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ARSENATE REMOVAL FROM AQUEOUS SOLUTIONS BY USING *RHAMUS FRANGULA* AND *CALAMI RHIZOMA*

BY

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Abstract. This paper reports the feasibility of using micro-particles of dried plants to remove As(V) from aqueous solutions under different experimental conditions. For this purpose, micro-particles of both *Rhamus frangula* and *Calami rhizoma* plants have been separately used as natural adsorbents without any pre-treatment. Effect of various process parameters, namely adsorbent dosage, contact time and initial arsenate solution concentration have been studied in batch system. The experimental data were analyzed using Freundlich adsorption isotherm model. The results revealed that As(V) is considerably adsorbed on both dried plants and the adsorption process was dependent on the physical–chemical characteristics of the adsorbent, adsorbate concentration and other studied parameters; therefore it could be an economical method for arsenate removal from aqueous systems.

Key words: Arsenate, dried plants, adsorption parameters.

1. Introduction

Arsenate is one of the main contaminants threatening water supplies all over the world hence its presence in drinking water is receiving increasing worldwide attention. According to the resolution of the World Health Organization (WHO) from January 2006, the maximum permissible concentration of arsenic in drinking water was decreased below 10 μg/L [1]. The newly recommended value was based on the increasing awareness of the toxicity of arsenium (particularly its carcinogenicity), and on the ability to quantitatively measure arsenium concentrations [2]. Adsorption is considered an efficient technology for removing heavy metals from wastewaters due to its effectiveness, low costs and the possibility of reusing the adsorbents. Here, we present two cheap and effective adsorbents, that can be used for arsenate adsorption from aqueous media. *Rhamus frangula* and *Calami rhizoma* are environmentally friendly materials, possessing medicinal proprieties and also high adsorption capacities. The adsorbents derived from the micro-particles of dried plants were used for As(V) ions removal from aqueous solutions under different experimental conditions, varying the adsorbent dosage, the contact time and the initial arsenate solution concentration as adsorption parameters. Experimental results fitted to Freundlich adsorption isotherm model, for different initial temperatures of the adsorption medium.

2. Materials and Methods

2.1. Materials, Solutions and Instrumentation

The environmentally friendly materials used in the present work were obtained from dried plants of *Calami rhizoma* and *Rhamus frangula* as Romanian plants with medicinal well known proprieties. Protein, carbohydrates and phenol compound contents, which have metal-binding functional groups such as carboxyl, hydroxyl, sulphate, phosphate and amino groups, seem to be responsible for plants high potential of retaining toxic ions from aqueous solutions [3]. The dried plants were washed several times with double distilled water in order to remove any trace of impurity and then dried in an oven. After drying, the organs were grounded with an electric grinder to obtain a fine powder.

Stock solution of arsenate was prepared by dissolving sodium arsenate (Na_2HAsO_4. $7H_2O$, Sigma, product of USA) in double distilled water. The stock solution was used afterwards for obtaining different initial arsenate solution concentrations by dilutions.

An analytical balance Precisa model XT 220A was used for weighting the adsorbent doses. The centrifuge HETTICH model EBA 21 was used to separate the micro-particles of plants from solution after adsorption experiments complete. A UV-Vis Spectrophotometer (Jasco, model V-550, Japan) was employed to measure the residual arsenate concentrations.

2.2. Methods

Adsorption kinetics experiments were performed using the batch reactor technique at room temperature [4]. Known amounts of adsorbent (dried plants) were placed in glass flasks containing 40 mL of arsenate solution of known concentrations. After a contact time t (T_c, min), the suspensions were centrifuged and the supernatant was filtered through a Whatman filter paper. The filtrates were then prepared for analysis according to the molybdate blue method, using the UV-Vis spectrophotometer, at a wavelength of 842 nm [5]. The removed As(V) ions concentration (C_r) was calculated as the difference between the initial concentration, C_0, and the concentration at time t ($C_r = C_0 - C_t$). The removed percentage of arsenate (%) by micro-particles of both plants was calculated according to the relation: % Removal = $(C_r/C_0)\cdot 100$; and the amount of arsenate adsorbed (Q_t, mg/g) was calculated using the following equation:

(1) $$Q_t = \frac{C_0 - C_t}{m} \times v,$$

where: C_0 is the initial arsenate solution concentration, [mg/L]; C_t − the arsenate solution concentration at a given time t, [mg/L]; v − the arsenate solution volume, [mL]; m − the adsorbent mass, [g].

