

OPTIMIZACIJA SINTEZE I ISPITIVANJE SORPCIONIH SVOJSTAVA HIBRIDNOG ADSORBENTA NA BAZI SILIKE ZA UKLANJANJE AS(V) JONA

OPTIMISATION OF SYNTHESIS AND TESTING OF ADSORPTION EFFICIENCY OF HYBRID SILICA BASED ADSORBENT FOR AS(V) IONS REMOVAL

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U ovom radu prikazana je sinteza hibridnog adsorbenta korišćenjem visoko poroznih sferičnih čestica silike kao osnovnog materijala, koje su modifikovane (3-amino)trimetoksisilanom (APTES) i impregnirane gvožđe-(oksi)hidroksidom u formi getita. Visokoorozna struktura materijala nosača, sferičnih čestica prečnika 1-2 mm, iskorišćena je radi dobijanja što veće aktivne površine adsorbenta te povećanja adsorpcionog kapaciteta, što je potvrđeno primenom infracrvene spektroskopije sa Furijeovim transformacijama (FT-IR) i skenirajuće elektronske mikroskopije sa energetske disperzivnom spektroskopijom (SEM-EDS). Primenom šaržne adsorpcije As(V) jona ispitana su adsorpciona svojstva materijala i mehanizam vezivanja As(V) jona, odnosno određen je adsorpcioni kapacitet novog materijala, termodinamički i kinetički parametri ovog procesa u različitim eksperimentalnim uslovima. Na kraju, uzimajući u obzir prezentovanu sintezu hibridnog adsorbenta i obećavajuće rezultate testiranja njegove primene, primetni su pozitivni tehnno-ekonomski parametri prilikom poređenja sa drugim komercijalnim adsorbentima i tehnikama uklanjanja arsena.

Ključne reči: *modification, porous spheres, goethite, adsorption, arsenic*

Hybrid adsorbent was prepared using a highly porous silica spheres as supporting material, modified with 3-aminopropyltriethoxysilane (APTES) and impregnated with iron oxy-hydroxide in goethite form. Highly porous structure of supported material of diameter 1-2 mm was used to obtain as much active surface of the adsorbent and increase the adsorption capacity, which was confirmed via Fourier Transform-Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). Equilibrium studies of the adsorbent properties were investigated through batch adsorption experiments in order to determine the adsorption capacity for As(V) ions and to understand the mechanism of adsorption and kinetic parameters of process in different experimental conditions. In addition, presented synthesis of hybrid adsorbent and promising testing results indicates positive techno-economic indicators in comparison to commercial adsorbents and arsenic removal techniques.

Key words: *modification; porous spheres; goethite; adsorption; arsenic.*

1 Introduction

Many novel porous materials have been used recently due to their wide application range in adsorption, separation, catalysis and sensors, as supporting materials suitable for further modification and functionalization [1]. High surface area allows diffusion and adsorption of larger molecules or ions for wide applications. Silica is widely employed as main building block of mesoporous materials because it is inexpensive, thermally stable, chemically inert, harmless and abundantly available in the Earth's crust [2]. Attachment of organic functional groups could attract attention for further development in which this could tune the hydrophilic-hydrophobic character of silica surface to give adsorbent

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chemical selectivity for specific molecules or ions [3]. Such an activated silica surface represents excellent support material. 3-aminopropyltriethoxysilane (APTES) is one of the most frequently used organosilane agents for the preparation of amino-terminated films on silica surface. Silanization begins with the hydrolysis of ethoxy groups in APTES, leading to the formation of silanols. APTES silanols then condense with surface silanols forming a monolayer of APTES via siloxane network in which amino groups with positive charges are oriented away from the underlying silica surface, as it is shown in Figure 1 [4].

