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Adsorption properties of a nanostructured hybrid material containing aluminium towards some metal ions

Research Article

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Abstract: In the present work the adsorption of some transition metal ions from aqueous solutions on a silica-based nanostructured hybrid material modified by aluminium was investigated. The novel organic-inorganic material was synthesized *via* a sol-gel method through hydrolysis and co-condensation reactions. Its structure was characterized by means of SEM, XRD and FTIR. Based on the data obtained the most probable cross-linking mechanism for the derived xerogel was proposed. The characterization of its texture parameters was carried out by low-temperature adsorption of nitrogen. The adsorption properties of this material with respect to Cu(II), Cr(III) and Pb(II) ions from single-component aqueous solutions and multi-component aqueous solutions containing also Cd(II) and Fe(III) were evaluated. The effect of contact time, acidity of initial solutions and metal ion concentrations was investigated using the batch method. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyze kinetic data. In all cases the adsorption was significantly affected by the pH value. Equilibrium modelling data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models. Best fit was observed for Langmuir model, which showed determination coefficients greater than 0.992 for all ions studied. The maximum adsorption capacities for single- and multi-component adsorption were calculated.

Keywords: *Silica-based nanostructured hybrid material • Removal of metal ions • Adsorption equilibrium*

1. Introduction

Pollution of water with metal ions represents an important environmental concern due to the toxicity of these metals and their further accumulation in humans throughout the food chain. Several methods are used for their removal from aqueous solutions, such as chemical precipitation, membrane filtration, ion exchange and sorption. To synthesize improved adsorbents for this purpose is a continuing research objective of environmental pollution control processes. Considerable efforts have been devoted to the preparation of nanoporous silica-based adsorbents due to their unique large surface area, well-defined pore size, pore shape and well modified surface properties. This application generally requires the materials to exhibit specific binding sites for metal ions. The preparation, characterization and application of organic-inorganic hybrid materials have become a fast expanding area of research in materials science. The new hybrid gels have the potential for providing interesting combinations of properties which cannot be achieved by other materials [1]. Modified silica containing materials can be used for technological applications such as extracting metal ions from aqueous and non-aqueous solutions because they show great adsorption capacity and specificity for metal ions [2-9].

The aim of the present paper is to study the adsorption properties of a novel di-urethanesil hybrid material modified by aluminium towards some metal ions from single and multi-component aqueous solutions.

2. Experimental procedure

2.1. Synthesis and characterization of the hybrid material

The organic-inorganic hybrid materials have been prepared as 80 wt.% tetramethoxysilane (TMOS), which was dissolved in tetrahidrofurane (THF) in ratio

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1:1 and hydrolyzed with acidified water (pH=1.5) for 10 min. Subsequently, an appropriate amount (20 wt.%) of trimethylsilil isocyanate (TMSI), previously dissolved in THF (1:1) was added. After 30 min of stirring at room temperature, 10 wt. % of aluminum sec-butoxide $Al(OBu)_3$ was added as a modifying agent in the presence of ethylacetoacetate (EtAcAc) in ratio 1:1 [10]. The mixture was further stirred for 40 min and then dried at room temperature. The schematic diagram for the preparation of the hybrid material containing Al is presented in Fig. 1.

The structure of the derived xerogel denoted as Si-10Al was investigated by means of XRD on a X-Ray Diffractometer System "Geigetflex" D/Max- C Series (Rigaкu, Japan) at 30 mA, 40V, with Cu-Kα radiation; FTIR (Mattson 7000, USA) in the range of 4000-400 cm^{-1} in KBr-pellets and SEM (S4000 Field Emission, Hitachi, Japan). The characterization of texture parameters of the alumosilica oxycarbonitride material was carried out by low-temperature adsorption of nitrogen (BET analysis performed on Gemini model 2370V5.00, Micrometrics, UK).

2.2. Adsorption studies

The adsorption properties of Si-10A with respect to Cu(II), Fe(III) and Pb(II) ions from single-component solutions and multi-component solutions containing Cu(II), Fe(III), Pb(II), Cr(III) and Cd(II) were determined by means of batch method. Experiments were carried out using

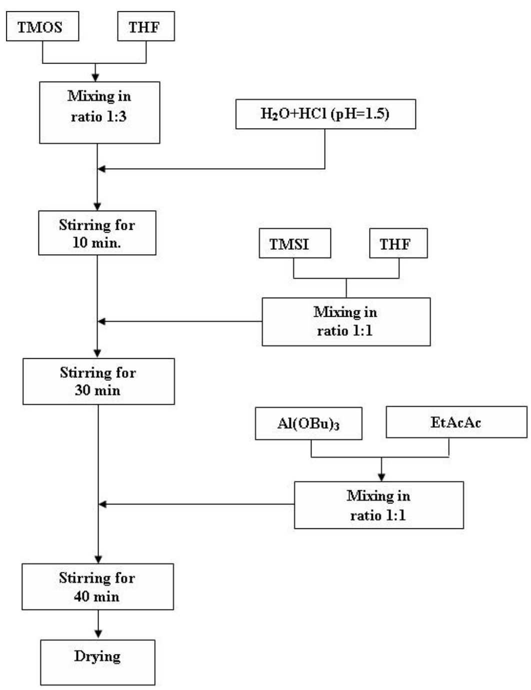

Figure 1. Schematic diagram for the synthesis of the hybrid material containing Al.