When adsorption process reaches equilibrium, the arsenate solution concentration C_t becomes the equilibrium concentration C_e and the amount of adsorbed arsenate Q_t becomes Q_{max}.

3. Results and Discussions

3.1. Effect of Adsorbent Dose

Adsorption equilibrium studies were conducted with 40 mL of arsenate solution of 100 mg/L initial concentration and varying adsorbent concentrations, ranging from 0–50 g/L (0.25–2.5 g of dried plants). The contact time of adsorbent with the As(V) solution was fixed to 12 h. Residual arsenate concentrations were measured as described in 2.1. and the variation of the adsorbent concentrations, [g/L], with the retained concentration of arsenate ions, [mg/L], was plotted. The equilibrium adsorbent concentration was found to be 25 g/L (1 g of each plant), and was used thenceforth in our studies.

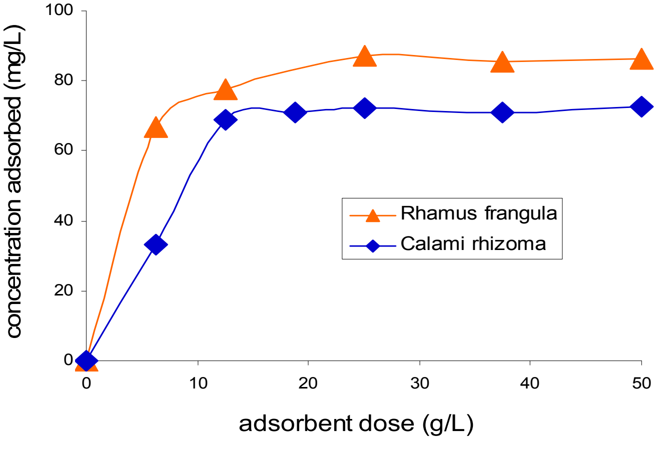

Fig. 1 − Effect of adsorbent dosage on As(V) removal by *Rhamus frangula* and *Calami rhizoma* (T = 25±2ºC, C_i = 100 mg/L, T_c = 12 h).

3.2. Effect of Contact Time and Initial Arsenate Solution Concentration

A series of 100 mL glass flasks each containing 1 g of adsorbent and 40 mL of arsenate solution of different initial concentrations were vigorously stirred with varying contact time (0–720 min) at ambient temperature (25±2°C). The initial arsenate solution concentration ranged from 100 to 1000 mg/L. The results indicated a maximum adsorption capacity of 94.5% for *Calami rhizoma* and 87% for *Rhamus frangula*. The adsorption equilibrium was achieved after 8 h of contact time with *Calami rhizoma* and 12 h of contact time with *Rhamus frangula* for an initial concentration of the arsenate solution of 100 mg/L.

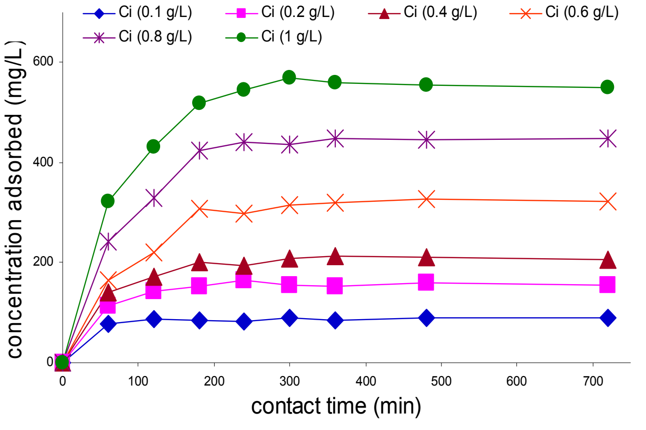

Fig. 2 – Time-dependent adsorption of As(V) on *Calami rhizoma* for different initial concentrations (T = 25ºC, adsorbent dosage = 25 g/L).

