temperature is 97.08 mg/g, 49.24 mg/g and 10.86 mg/g, respectively [16]. Therefore, this research was done to investigate the effects of generation 3 poly amidoamine dendrimer (PAMAM G3) as adsorbent for the removal of pentavalent arsenic from aqueous solutions.

Materials and Methods

In this laboratory-scale research, the effects of polyamidoamine dendrimer generation 3 (PAMAM G3) as adsorbent was studied for arsenic removal from aqueous solutions. PAMAM G3 was prepared by Color Research Institute of Tehran. The adsorbent chemical structure is shown in Figure 1. Table 1 illustrates the features of dendrimers 1 to 4 generation [11- 12]. All the chemicals used in this study had a high purity laboratory and provided by Merck Company. Aqueous solution pH adjusted by NaOH or HCl (1M). Arsenic concentration was measured by ICP based on the test 3500 of standard method. The effects of initial concentration of arsenic were studied using dendrimers. 0.1, 0.2, and 0.3 mL of dendrimers were added to 250 mL beaker containing arsenic with concentrations of 500, 1000, and 2000 mg/L. Experiments were conducted at optimal pH of 7. All experiments and preparation of standard solutions were carried out based on the guidelines of standard methods for water and wastewater examination. To prepare the solutions, distilled water (deionized) was used.

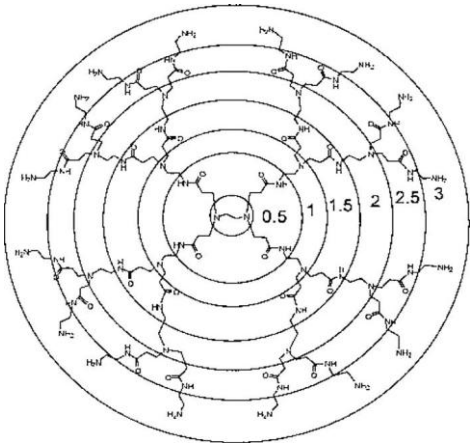

Figure 1: Poly amidoamines dendrimer generation 3 (PAMAM G3)

Table 1: Features of PAMAM dendrimers

Generation	Molecular weight	Measured diameter (Å)	Surface groups
0	517	15	4
1	1,43	22	8
2	3,26	29	16
3	6,91	36	32
4	14,22	45	64

Stock solution (1000 mg/L) was prepared using sodium arsenate salt ($Na_2HAsO_4.7H_2O$). Then, solutions with concentrations of 500 to 2000 mg/L were prepared from main stock solution. The effect of different variables such as adsorbent dosage, contact time, pH, and initial concentration was investigated for arsenic removal efficiency. Removal efficiency by PAMAM dendrimer was studied based on a variable parameter to obtain the optimum variables. In the first phase, experiments were performed by changing the factors of contact time, pH, and initial concentration. In this research, aqueous solutions containing different concentrations of arsenic were studied. Kinetic experiments were conducted by changing the contact time (15, 30, 60, 180 and 300 S), arsenic initial concentration (1000 mg/L), and the optimized dose of adsorbent (0.2 mL) at pH = 7. Data were analyzed using Langmuir, Freundlich and Dubinin-Radushkevich isotherm equations, along with pseudo first order and second order kinetic equations. The best kinetics and isotherms were determined by calculating the coefficient of determination. Reaction rate constants and above mentioned isotherms constants were calculated to interpret the processes of adsorption isotherms, adsorption capacity, and the type and energy of absorption. Arsenic removal efficiency was calculated using equation 1[5]:

Equation 1:
$$E = \frac{(C_i - C_t)}{C_i}$$

The maximum adsorption capacity (Q_t) per gram adsorbent as mg/g was calculated based on equation 2 [13- 17]:

Equation 2:
$$Q_t = \frac{V(C_i - C_t)}{m}$$

In these equations, *Ci* and *Ct* are the initial and final concentrations of arsenic (mg/L), respectively, *V* is the volume of solution (L), and *m* is the adsorbent dose (g).

Results

Effect of dendrimer concentration

The effect of dendrimer concentration on arsenic removal showed that by increasing the concentration of dendrimers to a certain level, the

removal efficiency increased and then decreased. Optimum concentration of dendrimer for arsenic removal was 0.2 mL. In high concentration of dendrimer, due to the availability of more active surface sites for adsorption arsenic, the removal efficiency also increased [18- 19].

