ANALELE ŞTIINŢIFICE ALE UNIVERSITĂŢII „AL. I. CUZA” IAŞI
Geologie. Tomul LIII, 2007

ANIONIC ADSORPTION IN METAL OXIDE-SOLUTION SYSTEMS

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Abstract

Although the adsorption process of single cationic specie has been extensively studied, a small attention has been given to removal of anionic species from their solutions or contaminants. Anionic complexes from solutions are effectively bound on the adsorbent surface. The industrial activities such as mining, metallurgy, energy etc., have a lot of problems with anionic complex (such as chromate, CrO_4^{2-}, seleniate, SeO_4^{2}, vanadate, VO_4^{3-}, nitrite, NO_2^- or nitrate, NO_3^- from their solutions).

In this study a non-competitive adsorption of NO_2^- ions to alumina surface was studied in an aqueous system. To express the magnitude of the process, we used Langmuir and Freundlich adsorption models and it was seen that the equilibrium data fitted well to both models in the concentration range studied. Different volumes (20 to 100 cm^3) of $NaNO_2$ solution of 10^{-3} to 10^{-1} M were used in experiments. Also, we used activated alumina (0.2 to 1.0 g) and a pH values around 4, mentioned with drops of either HCl or NaOH 0.1 N. The values of the constants obtained from graphical forms of the equations were used in the assessment of the adsorption intensity of the process. The results show that the maximum adsorption appears in the case of the more concentrated solution of $NaNO_2$ (10^{-1} M) and to small quantities of adsorbant material, both for Langmuir and for Freundlich isotherms (with some exceptions). The value of *k* constant from Langmuir equation shows a better affinity of mineral substratum for NO_2^- in

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diluted solutions comparable with the concentrated solutions of analyzed anion. In the same time, the value of *n* constant from Freundlich equation shows (with one exception) a better affinity for medium concentration of analyzed anion, comparable with the other solutions.

Key words: anionic adsorption, mineral oxide, Langmuir and Freundlich isotherms

Introduction

The removal of toxic cations and anions is one of the important environmental problems to be solved by the researchers. In order to find new adsorptive materials for these complex problems, minerals oxides like Al_2O_3, SiO_2 has focused attention and can represent an alternative to the classical chemical methods. The adsorption of contaminants to the mineral oxides arises from the coordination of the ions to the surface functional groups, especially OH groups (White, 2001, Harris, 1998). The kinetics of ions uptake, thought physical adsorption at the surface, is very rapid and occurs in a short time after the minerals comes into direct contact with the solution. Many minerals oxides are known to be capable to bind cations or anions to the surface hydroxyl groups from their structure.

The surface properties of aluminium oxides, which are considered to be an ideal adsorbent, are depending on the presence of aluminol groups (Dondur et al., 1995). At a sufficient concentration of ionic species in solution, these groups make such a surface hydrophilic. The OH groups act as the centers of adsorption during their specific interaction with adsorbates capable of forming a hydrogen bond with the OH groups, or of undergoing donor-acceptor interaction.

Adsorption of a single specie of ion on the mineral oxide is affected by several factors. These factors include the specific surface properties of minerals and the physicochemical parameters of the solution such as temperature, pH, initial concentration and adsorbent mass. Many other parameters affect the capacity of minerals to bind more than one chemical specie from solution (Kasprzyk-Hordern, 2004).

At the first stage of adsorption, a rapid equilibrium is established between the adsorbed specie on the mineral surface and unadsorbed specie from teh analysed solution. This equilibrium can be represented by adsorption isotherms. The mono-component adsorption is a function describing quantitatively, at a constant temperature, the relationship between the residual (equilibrium) specie concentration left in solution after binding (C_{eq}) and the amount of specie bound to the mineral surface (q_{eq}) (usually determined by difference). There are a lot of mathematicals models which describe the non-competitive adsorption onto solid surfaces. Among these, we used in this paper the Langmuir and Freundlich isotherm models which have been shown to be suitable for describing the short-term and mono-component adsorption of anions by minerals surfaces (Kasprzyk-Hordern, 2004).

The most difficult problem in describing the adsorption of chemical species (cations or anions) by solid surfaces is that in natural systems there are present more than one species and the interferences and competition phenomena are present. In these chemical systems more complex mathematical relationships are applied which take into account the adsorbed quantity of one component and the concentration of all other components from solution (Aksu et al., 1997, McKay et al., 1989).

Materials and methods

Sorption processes involve a solid phase (sorbent) and a liquid phase (solvent, usualy water) containing a dissolved species (sorbat). Due to the sorbent "affinity" for sorbate specie, the latter is attracted into the solid phase and bound there by different mechanisms. The process takes place until the equilibrium is established between the amount of solid-bound sorbates species and the amount remaining in solution, at a equilibrium concentration (c_e). The degree of the sorbent "affinity" for sorbates species determines its distribution between the solid and liquid phases. The calculation of the chemical specie uptake ($mg \cdot g^{-1}$) is based on the material balance of the sorption system; the sorbate amount, which is not in solution, must be onto the solid surface. The sorbate from the solid phase (the sorption uptake, Γ) can be calculated with the formula:

$$\Gamma = \frac{V(c_i - c_e)}{S} \qquad (1)$$

where V [L] = the volume of the solution contacted with the sorbat specie, c_i, c_e [$mg \cdot L^{-1}$] = the initial and equilibrium (final) concentration of sorbat species in solution, respectively, S [g] = the amount of the added sorbent used in experiment.