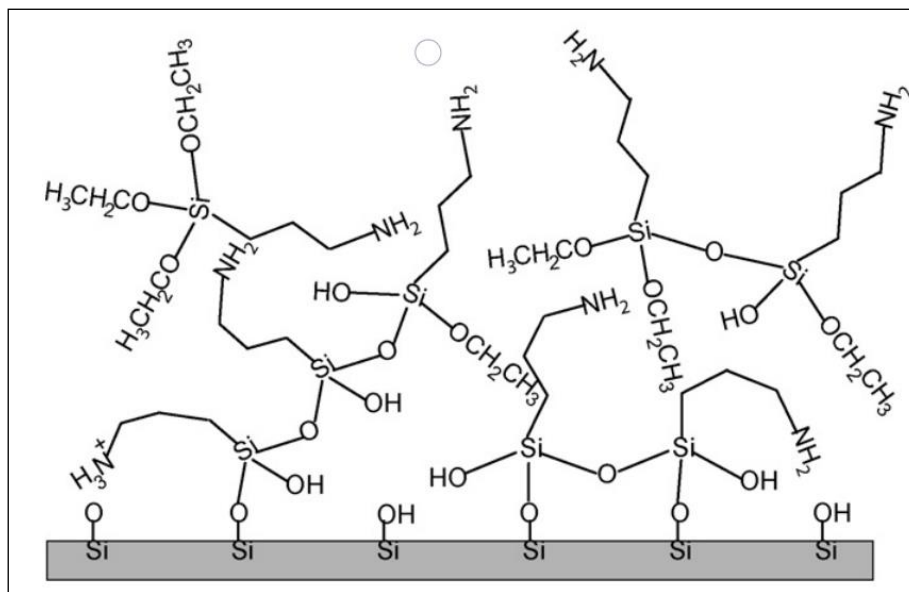


Figure 1. Schematic representation of adsorbed APTES on a silica surface in an anhydrous toluene solution [4]

Arsenic is a naturally occurring metalloid that is very mobile in the environment and highly toxic to all life forms. Among all existing arsenic species, the most prevalent forms which are commonly found in water, are the inorganic arsenite As(III) and arsenate As(V). Based on World Health Organization (WHO) guidelines, arsenic concentrations in drinking water should be strictly limited to 10 $\mu\text{g/L}$ [5].

In order to accomplish arsenic below recommended maximum contaminant level value, numerous of techniques and technologies were developed for natural water treatment, such as: oxidation/precipitation, precipitation/coagulation, nanofiltration, reverse osmosis, ion exchange, electrodiagnosis, adsorption and bioremediation [6]. Adsorption is a process that uses solids as medium for the removal of substances from gaseous or liquid solutions. This process is driven mainly by van der Waals forces and electrostatic forces between the adsorbate and the adsorbent surface. This makes it important to characterize first the adsorbent surface properties before it being used for adsorption [7]. Iron-based adsorption is an emerging technique for the treatment of arsenic-contaminated water. This can be explained by the fact that there exists a high affinity between inorganic arsenic species and iron [8]. Goethite (FeOOH), one of the most important iron oxy-hydroxide, having double bonds, possesses the capability of incorporating a range of environmentally important oxy-anions and cations in its complex matrix. Hence, it can be used as an adsorbent [9].

Utilization of iron oxides particles as adsorbents for arsenic species may have consequences associated with particle agglomeration which finally results in a drastic decrease in active surface area. To overcome this and similar problems, impregnation of oxide particles into porous materials or surface coatings can be a successful solution [5,8]. Although iron oxides are selective toward arsenate, high specific surface areas are required to achieve sufficiently high sorption capacity, which was the challenge of the present work.

In the present work, we present a simple approach to engineer hybrid highly porous silica based-goethite impregnated material for the adsorption of arsenic in water. Our approach for enhancing the activity of surface and to increase adsorption properties of material was to prepare amino-terminated

film on highly macroporous spherical silica particles using organosilane agent and precipitate iron-(hydr)oxide in goethite form.

2 Experimental

2.1 Synthesis of hybrid silica-based adsorbent

All the chemicals used in this study were analytical grade without further purification. Synthesis of hybrid material was performed in a slightly altered form in relation to procedure described in [11]. The commercial silica porous spheres were dried at 60 °C for 3h and cleaned firstly with a mixture of 3% hydrogen peroxide (H₂O₂) and 3% sulfuric acid (H₂SO₄) for 120 min, and then with a 5% hydrofluoric acid (HF), to provide better surface activation and prepare it prior to the modification process. After thoroughly rinsed with water and absolute ethanol, the material was stored in vacuum atmosphere at 60 °C before use. The material (10 g) was then submerged in xylene with simultaneous introduction of N₂ for 30 min, after which 1 mL of APTES (0.10 mas.% according to silica) was added in drops. Reaction was carried out for 24 h at room temperature, followed by the rinsing with 5 ml of 96% ethanol ten times. After this procedure and after thoroughly rinsed with xylene several times, the material was stored in vacuum atmosphere at 80 °C before further use.