The effect of arsenic initial concentration

The results showed that the equilibrium capacity decreased by an increase in the initial concentration of arsenic. It can be concluded that the active sites on adsorbent are reduced by increasing the concentration of arsenic [20].

The effect of pH on the adsorption of arsenic

The experiments were conducted in a wide range of pH 2-10. The effect of pH on the adsorption of arsenic by dendrimer is shown in Figure 2. The maximum adsorption of arsenic occurs at pH = 7.

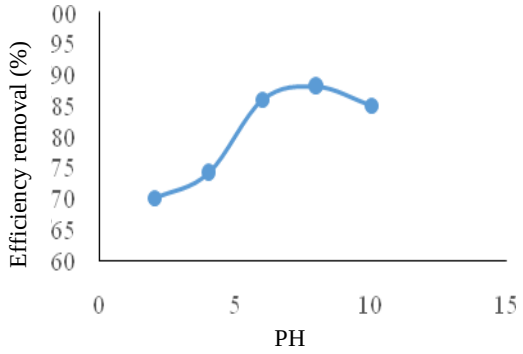

Figure 2: The effect of pH on the adsorption of arsenic (time = 60 S, Arsenic concentration = 1000 mg/L)

Adsorption isotherms

The adsorption isotherm indicates the adsorption capacity (q_e) and equilibrium concentration (C_e). Equilibrium adsorption isotherms, including Langmuir, Freundlich, and Dubinin-Radushkevich were applied (Figures 3a-3b-3c). According to the results (Table 2), Langmuir and Freundlich isotherm models describe the process of absorption more accurately.

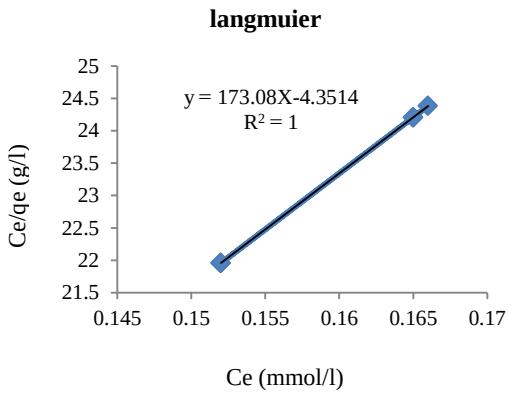

Figure 3a: Arsenic adsorption isotherm by dendrimer PAMAM based on Langmuir model (pH = 7)

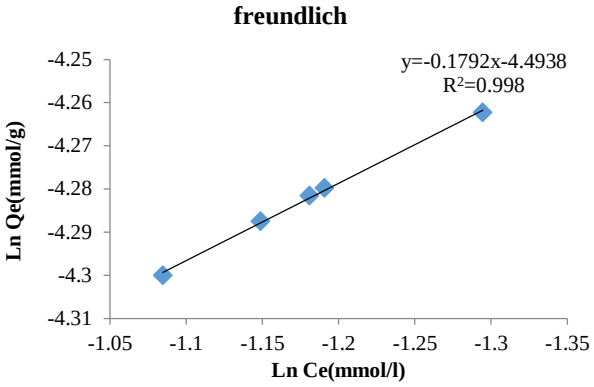

Figure 3b: Arsenic adsorption isotherm by dendrimer PAMAM based on Freundlich model (pH = 7)

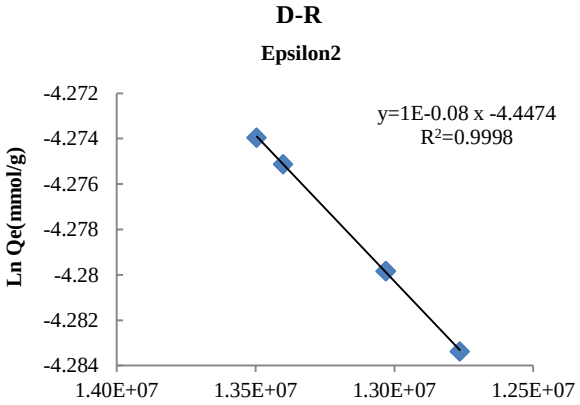

Figure 3c: Arsenic adsorption isotherm by dendrimer PAMAM based on Dubinin-Radushkevich (pH = 7)

Kinetics Adsorption Studies:

Adsorption Kinetics are used to control the absorption system such as mass transfer and chemical reactions progress. These models consist of the first and second pseudo order equations [5, 21-22]. The results of these models are presented in table 3. The results suggested that the model of Hoo et al. (pseudo second-order equation) with correlation coefficient of R^2 = 0.99 is more fitted than Lagergren et al. (pseudo first-order equation) with correlation coefficient of R^2 = 0.95.