stoppered 50 mL Erlenmeyer flasks containing about 0.1 g Si-10Al sample and 10 mL of aqueous solution of the metal ion(s) under study. The mixture was shaken at room temperature by an automatic shaker. In order to optimize contact time for adsorption, kinetic experiments were carried out. The time interval was from 30 min to 5 h. Kinetic adsorption experiments were performed using solutions with initial ions' concentrations of 10 mg L^{-1} (pH 5.0). On reaching equilibrium, the adsorbent was removed by filtration through a Millipore filter (0.2 µm). The initial and equilibrium concentrations of the metal ions were determined by flame AAS on a Pye Unicam SP 192 flame atomic absorption spectrometer (UK).

The effect of acidity on the removal efficiency of the adsorbent studied was investigated over the pH range 2.0–5.5 (pH-meter model pH 211, Hanna instruments, Germany) employing an initial concentration of 20 mg L^{-1} for all ions investigated. This allowed for establishing optimal pH value for each metal ion. At this optimal pH value, adsorption of the metal ion concerned is significant and no precipitation of metal hydroxide occurs. Thus, to determine the effect of the initial metal ions' concentrations on the adsorption capacity initial concentrations in the range 5−100 mg L^{-1} at pH 5.0 were chosen.

Analytical grade reagents were used in all experiments. The working solutions containing different concentrations of Cu(II), Fe(III), Pb(II), Cr(III) and Cd(II) ions were prepared by stepwise dilution of stock solutions (Titrisol Merck, Germany). All adsorption experiments were replicated and the average results were used in data analyses.

3. Results and discussion

3.1. Characterization of the hybrid material

The structure of Si-10Al was investigated by means of XRD, FTIR and SEM (Fig. 2). As shown in [10], the XRD pattern reveals that the derived xerogel is X-ray amorphous (Fig. 2a). From the FTIR spectrum of Si-10Al (Fig. 2b) it is obvious that the band observed in the frequency range from 1600 to 1750 cm^{-1} corresponds to vibrations of the urea- and urethane-bonds, which are formed during the polycondensation processes. The peaks at 1080 cm^{-1} and 480 cm^{-1} are due to both stretching and deformation vibration of Si-O-Si bonds, the deformation vibration corresponding to $Si\text{-}(CH)_3$ groups appears at 845 cm^{-1} and 765 cm^{-1}. The peak at 950 cm^{-1} is due to SiO stretching of SiOH on surface, while the peak at 3400 cm^{-1} is due to OH stretching of SiOH or sorbed water.

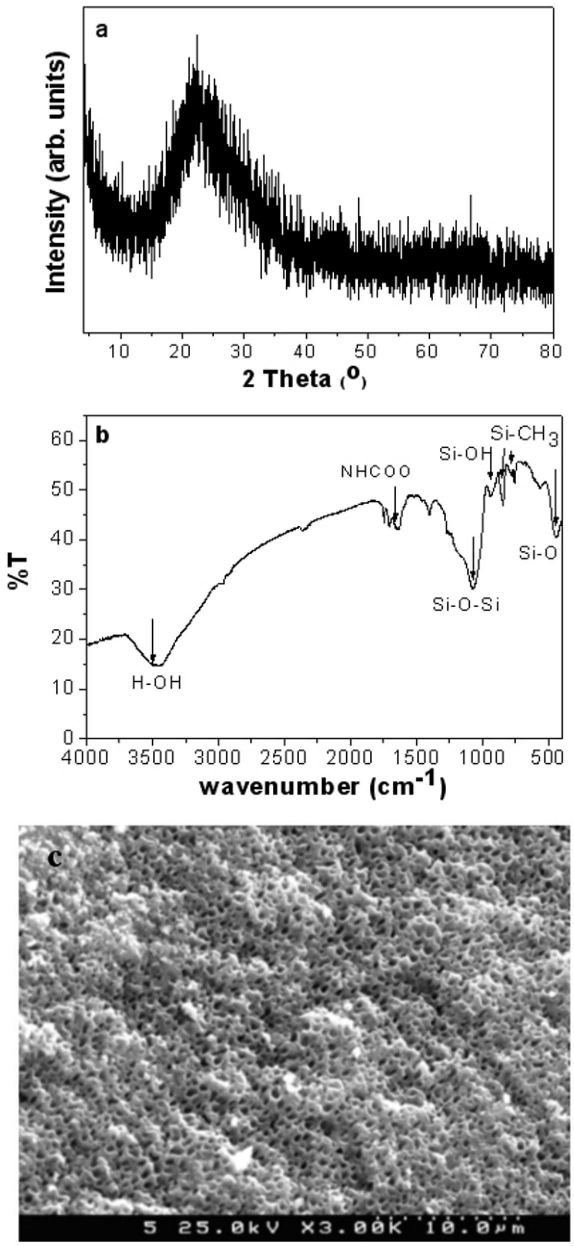

Figure 2. Investigation of the hybrid material Si-10Al by means of: a) XRD; b) FTIR and c) SEM