The first step of iron oxy-hydroxide precipitation was carried by the procedure bellow. Modified silica material (4 g) was submerged in xylene again. The reaction was conducted continuously with simultaneous introduction of N₂ for 30 min, by drop-wise addition of 2 mL FeSO₄·7H₂O solution with concentration of 2 mol/L for 15 min and simultaneously mixing of reactants. The oxidation was performed by changing the nitrogen with air introduction and neutralizing the reaction by addition of 1 mL sodium bicarbonate concentration of 2.6 mol/L for 30 min, which caused the precipitation of iron oxide into goethite (GT) form. The reaction was conducted for 48 h until the green-blue color of the solution changed to ocher shade. The material was rinsed with xylene and stored in vacuum atmosphere at 80 °C for 24 h to dry. The procedure for the precipitation of iron oxy-hydroxide was repeated in an analogous manner (the second and the third step), and the obtained adsorbent was named S-APTES-GT.

2.2 Material characterisation

Prepared material was characterized by several characterization techniques. The morphology of the samples was characterized via SEM-EDX analysis (TESCAN MIRA3) and FTIR analysis (Bomem MB-102) was used to identify the functional groups of the resulted material scanned in the range of 500-4000 cm⁻¹ in transmission mode.

2.3 Batch adsorption studies

In order to investigate the effect of adsorbent dosage, temperature and contact time on adsorption performance, batch experiments were performed. The adsorbents doses of 0.1 – 1.0 g/L were agitated with 10 mL of As(V) solution (4 mg/L) at pH 6.8 ± 0.1 for 720 min in order to investigate the mass balance. Batch kinetic experiments were carried out at different contact times 5-720 min contacting 1.0 g/L of prepared adsorbent and 10 mL of As(V) solution (4 mg/L) at pH 6.8 ± 0.1. For isotherm studies, 10 mL of As(V) solution of concentration 4 mg/L were shaken with adsorbents doses of 0.1 – 1.0 g/L for 720 min (250 rpm) at different temperatures (298, 308 and 318 K).

The content of As(V) ions in the resultant filtrates were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce). The adsorbent isotherm and capacity were calculated according to following equation (1):

$$q = \frac{C_0 - C_e}{m} V \quad (1)$$

where q is a adsorption capacity in mg/g, C_0 and C_e are initial and final As(V) concentrations in mg/L, respectively, V is the volume of solution in L, and m is mass of adsorbent in g. Prior to analysis, the aqueous samples were filtered through 0.2 μm membrane filter, acidified with concentrated nitric acid, stored in polyethylene containers and analyzed day after collection.

3 Results and discussion

3.1 Characterization of adsorbent

SEM images of S-APTES-GT are presented in Figure 2, to illustrate adsorbent porosity (a, b) and surface coverage of iron oxide (c, d). Spherical particles are 1-2 mm in diameter (a), images *c* and *d* revealed porous structures with disorganized structural channels and a lot of macropores and micropores. These pores facilitate the diffusion of As(V) ions to the interior of S-APTES-GT by providing a larger contact surface means more binding sites for ions. One of the most important observations is that iron oxide did not blow up the pore of the material.