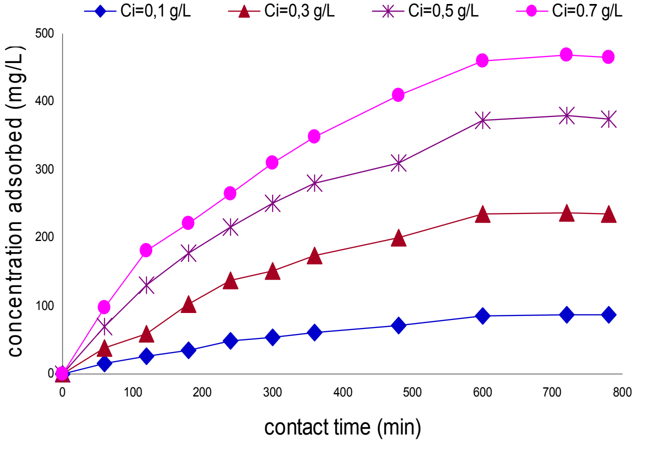

Fig. 3 – Time-dependent adsorption of As(V) on *Rhamus frangula* for different initial concentrations (T = 25ºC, adsorbent dosage = 25g/L).

3.3. Adsorption Isotherm Studies

Adsorption isotherm studies were performed adding 1 g of both dried plants individually in solution containing 40 mL of various initial arsenate solution concentrations, 200–1000 mg/L and different temperatures, ranging from 25 to 45ºC. The obtained adsorption data were then fitted to Freundlich adsorption isotherm [6], which is the earliest relationship known describing the adsorption equilibrium and is expressed by eq. 2, and its linear form in eq. 3:

(2) $$q_e = K_f \, C_e^{1/n}$$

(3) $$Ln\, q_e = Ln\, K_f + \frac{1}{n} Ln\, C_e$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. The values of K_f and n were calculated from eq. 3 and Freundlich plots (Figs. 4 and 5).

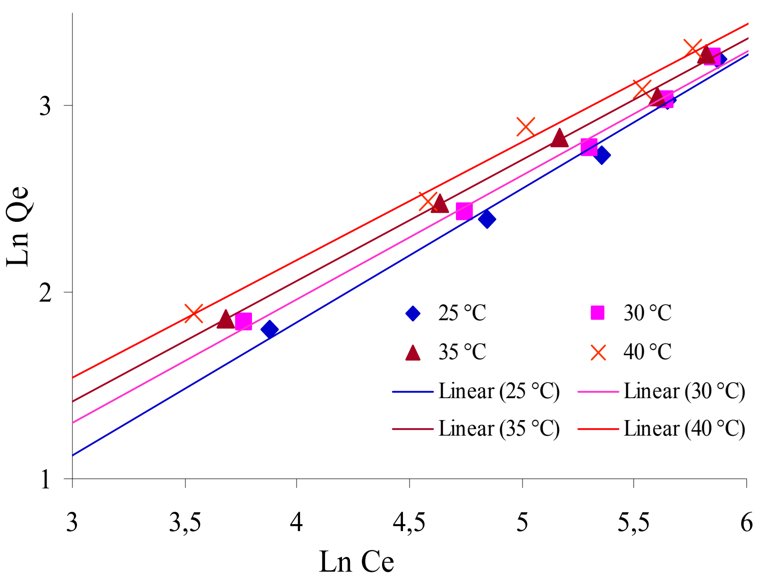

Fig. 4 – The plot of ln Q_e *versus* ln C_e for the determination of Freundlich isotherm parameters for As(V) adsorption on *Calami rhizome.*