Evidence for the chemical homogeneity of hybrid materials can be considered from the presence of peaks at 648 cm^{-1}, which in bibliographic data refers to the presence of heterometallic (Si-OAl(Si) bonds, as well as the linkages at 547 cm^{-1} due to deformation vibration of O-Si (Al)-O). According to these results the hybrid structure is built from SiO_2-AlO_6 polyhedra and Si-CH_3 repeating structural units, grafted onto siloxane network by urethane (-NHC(=O)-) bridges in the presence of ureasil monomers [11]. Therefore the organic and the inorganic parts in the gels are linked to each other *via*

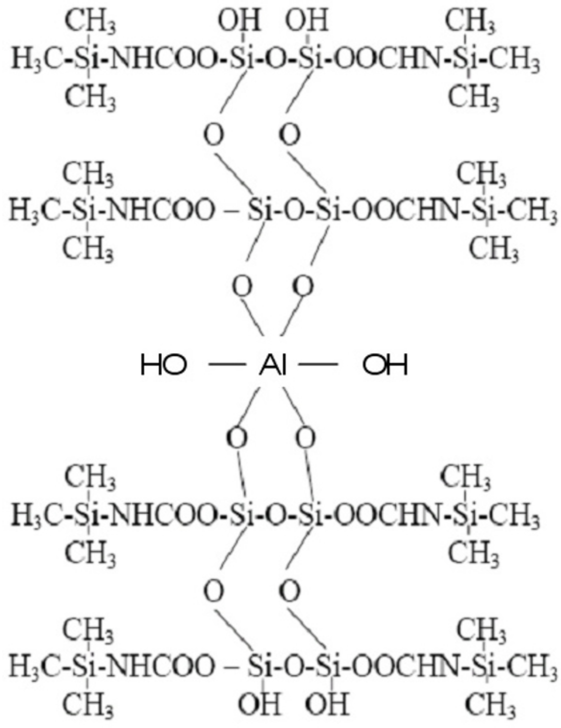

Figure 3. Structure of the silica-based hybrid material Si-10Al.

covalent bonds and form a single homogeneous phase. The pore morphology formation in the Si-10Al was well interpreted by means of SEM. From the SEM study (Fig. 2c) it was observed that the derived xerogel possesses high degree of open porosity with a characteristic pore size in the range of 0.2 μm to 0.6 μm. All analytical data pointed out, that the structure of Si-10Al can be described as amorphous porous material built from Si-O-Al and Si-CH_3 repeated structural units covalently bonded onto the siloxane network by urethane (-NHC(=O)-) bridges to form a di-urethanesil backbone. The possible structure of the silica-based di-urethanesil hybrid material Si-10Al is presented in Fig. 3.

Low temperature nitrogen adsorption on the derived xerogel Si-10Al (Fig. 4) is expressed by II–type isotherm. The nitrogen adsorption isotherm was used for evaluation of textural parameters and the following values were obtained: specific surface area – 764 $m^2\ g^{-1}$; total pore volume – 0.58 $cm^3\ g^{-1}$ and average pore radius – 1.5 nm.

3.2. Adsorption studies

3.2.1. Kinetic studies

The effect of contact time on the amount of adsorbed metal ions on the investigated material Si-10Al from multi-component solutions is presented in Fig. 5.

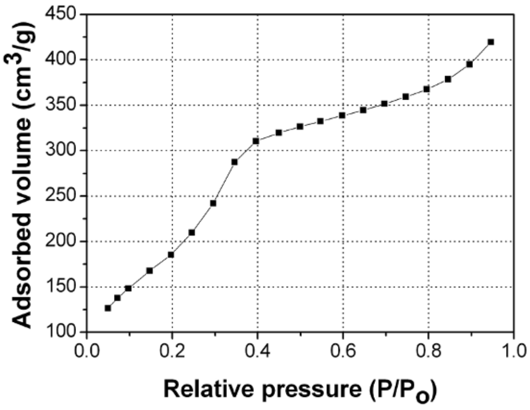

Figure 4. Low temperature nitrogen adsorption isotherm on the derived xerogel Si-10Al

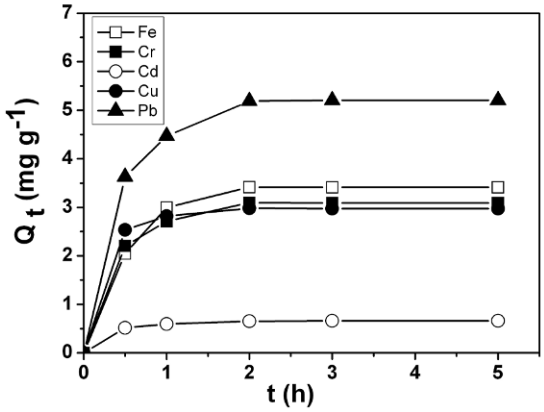

Figure 5. Effect of contact time on the amount of adsorbed Fe(III) - □, Cu(II) - ●, Cr(III) - ■, Cd(II) - ○ and Pb(II) - ▲ ions (C_o 10 mg L^{-1} at pH 5.0) on Si-10Al

Adsorption on this material is found to increase with increase in contact time and reached a maximum value within two hours. At contact time more than 120 min the amount of adsorbed ions remained unchanged. Thus we fixed two hours as the optimum contact time for all further experiments. This short time period required to attain equilibrium suggests an excellent affinity of the adsorbent for the investigated metal ions from aqueous solution. Highest adsorption rate was found for Pb(II) ions and lowest – for Cd(II) ions.