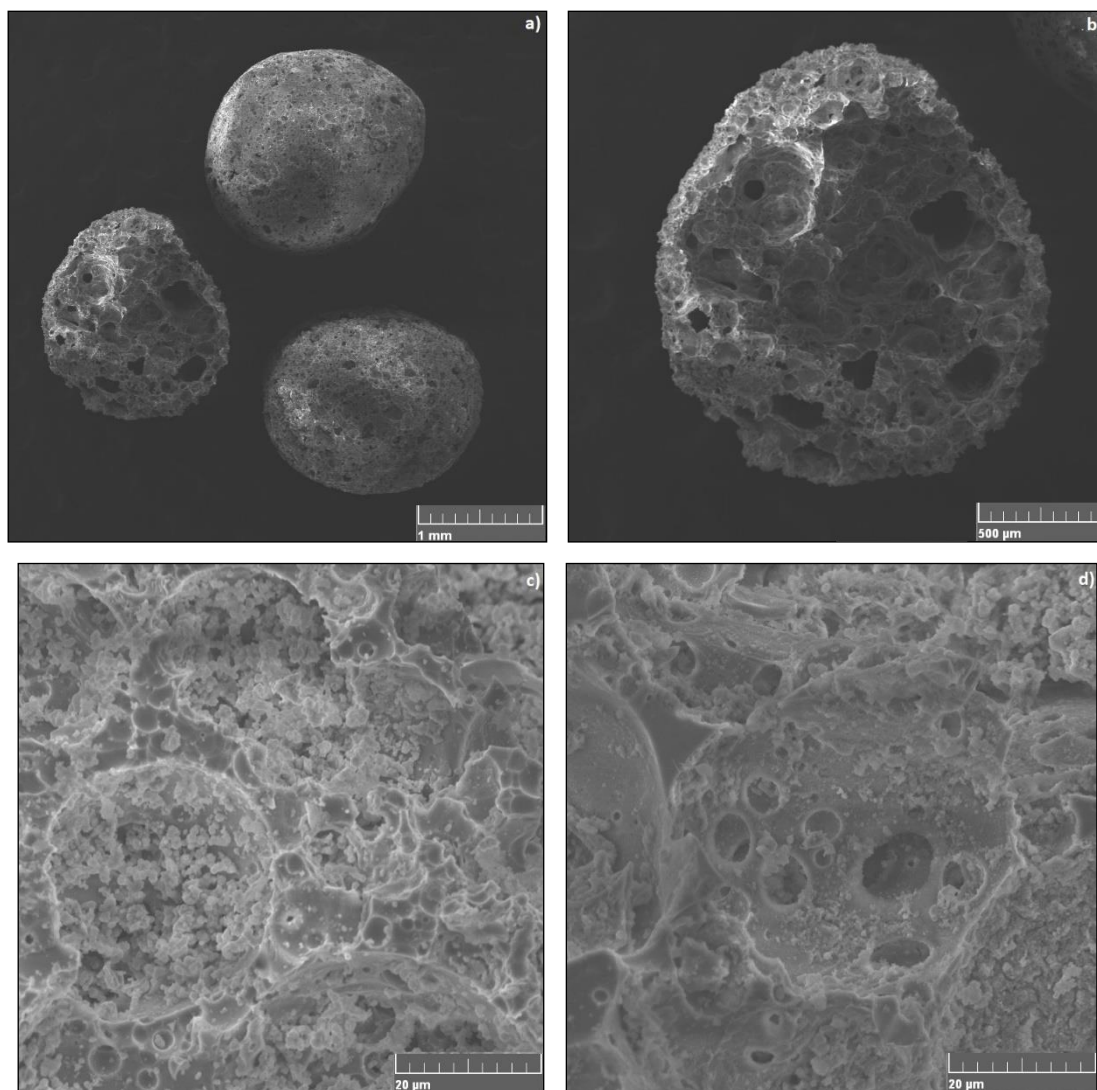


Figure 2. SEM images of hybrid silica based adsorbent: adsorbent particles (a), halved particle (b), adsorbent surface area (c) and surface inside sphere particle with micropores and mesopores (d)

The EDX spectrums for S-APTES-GT showed the presence of Si, O, Fe, Mg, Na, Ca, S, Cl, K and Ge peaks, Figure 3. Elemental analysis revealed that the main constituents of the obtained adsorbent are silicon and iron compounds. Simultaneously, the high content of oxygen shown during EDX analysis may suggest their presence in the oxide and oxy-hydroxide form.

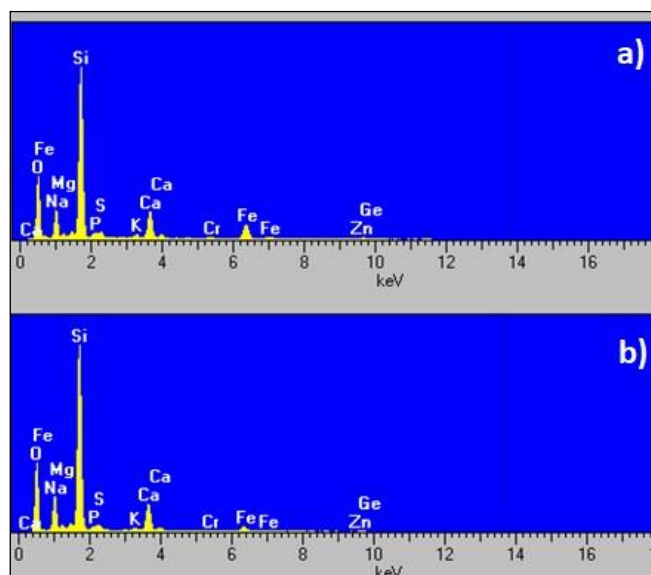


Figure 3. EDX spectrums for S-APTES-GT on sphere surface (a) and in the center of sphere (b)

A significant presence of Fe is observed on the surface of the sphere then in the center of sphere (Table 1), but it indicates successful precipitation of iron oxide through the porous silica material.