Table 2: Langmuir and Freundlich isotherm parameters in Arsenic adsorption

Freundlich model			Langmuir model		
R^2	K_F (mmol g^{-1})	b_F (L g^{-1})	R^2	K_L (L $mmol^{-1}$)	Q_L (mmol g^{-1})
0.998	0.04	0.5	1	39.78	0.01

Table 3: Pseudo first and second -order Kinetics parameters in Arsenic adsorption

Pseudo second-order equation			Pseudo first-order equation			Initial Concentration (µg L^{-1})
R^2	K_{II} (g mg^{-1} min^{-1})	Qe (mg g^{-1})	R^2	K_I (min^{-1})	Qe (mg g^{-1})	
0.99	0.05	233.17	0.95	0.02	0.03	500
1	0.07	198.07	0.90	0.01	0.03	1000
1	0.11	137.25	0.96	0.01	0.07	2000

Discussion

pH is one of the parameters that effect arsenic water and have primary amine groups at the end of each branch which can affect the pH of solution. These functional groups can be modified and linked with different target molecules [23]. The pH of the solution affects the surface charges and ionic arsenic compounds. These conditions control the arsenic adsorption. At acidic condition (pH < 2), the prevailing form of arsenic is H_3AsO_4, a non-ionic compound without electrostatic adsorption. In pH between 3 to 4 there is $H_2AsO_4^-$ and at pH from 4 to 9, $H_2AsO_4^{-2}$ is observed [5- 6]. PAMAM dendrimer have a unique structure which can accept host metal molecules [8]. Therefore, electrostatic adsorption and also organic features and molecular structure of dendrimer have an important role in arsenic adsorption. At pH = 7, there is an electrostatic attraction between the positively charged dendrimers and negatively charged arsenic.

By increasing the solution pH, due to the competition between OH ions and arsenic ions for adsorption, the number of positively charged sites on the surface of dendrimer is reduced. These conditions are not desirable for arsenic adsorption and decline the absorbent capacity for arsenic [9]. On the other hand, in high pH, surface charges of dendrimer become negative, which decrease the tendency to absorb arsenic through electrostatic process [6]. In this study, the optimal pH (pH = 7) was in the same as other studies. Based on the findings of other researches, at pH from 4 to 9, pentavalent form of arsenic was very active and complex with adsorbents [5- 6]. In addition, it has been shown that the optimum pH for adsorption of pentavalent arsenic is between 6 to 8 [24- 25].

Effect of dendrimer concentration on arsenic adsorption

Dendrimers have certain capacity for adsorption [26- 27]. Thus initial concentration of adsorbate is important [19]. Because in high concentration of dendrimers, the more active surface sites are available for adsorption; by increasing the concentrations of dendrimers, the removal efficiency increased and then declined. Dendrimers are known as ligands soluble in water, which remove toxic metal ions from water. Tertiary amine functional groups in polyamidoamines dendrimers create acid-base and hydrogen bonding [9]. Since anions have full orbitals, they cannot be covalently bound to ligand and are removed from water. The polyamidoamine is a powerful chelating agent, so that it can chelate with cations such as transition metals, lanthanides, and actinides. These ligands are recyclable and selectable by changing pH [7- 9]. Azhdarpour indicated in his study that adsorbent dosage is an important and effective parameter for arsenic removal. According to the results, much absorbent had no effect on arsenic removal efficiency [28].