In order to understand the adsorption kinetics of the investigated metal ions, three kinetic models - pseudo-first-order, pseudo-second-order and intraparticle diffusion model - have been applied to the experimental data.

Pseudo-first-order [12] and pseudo-second-order [13] equations are as follows:

$$\log (Qe - Qt) = \log (Qe) - (k_1/2.303)t \quad (1)$$

$$(t/Qt) = (1/k_2Qe) + (1/Qe)t \quad (2)$$

where **Qt** is the amount of metal ions adsorbed for a certain time **t** (mg g^{-1}) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}); **Qe** is the equilibrium adsorption capacity (mg g^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). k_1 values were calculated from the slope of the **log (Qe − Qt)** *versus* **t** plots; k_2 values were calculated from the slope of the **t/Qt** *versus* **t** plots. The intercepts of these curves were used to determine the equilibrium capacity **Qe**. The values obtained are presented in Table 1.

The theoretical **Qe** values estimated from the pseudo-first-order kinetic model differ from the experimental values, thus the corresponding correlation coefficients were found to be lower than those for the pseudo-second-order model (see Table 1). On the other hand, the theoretical values obtained from the pseudo-second-order kinetic model are very close to the experimental **Qe** values. Thus we proved that the adsorption of all investigated ions can be described by the pseudo-second-order kinetic mechanism.

In order to assess the nature of the diffusion process responsible for the adsorption of the investigated ions onto the hybrid material, attempts are made to calculate the pore diffusion coefficients. The intraparticle diffusion equation [14,15] is expressed as:

$$Qt = k_{id}\, t^{1/2} + C \quad (3)$$

where **C** is the intercept, and k_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{1/2}$). By using this model, the plots **Qt** *versus* $t^{1/2}$ should be linear if the intraparticle diffusion is involved in the adsorption process. If these lines pass through the zero point then the intraparticle diffusion is the rate-controlling step [16]. If the plots do not pass through the zero point, the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption simultaneously. From the slope of the linear part of the plot the values of the rate parameter, k_{id} for the intraparticle diffusion can be calculated. The intercept **C** gives an idea concerning the boundary layer thickness, the larger intercept the greater is the boundary layer [17,18]. The values of k_{id} and **C** are presented in Table 1. The correlation coefficients for the intraparticle diffusion model are also lower than that of the pseudo-second-order kinetic model. These results confirm that the pseudo-second-order mechanism is predominant for the adsorption of Cu(II), Fe(III), Cr(III), Cd(II) and Pb(II) onto Si-10Al.

Table 1. Kinetic parameters of adsorption of Fe(III), Cr(III), Cd(II), Cu(II) and Pb(II) ions from multi-component aqueous solutions onto Si-10Al

Metal ions	Pseudo-first order constants			Pseudo-second order constants			Intraparticle diffusion constants			$Q_{e, exp}$ (mg g^{-1})
	Q_e (mg g^{-1})	k_1 (min^{-1})	r^2	Q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	r^2	k_{id} (mg g^{-1}min$^{-1/2}$)	C (mg g^{-1})	r^2	
Fe(III)	3.271	0.015	0.994	3.636	0.066	0.997	0.197	0.745	0.888	3.513
Cr(III)	2.887	0.015	0.988	3.227	0.096	0.999	0.171	0.799	0.866	3.090
Cd(II)	0.532	0.013	0.988	0.684	0.012	0.999	0.019	0.487	0.872	0.662
Cu(II)	2.573	0.015	0.973	3.023	0.074	0.999	0.154	0.960	0.812	2.971
Pb(II)	6.868	0.021	0.970	5.467	0.085	0.999	0.291	1.290	0.852	5.207

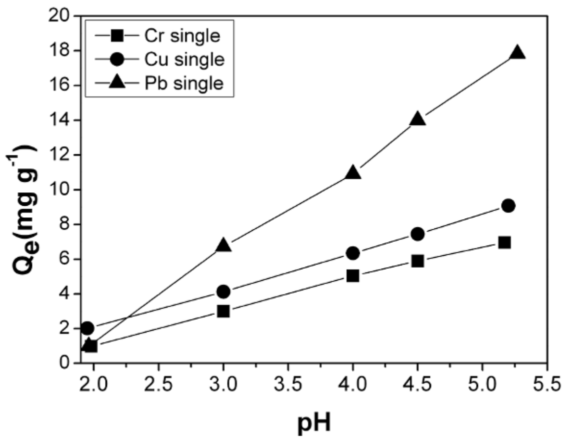

Figure 6. Effect of pH on metal adsorption onto Si-10Al

3.2.2. Effect of pH on adsorption efficiency

Since the binding of metal ions by surface functional groups was strongly pH dependent, the pH of the aqueous solution is an important controlling parameter in the adsorption process. The pH of solution controls the electrostatic interactions between the adsorbent and the adsorbate. It is known that increase of pH decreases the competition between the hydroxonium and metal ions for surface sites and results in increased uptake of metal ions by the adsorbents. Thus it is possible to manage metal removal from aqueous solutions by changing the pH value. The increase in metal uptake by adsorbents of different type due to increasing the pH of solution has been reported by several authors [7,19-22].