Table 1. Chemical composition of S-APTES-GT

Element	Content on sphere surface [%]	Content in sphere center [%]
O	50.14	54.13
Na	7.76	8.63
Mg	0.63	0.89%
Si	24.12	25.11
S	0.48	0.48
Cl	0.11	0.06
K	0.72	0.63
Ca	5.97	5.73
Fe	8.44	2.46
Ge	1.63	1.88
Total	100.00	100.00

Successful modification of silica surface with 3-aminopropyltriethoxysilane and presence of iron oxide and adsorbed arsenate on adsorbent surface were confirmed by FI-IR analysis, Figure 4.

The compositions of the obtained material before and after modification and adsorption experiments were characterized with FT-IR spectroscopy, Figure 4. For the material samples, the absorption at ca. 1010 cm^{-1} results from Si-O-Si anti-symmetric stretching vibrations which implies the existence of a SiO_2 [12]. The presence of N-H bending vibration in S-APTES-GT graphs around 692 and 1630 cm^{-1} confirms the existence of amino groups [13]. Also, the broad peaks at $3300\text{--}3600\text{ cm}^{-1}$ were due to the NH_2 stretch of the amine group overlapped with OH vibration. The peaks at ca. 570 cm^{-1} that appear are assigned to the stretching modes of Fe-O on treated material. Appearance of new peak for S-APTES-GT at 892 cm^{-1} in the spectrum originated from As-O stretching vibration of coordinated arsenic species after adsorption, but As-O stretching vibration of coordinated arsenic

species also appeared at 796 cm^{-1} , corresponding to the frequency of the As–O–Fe band of complexed arsenate [14].

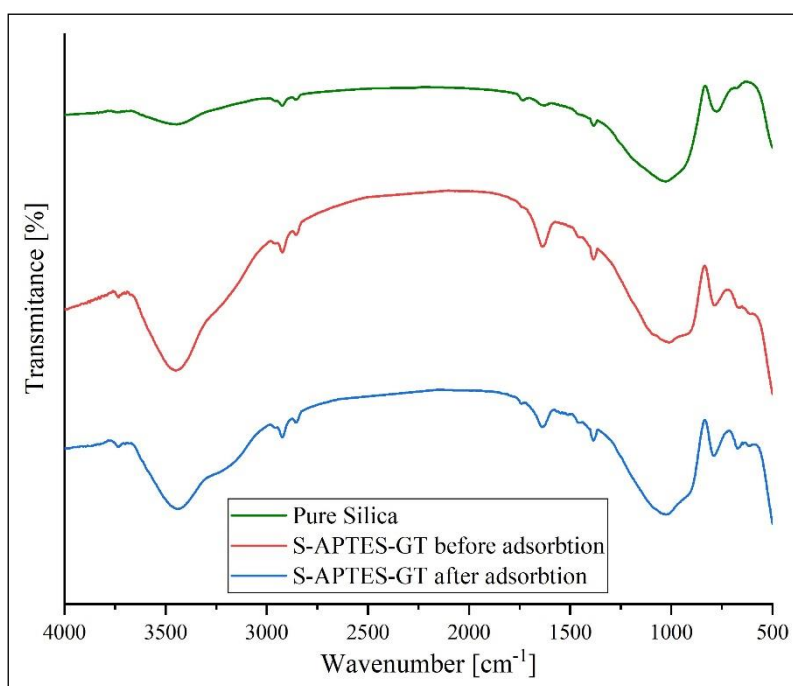


Figure 4. FT-IR spectra of the obtained silica based material before and after modification and adsorption experiments

3.2 Batch adsorption studies

3.2.1 Effect of adsorbent dosage and temperature

The effects of S-APTES-GT doses on As(V) adsorption are shown in Figure 5. The amount of As(V) adsorbed (q_e) by the different doses 0.01-1.0 g/L of S-APTES-GT was reduced from 33.78 to 3.56, from 37.27 to 3.63 and from 37.6 to 3.65 mg/g, for done adsorption experiments at 298, 308 and 318 K, respectively (Figure 5a). The dose of 0.1 g/L gave the highest q_e value but dose of 0.01 g/L gave the highest adsorbent capacity (Figure 5b). Adsorption performance, both amount of As(V) adsorbed and adsorbent capacity, slightly increases at higher temperature (Figure 5a and 5b).