Adsorption isotherm

Adsorption is a mass transfer process and isotherms are used for determination of adsorbent performance. Isotherm data are adjusted in different models to obtain an appropriate model for process. Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were used to interpret laboratory data. Equations of these isotherms:

Langmuir isotherm, Equation 3:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_L} + \frac{1}{Q_L K_L}$$

Freundlich isotherm, Equation 4:

$$\ln Q_e = b_F \ln C_e + \ln K_F$$

Where, C_e is equilibrium concentration adsorbent (mg/L), Q_e is the ratio mass of adsorbate to mass of adsorbant (g/mg) at equilibrium, K_f and n are Freundlich adsorption constants [22]. The Langmuir isotherm can be interpreted by a no dimension constant called separation factor [5]. If the value of separation factor (equation 5) is between 0 and 1, absorption process is considered desirable while if it is > 1, the process is considered undesirable [6]. Equation 5:

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

Where C_{max} is the maximum concentration of metal ion as mg/L.

In this study, the concentration of arsenic was from 500 to 2000 µg/L, thus separation factor was between 0.04 and 0.06. This value indicates that the adsorption of arsenic by dendrimer is desirable. In other words, dendrimer material is an appropriate absorbent for arsenic removal.

Dubinin-Radushkevich

Thermodynamic parameters of adsorption are determined by Dubinin-Radushkevich with Equation 6:

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

Where β is the coefficient of average free energy of adsorption (mol/J) ², Q_m maximum absorption capacity, and ε is the polany potential as j/mol. figure 3c shows the values of Ln Q_e versus ε². The constant coefficients of Freundlich isotherm are calculated by linear regression (Table 2).

According to the results, Correlation coefficients of Dubinin- Radushkevich and Freundlich isotherms are 0.998 and 0.997, respectively, which indicated these isotherms describe arsenic adsorption as well as Langmuir model.

Kinetic Adsorption Studies

The most popular kinetic models are the Lagergren pseudo-first order and pseudo-second order kinetics [22]. For many adsorption processes, the pseudo-first order kinetic was found to be suitable for only the initial 20 to 30 minutes of interaction time but not for the whole range of contact times. Equation 8:

$$\ln(Q_e - Q_t) = -K_1 t + \ln Q_e$$

Where, k_1 is the adsorption rate constant as 1/min, Q_e and Q_t are arsenic adsorption at equilibrium and t (time) as (g/mg), respectively. K_1 and Q_e can be evaluated from the graph of ln (Q_e-Q_t) versus t, if a straight line, and hence the adsorption follows a pseudo first order kinetics model.

If the adsorption system follows a pseudo-second order kinetic, the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate.

The equation below describes the pseudo second order kinetic: Equation 9:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2}$$

Where K_2 is the constant rate of second rate reaction as min.mg/g. then a plot of t/Qt versus t would be linear and K_2 and Q_e can be determined from the intercept and gradient of the graph. The values of constants of equations are presented in table 2. As shown in the table, correlation coefficient is from 0.96 for pseudo-first order to 1 for pseudo-first order. Thus it is concluded that the pseudo-second order kinetic is more acceptable for this process. One of the advantages of the pseudo-second order equation for estimating q_e values, is its small sensitivity to the influence of random experimental errors. The calculated of Q_e is close to practical of Q_e (resulted from experiments). Therefore, the kinetics of pseudo second order can explain arsenic adsorption better than pseudo first order kinetics. These findings agree with Khazaie and Azhdarpour [22, 28].

Conclusion

Nowadays, removal of heavy metals from wastewater and water resources is one of the most important issues in environment sciences. The nanotechnology has some advantages such as cost benefit, producing large amounts of absorbent, high efficiency, lack of sludge production, and the possibility of recycling metals. This study points out that dendrimers (PAMAM G3) have a high adsorption capacity for arsenic removal from aqueous solutions. Adsorption kinetics was studied using pseudo first and pseudo second order equations. The effects of variables such as concentration of arsenic, concentration of dendrimers and pH were investigated. Data have a suitable correlation with Langmuir isotherm. Although dendrimers have benefits in water and wastewater treatment, preparation of these materials is a challenge, because production of each generation, with variable removal efficiency, is time consuming. Each successive generation results in a dendrimer roughly twice the molecular weight of the previous generation. Furthermore,

higher generation dendrimers have more exposed functional groups on the surface, which can be later used for customizing the dendrimer in a given application.

Acknowledgments

The authors aim to acknowledge the Department of Environmental Health Engineering and the Student Research Centre, School of Health in Isfahan University of Medical Sciences, for supporting and the laboratory staff of the department for their technical support in this research.

Funding

The work was unfunded.

Conflict of interest

We have no competing interests.

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