This trend has been discussed also in terms of a possible hydrolysis of adsorbate species and the formation of some surface compounds. In fact, adsorbents are characterized by the presence of surface functional groups such as silanol and uretan groups in the case of Si-10Al (Fig. 2b). The pattern of increase varies for individual metals as driven by solution phase equilibrium of oxide/hydroxide complexes and precipitates [23].

The amounts of adsorbed ions onto the investigated material Si-10Al as a function of pH of initial solutions are presented on Fig. 6. The effect of pH on metal adsorption on Si-10Al samples was studied in the pH range from 2.0 to 5.5. The pH was limited to values equal to 5.5 because of precipitation of metal hydroxide at higher pH values. As expected, the adsorption of the investigated metal ions strongly depends on acidity of the initial solutions. With the increase of pH-values the amounts of adsorbed ions increases and the optimum pH range is found to be above 5.0. Most affected by pH changes is the adsorption of Pb(II).

3.2.3. Adsorption isotherms

Experimental adsorption isotherms for single-component solutions are presented in Fig. 7. For this study, aqueous solutions with concentrations from 5 to 100 mg L^{-1} of each ion were prepared. In all cases an increase of adsorption with increase of the corresponding ion concentration in the solution is observed. These results indicate that energetically less favourable sites become involved with increasing ion concentrations.

It was found that for the hybrid material Si-10Al the amount of adsorbed ions increases in the order:

Cr(III) < Cu(II) < Pb(II)

The adsorption of metal ions is a result of physicochemical and stereochemical factors, which depends both on ionic and adsorbent properties. The most significant ionic properties are the hydrated radii, the hydration enthalpy of cations and hydrolysis ability. The concept of rejection of some water molecules, which is related to hydration enthalpies of the cations, could explain the high selectivity for Pb^{2+} (−357.3 kcal mol^{-1}) compared to the lower selectivity for Cu^{2+} (−502 kcal mol^{-1}) and the lowest for Cr^{3+} (−1047 kcal mol^{-1}). The metals studied, except Pb^{2+}, form stable complexes with water molecules. The difference is that Cr^{3+} has a coordination number of 6 and thus it forms octahedral complexes, while Cu^{2+} has a coordination number of 4 and thus forms tetrahedral complexes [24]. In this way the sequence above could be explained.

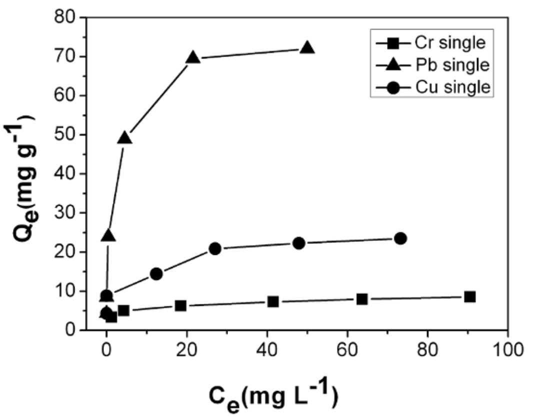

Figure 7. Adsorption isotherms for single-component solutions of Cu(II) - ●, Cr(III) - ■ and Pb(II) - ▲ onto Si-10Al

The equilibrium isotherms are very important in designing adsorption systems. The adsorption isotherm describes the distribution of the adsorbed molecules between the liquid and solid phases at equilibrium state. Concentration variation method is used to calculate the adsorption characteristic of both adsorbent and process. The elucidation of isotherm data by fitting them to different isotherm models is a substantial step in the adsorption study. There are several isotherm equations available for evaluation of experimental adsorption equilibrium data. In this study the equilibrium experimental data for the adsorbed metal ions on the investigated material Si-10Al were analyzed using Langmuir (4), Freundlich (5) and Dubinin–Radushkevich (6) isotherm models. The linear forms of these isotherms are as follows:

$$C_e/Q_e = 1/K_L Q_0 + C_e/Q_0 \tag{4}$$

where C_e is the concentration of metal ions in the equilibrium solution (mg L^{-1}), Q_e is the amount of metal ions adsorbed (mg) by per unit mass of adsorbent (g), Q_0 , the maximum adsorption capacity (mg g^{-1}); K_L, the constant of the Langmuir equation related to the enthalpy of the process.

$$\ln Q_e = \ln k_F + (1/n) \ln C_e \tag{5}$$

where k_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

$$\ln Q_e = \ln Q_0 - \beta\varepsilon^2 \tag{6}$$

where β is the constant of the adsorption energy (mol^2 J^{-2}), and ε is the Polanyi potential, described as:

$$\varepsilon = RT \ln(1+1/C_e) \tag{7}$$

where R is the gas constant (J mol^{-1} K^{-1}) and T is the temperature (K). The mean adsorption energy E (KJ mol^{-1}) can be calculated from parameter β as follows:

$$E = 1/(-2\beta)^{1/2} \tag{8}$$

The corresponding correlation coefficients and the isotherm constants are calculated and presented in Table 2.