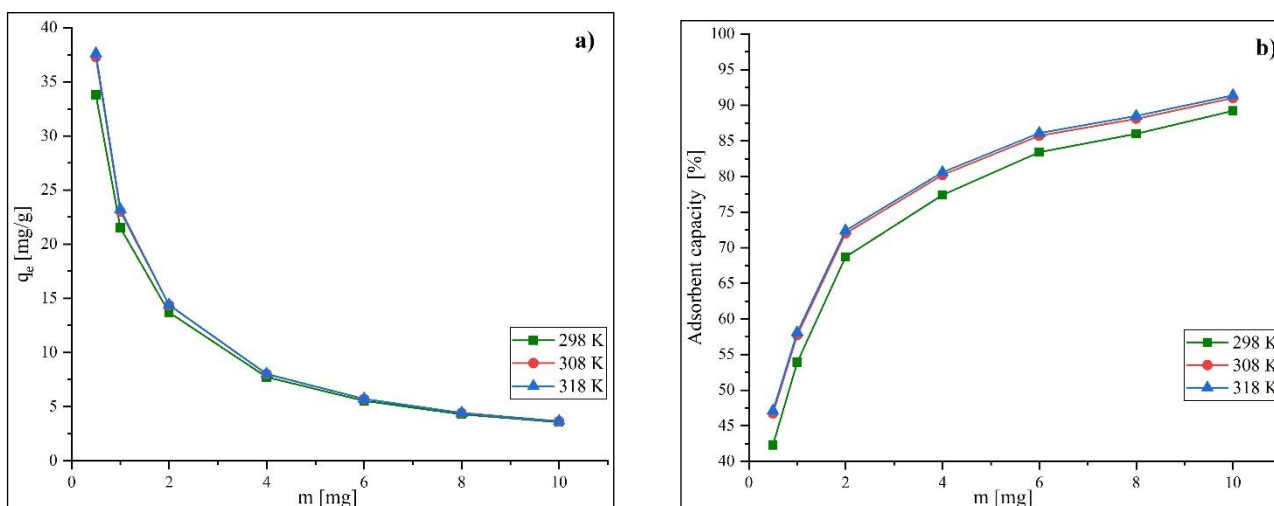


Figure 5. Amount of As(V) adsorbed (a) and adsorbent capacity (b) of S-APTES-GT at 298, 308 and 318 K

3.2.2 Kinetics studies

The adsorption kinetic study is very important in the adsorption process because it provides valuable information for the design of the adsorption system. Experiments were conducted at 298 K, varying contact time from 5 to 720 min. The kinetic of adsorption process were described by pseudo-second-order and intra-particle diffusion kinetic models. The linear form of the pseudo-second-order model can be expressed as the following equation (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where k_2 is the pseudo-second-order rate constant (min^{-1}). The k_2 and q_e can be calculated from the slope and intercept of the linear plot of t/q_t versus t [15].

The intra-particle diffusion model can be expressed as the following equation (3):

$$q_t = k_{int} t^{1/2} + C \quad (3)$$

where k_{int} is the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C is intercept. The k_{int} can be obtained from the slope of the linear plot of q_t versus $t^{1/2}$ [16]. The intra-particle diffusion model showed multi-linearity suggesting that the adsorption of As(V) on the S-APTES-GT may occur more than one sorption steps. The rate constant and experimental data of kinetic models are shown in Table 2.

Table 2. Kinetic parameters for As(V) adsorption on the S-APTES-GT

<i>Pseudo-second-order model</i>	
$q_{e,cal}$ (mg/g)	9.993
k_2 (g/mg min)	0.00462
R^2	0.995
<i>Intraparticle diffusion model</i>	
k_{int1} ($\text{mg/g min}^{1/2}$)	1.105
R^2	0.995
k_{int2} ($\text{mg/g min}^{1/2}$)	0.376
R^2	0.999

Based on results, the correlation coefficient values ($R^2 > 0.990$) of the intra-particle diffusion model and pseudo-second-order model agree with experimental values. This suggests that the adsorption of As(V) on the S-APTES-GT follows pseudo-second-order model and the adsorption involved complexation and ion-exchange mechanism [17]. Also, the successful application of the pseudo-second-order model suggests that the chemisorption processes could be a rate-limiting step [18].

3.2.3 Sorption isotherm models

Two isotherm models, Langmuir and Freundlich, were applied for analyzing the As(V) adsorption process on S-APTES-GT surface in accordance to the obtained experimental data. Sorption experiments were conducted at contact time of 720 min to ensure equilibrium. The Langmuir isotherm model is based on the assumption of a monolayer adsorption process onto a homogeneous surface, with constant adsorption energy and without transmigration of adsorbate in the plane of the surface. This isotherm model has been represented by the following equation (4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_m is the maximum amounts of As(V) ion adsorbed on the adsorbent (mg/g), C_e is the equilibrium concentration (mg/L) and K_L is the Langmuir constant (L/mg), related to the affinity of the

binding sites [19]. The dimensionless constant (R_L) describes feasibility of Langmuir isotherm model and favorability of adsorption process. It is expressed as the following equation (5):

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the highest initial ions concentration (mg/L). The R_L values were evaluated at different temperatures.