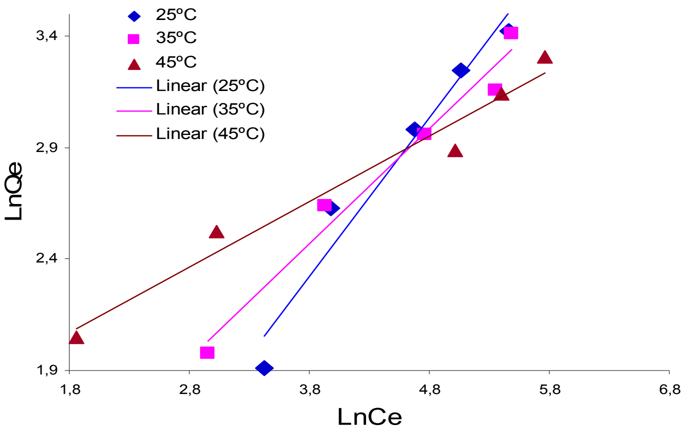

Fig. 5 – The plot of ln Q_e *versus* ln C_e for the determination of Freundlich isotherm parameters for As(V) adsorption on *Rhamus frangula.*

The values for Freundlich constants and correlation coefficients (r^2) for the two adsorbents are presented in Table 1. The values of n between 1 and 10 represent a favorable adsorption [7]. As we can observe from table 1, the values of n are between 1.4 and 3.4 for adsorption onto *Rhamus frangula* and between 1.39 and 1.58 for adsorption onto *Calami rhizoma*, indicating that arsenate ions are favourably adsorbed by both dried plants, at all studied temperatures. Freundlich model had a good agreement with the data for arsenate adsorption, also evidenced by the high r^2 values. The r^2 values are increasing with the increasing of the temperature, which shows that the temperature is a contributing factor in the adsorption processes. These experiments confirm the efficiency of the micro-particles of dried plants to remove As(V) from aqueous solution.

Table 1

Kinetic Parameters of Freundlich Model for As(V) Adsorption on Rhamus Frangula and Calami Rhizoma for Different Initial Arsenate Concentrations (T = 25-45ºC, Adsorbent Dosage = 25 g/L)

Adsorbent \ Adsorption parameter	r^2		n	K_f
Rhamus frangula	25ºC	0.957	1.401	0.677
	35ºC	0.975	1.937	1.658
	45ºC	0.969	3.401	4.664
Calami rhizoma	25ºC	0.988	1.398	0.361
	30ºC	0.991	1.505	0.499
	35ºC	0.997	1.540	0.586
	40ºC	0.990	1.584	0.703

4. Conclusions

In this study micro-particles of dried plants, *Rhamus frangula* and *Calami rhizoma,* were used as adsorbents for As(V) removal from aqueous solutions. Both, *Rhamus frangula* and *Calami rhizoma,* have high arsenate removal efficiency and were able to reduce the arsenate concentrations with over 85%. The results also showed that the amount of adsorbed As(V) was dependent on the studied adsorption parameters (adsorbent dosage, initial arsenate concentration and contact time). The equilibrium studies indicated that Freundlich model described well the As(V) adsorption on *Rhamus frangula* and *Calami rhizoma*. The environmentally friendly materials used in this study are suitable candidates as adsorbents for As(V) removal from aqueous media, also considering that these adsorbents are naturally abundant and low-cost materials.

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ÎNDEPĂRTAREA IONILOR ARSENAT DIN MEDII APOASE UTILIZÂND *RHAMUS FRANGULA* ŞI *CALAMI RHIZOMA*

(Rezumat)

În această lucrare este prezentat studiul procesului de adsorbţie al ionilor As(V) pe adsorbanţi de tip plante uscate, cu variaţia diferiţilor parametri experimentali.

În acest scop au fost folosite micro-particule de *Rhamus frangula* şi *Calami rhizoma*, ca atare, fără alte modificări. Procesul de adsorbție s-a realizat în sistem static, cu variația unor parametri de adsorbție, precum, concentrația adsorbantului, concentrația inițială a soluției de arsenat şi timpul de contact. Rezultatele experimentale au fost analizate cu ajutorul modelului izotermei de adsorbție Freundlich. Astfel, rezultatele au evidențiat o capacitate crescută a celor două plante de reținere a ionilor arsenat, care este dependenta de caracteristicile fizico-chimice ale adsorbantului, de concentrația sorbentului şi alți parametri investigați; prin urmare, aceasta poate fi o metodă economică şi ecologică de îndepărtare a ionilor arsenat din medii apoase.