The Langmuir model supports the following hypothesis: the adsorbent has a uniform surface which means absence of interactions between the solid molecules; the sorption process takes place in a single layer. According to the determination coefficients r^2 (values from 0.994 to 0.999, Table 2) the fit to his model is excellent. The Q_0 values calculated from the Langmuir model vary from 8.72 mg g^{-1} for chromium ions to 72.69 mg g^{-1} for lead ions. It is obvious that highest equilibrium adsorption capacity Q_0 was obtained for the Pb(II) ions.

The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor R_L.

$$R_L = 1/(1 + K_L C_0) \tag{9}$$

The R_L values for the investigated adsorbent are found to vary within the ranges: 0.001 - 0.014 (for lead ions); 0.036 – 0.428 (for chromium ions) and 0.008 – 0.138 (for copper ions). All values are between 0 and 1, which indicates favourable adsorption for all investigated ions [25,26]. In addition, the values of the separation factor (R_L) prove that the nanostructured hybrid material Si-10Al is a potential adsorbent for Pb(II), Cu(II) and Cr(III) removal from aqueous solutions.

The Freundlich model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species adsorbed onto the surface of the solid when increasing the concentration of certain species in the liquid phase. According to the determination coefficients r^2 calculated from the Freundlich model (values from 0.945 to 0.978, Table 2) the fit of this model is also very good, but not as good as the fit of the Langmuir model. The constants k_F and n are calculated for all investigated ions and presented in Table 2. Higher values for k_F indicate higher affinity for adsorption. In our study all n-values are in the range of 2.305 to 4.826 (Table 2), which indicates favourable adsorption onto the nanostructured hybrid material Si-10Al [27-29].

According to the determination coefficients r^2 values calculated from the Dubinin-Radushkevich model (values from 0.836 to 0.979, Table 2) the fit of this model

Table 2. Isotherm constants for single- and multi-component adsorption of metal ions onto Si-10Al

Adsorption	Metal Ions	Langmuir parameters			Freundlich parameters			Dubinin-Radushkevich parameters		
		Q_0 (mg g^{-1})	K_1 (L mg^{-1})	r^2	k_F (mg^{1-n} L^n g^{-1})	n (L mg^{-1})	r^2	Q_m (mg g^{-1})	E (KJ mol^{-1})	r^2
Single-Component	Cr(III)	8.72	0.267	0.994	3.41	4.826	0.978	3.82	9.19	0.891
	Cu(II)	23.44	1.250	0.998	4.26	2.305	0.978	4.89	5.57	0.836
	Pb(II)	72.69	14.350	0.999	13.23	3.232	0.945	9.31	3.91	0.979
Multi-Component	Fe(III)	6.22	0.167	0.998	1.94	3.865	0.918	2.51	2.54	0.892
	Cr(III)	8.24	0.134	0.998	2.05	3.242	0.972	2.75	7.27	0.899
	Cd(II)	2.39	0.044	0.992	0.19	1.851	0.982	0.40	5.94	0.828
	Cu(II)	5.07	0.284	0.998	4.07	5.407	0.923	2.73	9.66	0.883
	Pb(II)	10.31	0.301	0.998	4.21	4.926	0.815	4.50	8.10	0.851

is also good but worse as compared to both Langmuir and Freundlich models.

The value of *E* is very useful to predict the type of adsorption and give information about chemical and physical adsorption. It is known that energy of adsorption in the range of 2–20 kJ mol^{-1} could be considered physisorption in nature [30]. As shown in Table 2, the values obtained in the present work are in the range of 3.91 to 9.19 KJ mol^{-1}. This indicates that the type of adsorption for all investigated ions onto the nanostructured hybrid material Si-10Al is essentially physical.

Langmuir, Freundlich and Dubinin-Radushkevich equations are based on entirely different principles and the fact that the experimental results fit to one or other equation indicates only purely mathematical fit. It is important to note that every model has its own limitations in accurately describing equilibrium data. From data listed in Table 2 we consider that the mechanism of adsorption of metal ions on the nanostructured hybrid material containing aluminium cannot be attributed directly to the Langmuir, Freundlich or Dubinin–Radushkevich models (the r^2 values suggest that all three isotherm models provide good correlations for the adsorption of the investigated ions). However, it can be concluded that the adsorption isotherms of all investigated ions exhibit mainly Langmuir behaviour (determination coefficients greater than 0.994), which indicates for the most part homogeneous surface binding and monolayer adsorption.