The Freundlich isotherm, based on the assumption of chemisorption onto heterogeneous surface with different sites energies, can be expressed in its non-linear form (6):

$$q_e = K_F C_e^{1/n} \quad (6)$$

where q_e , K_F , C_e and $1/n$ represents the amount of the adsorbate per unit weight of adsorbent (mg/g), a constant relating to adsorption capacity (Freundlich constants), equilibrium As(V) ion concentration in the solution (mg/L) and adsorption intensity, respectively [20].

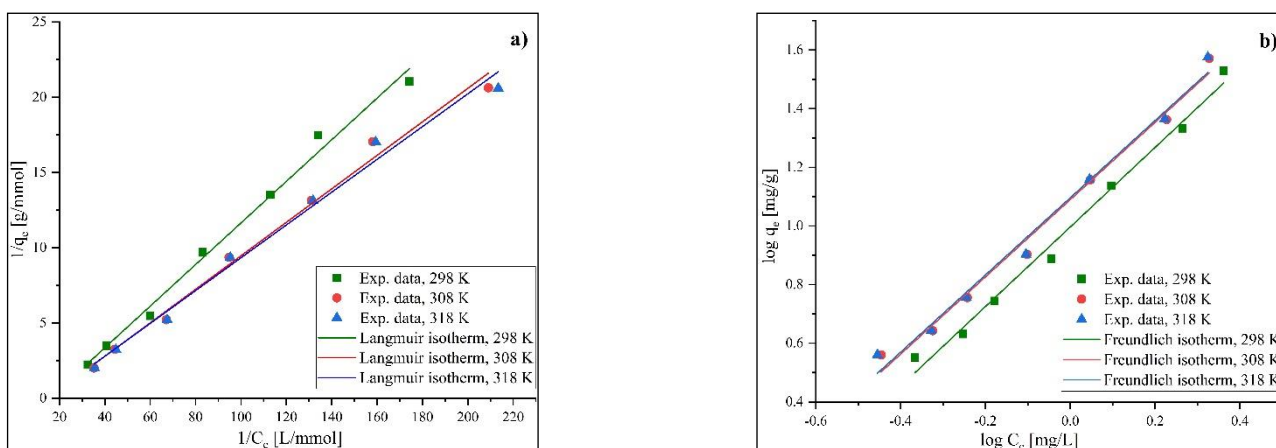


Figure 6. Langmuir (a) and Freundlich (b) linearized isotherm models for the As(V) adsorption on the S-APTES-GT at 298, 308 and 318 K

The Langmuir and Freundlich linearized isotherm models for the As(V) adsorption on the S-APTES-GT at different temperatures are presented in Figure 6. Isotherms parameters for adsorption are presented in Table 3. The values of correlation coefficients R^2 revealed that the Langmuir and Freundlich isotherm models provide almost the same experimental data. This indicates that the adsorption of As(V) on the S-APTES-GT occurs at monolayer and multilayer adsorption and adsorption at heterogeneous sorbent surface.

Table 3. Langmuir and Freundlich isotherm parameters for adsorption of As(V) on the S-APTES-GT

Models	Linear plot	Parameters	Results		
			298 K	308 K	318 K
Langmuir	$1/q_e$ vs $1/C_e$	R^2	0.992	0.991	0.988
		q_m [mg/g]	34.49	45.04	47.93
		K_L [L/mg]	0.210	0.200	0.191
Freundlich	$\log q_e$ vs $\log C_e$	R^2	0.990	0.989	0.987
		K_F [mg/g(L/mg) $^{1/n}$]	9.918	12.292	12.480
		$1/n$	1.356	1.317	1.316

4 Conclusion

In this work, the synthesis of hybrid material S-APTES-GT and possibility of its application for removal of As(V) was investigated. The experimental results showed that operating parameters such as adsorbent dosage, temperature and contact time greatly affected the adsorption capacity. The adsorption capacity range of S-APTES-GT was from 34.49 to 47.93 mg/g in the temperature interval from 298 to 318 K, respectively. The kinetic studies of As(V) adsorption showed a good fitting with pseudo-second order kinetic model and intra-particle diffusion model. The complexation and ion-exchange mechanism were involved in As(V) adsorption on the S-APTES-GT. On the basis of the present investigation, the synthesized silica based hybrid material can be utilized as an efficient and eco-friendly low-cost adsorbent, because it can successfully and rapidly remove dissolved As(V) ions from water. Therefore, it can be further examined and considered as a cheaper alternative to commercial columns for continual adsorption processes. Since this material has proved to be good adsorbent for As(V) removal, further investigation will continue.