3.2.4. Comparison of estimated adsorption capacities of Pb(II), Cu(II) and Cr(III) with those of other silica based adsorbents

The adsorption capacities of silica based adsorbents modified with different organic compounds with respect to Pb(II), Cu(II) and Cr(III) reported in the literature are compared to those obtained for the hybrid material Si-10Al in the present study. The values of adsorption capacities are presented in Table 3. It is obvious that the hybrid material Si-10Al is superior with respect to lead removal, while the values obtained for copper and chromium are comparable to most of the data reported in literature. Thus it could be concluded that the hybrid material Si-10Al can be used as a potential adsorbent for effective removal of Pb(II), Cu(II) and Cr(III) ions from contaminated aqueous solutions.

3.2.5. Multi-component adsorption studies

A practical consideration of the problem reveals that most of the effluent solutions represent a case of multi-metal situation rather than mono-metal one. In such a scenario it becomes essential to study not only single-component adsorption, but also effects of the presence of co-cations on the adsorption capacity [22].

For such studies, model multi-component aqueous solutions containing the metal ions Pb(II), Cu(II), Cr(III), Fe(III) and Cd(II) were prepared in order to investigate their competitive adsorption on Si-10Al and the influence of the other ions on their removal.

Experiments were carried out in different concentrations and acidity. The adsorption was significantly affected by pH and follows the same trend as that of the single-component adsorption, discussed above. Experimental adsorption isotherms for multi-component solutions are presented in Fig. 8.

Equilibrium modelling data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models and the corresponding constants are presented in Table 2. Best fit was observed for Langmuir model, which showed determination coefficients greater than 0.992 for all ions studied. Thus we proved that the Langmuir isotherm most adequately described the multi-component adsorption processes of the investigated ions as it was in the case for single-component adsorption.

The maximum adsorption capacities for multi-component adsorption were also calculated (Table 2). Highest adsorption capacity was achieved again for

Table 3. Comparison of the adsorption capacities for Pb(II), Cu(II) and Cr(III) in the present study with those reported in the literature

Silica based adsorbent modified with:	Adsorption capacity ($mg\ g^{-1}$) Pb(II)	Cu(II)	Cr(III)	Reference
5-Amino 1,3,4-thiadiazole-2-thiol	1.54	1.21	-	[31]
2,2-Thiodiethanol	2.00	-	-	[6]
Trialkylmethylammonium bis 2,4,4-trimethylpentylphosphinate	-	-	2.96	[32]
Bis (2,4,4-trimethylpentyl) phosphinic acid	-	-	5.83	[32]
Aminopropyl	-	22.22	-	[33]
Imidazole functionalized polystyrene	26.91	9.52	0.87	[34]
Tetrakis (4-carboxyphenyl) porphyrin	-	62.33	-	[35]
3-Mercaptopropyltriethoxysilane	-	36.42	-	[36]
3-Mercaptopropyltrimethoxysilane	66.04	38.12	13.84	[37]
Polystyrene	-	81.85	-	[8]
3-Aminopropyltrimethoxisilane	57.74	-	-	[9]
Aluminum sec- butoxide	72.69	23.44	8.72	Present study

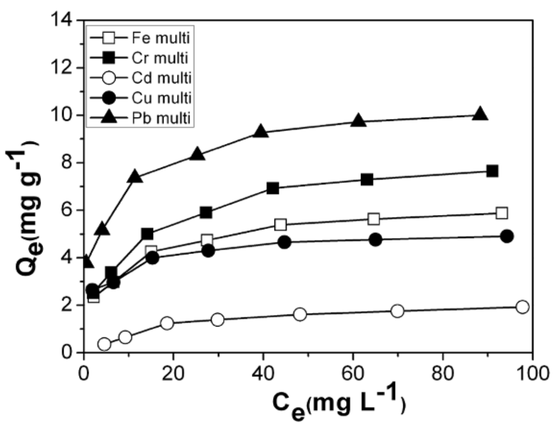

Figure 8. Adsorption isotherms for multi-component solutions containing Cu(II) - ●, Fe(III) - □, Cr(III) - ■, Cd(II) - ○ and Pb(II) - ▲ onto Si-10Al

Pb(II) ions, but it is significantly affected by the presence of competitive ions. On the other hand, the adsorption of Cr(III) on Si-10Al is practically not affected by the presence of Cu(II), Fe(III), Cd(II) and Pb(II).

4. Conclusions

The nanostructured hybrid material Si-10Al can be described as an amorphous porous material built from Si-O-Al and Si-CH_3 repeated structural units covalently bonded onto a siloxane network by urethane (-NHC(=O)-) bridges to form a di-urethanesil backbone.

The adsorption properties of this material with respect to Cu(II), Cr(III) and Pb(II) ions from single-component aqueous solutions and multi-component aqueous solutions containing also Cd(II) and Fe(III) was studied using the batch method.

The influence of contact time and acidity of initial solutions on their adsorption was investigated. Results from kinetic studies confirm that pseudo-second-order mechanism is predominant for the adsorption of all investigated ions onto Si-10Al.

The optimum pH range is found to be above 5.0. The maximum adsorption capacities for multi- and single-component adsorption were calculated. In both cases highest adsorption capacity was achieved for Pb(II) ions, but it is significantly affected by the presence of competitive ions. On the other hand, the adsorption of Cr(III) on Si-10Al is practically not affected by the presence of Cu(II), Fe(III), Cd(II) and Pb(II).