5 References

- [1] **Alothman Z. A.**, A review: Fundamental aspects of silicate mesoporous materials, *Materials (Basel)*, vol. 5 (2012), no. 12, pp. 2874–2902.
- [2] **Nandiyanto A. B. D., Kim S. G., Iskandar F., Okuyama K.**, Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable pores and outer diameters, *Microporous Mesoporous Mater.*, vol. 120 (2009), no. 3, pp. 447–453.
- [3] **Djokić V. R. et al.**, “Preparation of TiO₂/carbon nanotubes photocatalysts: The influence of the method of oxidation of the carbon nanotubes on the photocatalytic activity of the nanocomposites,” *Ceram. Int.*, vol. 38 (2012), no. 8, pp. 6123–6129.
- [4] **Kim J., Seidler P., Wan L. S., Fill C.**, Journal of Colloid and Interface Science Formation, structure and reactivity of amino-terminated organic films on silicon substrates, *J. Colloid Interface Sci.*, vol. 329 (2009), no. 1, pp. 114–119.
- [5] **WHO**, *Guidelines for drinking water quality recommendations*, Geneva, 1993.
- [6] **Faria M. C. S. et al.**, Arsenic removal from contaminated water by ultrafine δ -FeOOH adsorbents, *Chem. Eng. J.*, vol. 237 (2014), pp. 47–54.
- [7] **Nicomel N. R., Leus K., Folens K., Van Der Voort P., Du Laing G.**, Technologies for arsenic removal from water: Current status and future perspectives, *Int. J. Environ. Res. Public Health*, vol. 13 (2015), no. 1, pp. 1–24.
- [8] **Gupta A., Yunus M., Sankararamkrishnan N.**, Zerovalent iron encapsulated chitosan nanospheres - A novel adsorbent for the removal of total inorganic Arsenic from aqueous systems, *Chemosphere*, vol. 86 (2012) no. 2, pp. 150–155.
- [9] **Jaiswal A., Banerjee S., Mani R., Chattopadhyaya M. C.**, Synthesis, characterization and application of goethite mineral as an adsorbent, *J. Environ. Chem. Eng.*, vol. 1 (2013), no. 3, pp. 281–289.
- [10] **Basu H., Singhal R. K., Pimple M. V., Reddy A. V. R.**, Arsenic removal from groundwater by goethite impregnated calcium alginate beads, *Water. Air. Soil Pollut.*, vol. 226 (2015), no. 2.
- [11] **Veličković Z. et al.**, Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes, *Chem. Eng. J.*, vol. 181–182 (2012), pp. 174–181.
- [12] **Chen L. et al.**, Designed fabrication of unique eccentric mesoporous silica nanocluster-based core-shell nanostructures for pH-responsive drug delivery, *ACS Appl. Mater. Interfaces*, vol. 5 (2013), no. 15, pp. 7282–7290.
- [13] **Hao S., Verlotta Aprea A., P., Pepe F., Caputo D., Zhu W.**, Optimal synthesis of amino-functionalized mesoporous silicas for the adsorption of heavy metal ions, *Microporous Mesoporous Mater.*, vol. 236 (2016), pp. 250–259.
- [14] **Taleb K. A. et al.**, Efficient pollutants removal by amino-modified nanocellulose impregnated with iron oxide, *J. Serbian Chem. Soc.*, vol. 81, no. 10, pp. 1199–1213, 2016.

- [15] **Ho Y. S., Mckay G.**, Pseudo-second order model for sorption, *Process Biochem.*, vol. 34 (1999) pp. 451–465.
- [16] **Weber J., Morris W.**, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div.*, vol. 89 (1963), pp. 31–60.
- [17] **Ouyang X. K. et al.**, Partially hydrolyzed bamboo (*Phyllostachys heterocycla*) as a porous bioadsorbent for the removal of Pb(II) from aqueous mixtures, *J. Agric. Food Chem.*, vol. 62 (2014), no. 25, pp. 6007–6015.
- [18] **Visa M.**, Tailoring fly ash activated with bentonite as adsorbent for complex wastewater treatment, *Appl. Surf. Sci.*, vol. 263 (2012), pp. 753–762.
- [19] **Langmuir I.**, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.*, vol. 40 (1918), pp. 1361–1368.
- [20] **Freundlich H. M. F.**, Over the adsorption in solution, *J. Phys. Chem.*, vol. 57 (1906), pp. 384–470.