Equilibrium modelling data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models. In the present study, best fit was observed by the Langmuir model, which exhibits determination coefficients greater than 0.992 for all systems studied. Thus we proved that Langmuir isotherm most adequately described the adsorption processes of the investigated ions. The hybrid material Si-10Al can be used as potential adsorbent for the effective removal of Pb(II), Cu(II) and Cr(III) ions from contaminated aqueous solutions.

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References

[1] M.C. Goncalves, V. de Z. Bermudez, D. Ostrovskii, L.D. Carlos, Electrochim. Acta. 48, 1977 (2003)
[2] M.E. Mahmoud, M.M. Osman, M.E, Amer, Anal. Chim. Acta. 415, 33 (2000)
[3] M.E. Mahmoud, O. F. Hafez, M. M. Osman, A. A. Yakout, A. Alrefaay, J. Hazard. Mater. 176, 906 (2010)
[4] R.S.A. Machado, Jr., M.G. da Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, Talanta 63, 317 (2004)
[5] P.K. Jal, S. Patel, B.K. Mishra, Talanta 62, 1005 (2004)
[6] P. Tzvetkova, P. Vassileva, N. Nikolova, L. Lakov, O. Peshev, J. Mater. Sci. 39, 2209 (2004)
[7] M. Puanngam, F. Unob, J. Hazard. Mater. 154, 578 (2008)
[8] Q. Xu, P.Yin, G. Zhao, G. Yin, R. Qu, Cent. Eur. J. Chem. 8, 214 (2010)
[9] A. Heidari, H. Younesi, Z. Mehraban, Chem. Eng. J. 153, 70 (2009)
[10] Y. Ivanova, T. Gerganova, M.H.V. Fernandes, I.M.M. Salvado, Cent. Eur. J. Chem. 7, 42 (2009)
[11] B. Stuart, W.O. George, P.S. McIntyre, Modern Infrared Spectroscopy (John Wiley & Sons, Chichester, 1996)
[12] H. Leinonen, J. Letho, Waste Manag. Res. 19, 45 (2001)
[13] Y.S. Ho, G. McKay, Process. Biochem. 34, 451 (1999)
[14] W.J. Weber, J.C. Morris, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89, 31 (1963)
[15] S.J. Allen, G. McKay, K.Y.H. Khader, Environ. Pollut. 56, 39 (1989)
[16] Y.S. Ho, G. McKay, Process. Biochem. 38, 1047 (2003)
[17] G. McKay, M.S. Otterburn, J.A. Aga, Water Air Soil. Pollut. 24, 307 (1985)
[18] G. Bayramoglu, B. Altintas, M.Y. Arica, Chem. Eng. J. 152, 339 (2009)
[19] S.E. Samra, Adsorpt. Sci. Technol. 18, 761 (2000)
[20] M.M. Rao, G.P.C. Rao, K. Seshaiah, N.V. Choudary, M.C. Wang, Waste Manage 28, 849 (2008)
[21] P. Vassileva, D. Voikova, J. Hazard. Mater. 170, 948 (2009)
[22] P. Vassileva, A. Detcheva, Adsorpt. Sci. Technol. 28, 229 (2010)
[23] B.E. Reed, J. Maqbul, B.Tomas, Water Environ. Res. 68, 877 (1996)
[24] J.V. Inglezakis, A.A. Zorpas, M.D. Loizidou, H.P. Grigoropoulou, Sep. Pur. Technol. 46, 202 (2005)
[25] G. Rojas, J. Silva, J. A. Flores, A. Rodriguez, M. Ly, H. Maldonado, Sep. Pur. Technol. 44, 31 (2005)
[26] A.A. Atia, A.M. Donia, W.A. Al-Amrani, Desalination 246, 257 (2009)
[27] B.H. Hameed, F.B.M. Daud, Chem. Eng. J. 139, 48 (2008)
[28] K. Saltalı, A. Sarı, M. Aydın, J. Hazard. Mater. 141, 258 (2007)
[29] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, J. Colloid. Interface Sci. 282, 20 (2005)
[30] J.M. Smith, Chemical Engineering Kinetics (McGraw-Hill New York, 1981)
[31] P. Tzvetkova, P. Vassileva, R. Nickolov, J. Porous Mater. 17, 459 (2010)
[32] Y. Liu, L. Guo, L. Zhu, X. Sun, J. Chen, J. Chem. Eng. 158, 108 (2010)
[33] J. Aguado, J.M. Arsuaga, A.Arencibia, M. Lindo, V. Gascón, J. Hazard. Mater. 163, 213 (2009)
[34] P. Yin, Q. Xu, R. Qu, G. Zhao, Y. Sun, J. Hazard. Mater. 173, 710 (2010)
[35] E.-Y. Jeong, M.B. Ansari, Y.-H. Mo, S.-E. Park, J. Hazard. Mater. 185, 1311 (2011)
[36] X. Xue , F. Li, Micropor. Mesopor. Mater. 116, 116 (2008)
[37] S. Wu, F. Li, R. Xu, S. Wei, G. Li, J. Nanopart. Res. 12, 2111 (2010)