The Langmuir isotherm is described in terms of how much adsorbed aqueous specie is adsorbed onto solid phase. The isotherm equation is of a hyperbolic form:

$$\Gamma = \Gamma_{\max} \frac{k \cdot c_e}{1 + k \cdot c_e} \qquad (2)$$

where k = the equilibrium constant of adsorption process, Γ_{max} = the value of maximum adsorption. The value of Γ_{max} can be explained as the number of binding sites that are available for adsorption, while Γ as the number of binding sites that are in fact occupied by the sorbate at the concentration c_e (Hurduc, 1979, Isac et al., 1995).

The linearization of Langmuir equation permits us to find the main constants of the adsorption process.

$$\frac{c_e}{\Gamma} = \frac{c_e}{\Gamma_{\max}} + \frac{1}{k \cdot \Gamma_{\max}} \qquad (3)$$

From the graph of (c_e / Γ) = f (c_e) we can find the values of ($\Gamma_{\max}$, k). The Langmuir isotherm considers sorption as a chemical phenomenon, so the Langmuir constant k is related to the energy of adsorption (the higher constant means a higher affinity of the sorbent for the sorbate specie).

The Freundlich isotherm equation is exponential type (Hurduc, 1979, Isac et al., 1995):

$$x = K_F \cdot c_e^{(1/n)} \qquad (4)$$

where K_F, n are Freundlich constants and x = the sorption uptake.

The Freundlich relation is an empirical one; it does not indicate a finite uptake capacity of the sorbent and can be applied in the low concentration range. Freundlich equation can be liniarized, and a plot of ln x = f (ln c_e) permite us to determine the empirical coefficients n and K_F.

$$\ln x = \frac{1}{n} \ln c_e + \ln K_F \qquad (5)$$

Other sorption isotherm relationships are listed in the table below, all of them having advantages or disadvantages. These equations are mathematics models for describing the relationship between (Γ or x) adsorption vs (c_e) equilibrium concentrations of adsorbate species from solutions. Some of these equations are presented in table 1.

Tab. 1. Some sorption isotherm relations used in literature (Niu and Volesky, 2001, Volesky, 2001)

Adsorption isotherm	Equation
Mixed equation (LANGMUIR+ FREUNDLICH)	$\Gamma = \Gamma_{\max} \frac{kC_e^{1/n}}{1 + kC_e^{1/n}}$
RADKE-PRAUSNITZ	$\frac{1}{\Gamma} = \frac{1}{aC_e} + \frac{1}{bC_e^{\beta}}$

REDDLICH-PETERSON	$\Gamma = \dfrac{aC_e}{1+bC_e^{1/n}}$
BRUNAUER-EMMET-TELLER (BET)	$\Gamma = \dfrac{BCQ^0}{(C_e - C)[1+9B-1)C/C_e]}$
DUBININ-RADUSHKEVICH	$\dfrac{W}{W_0} = \exp[-k(\dfrac{\varepsilon}{\beta})^2]$

In this paper the adsorption of NO_2^- anion by aluminium oxide dust was studied. A stock solution was prepared through dissolving the exact quantity of sodium nitrite (Merck reagent $NaNO_{2)}$. The test solutions were prepared by dilution of 10^{-1} M to 10^{-2} M and 10^{-3} M, respectively, from the stock solution. In experiment were used different volumes (20 to 100 mL) of the above concentrations. The pH of the working solutions was mentioned at constant value ($pH \approx 4$) with some droplets of NaOH/HCl 10^{-1} M added before starting the experiments. For adsorption studies 0.2 to 1.0 g of aluminium oxides (d=0.3-0.6 mm) was suspended in different volumes of NO_2^- solution, (see fig. 1). In order to simplified the methodology, we used in the experiments different amounts of aluminium oxides (0.2, 0.4; 0.6; 0.8 and 1.0 g, respectively) and different volumes of NO_2^- solution (20, 40, 60, 80 and 100 mL, respectively) by different concentrations (10^{-1} M, 10^{-2} M and 10^{-3} M, respectively). All the flasks were agitated on a magnetic stirrer for 10 - 15 min, until o chemical equilibrium was attained. After mixing, the solutions were filtered, and the content of NO_2^- anion at equilibrium was measurement through ionic chromatography (Shimadzu HIC 6A device with UV detector 209 nm).

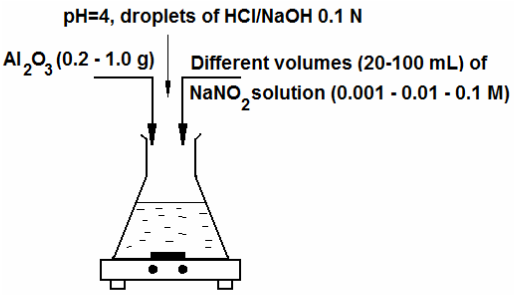

Fig. 1. Working methodology used in the experiments

Results

In order to calibrate the instrument, we used a $NaNO_2$ Merck reagent and the calibration curve is presented in fig. 2.

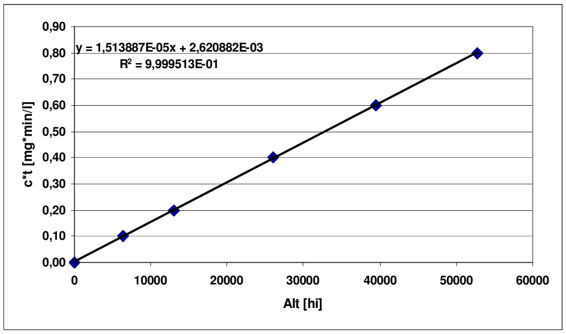

Fig. 2. Calibration curve obtained for ionic cromatograph

Although the adsorption of numerous cations by mineral oxides has been investigated by researchers, the adsorption of anions by mineral oxides has not been extensively investigated. In this study a non-competitive adsorption was studied using two mathematical models of isotherms, Langmuir and Freundlich isotherms, respectively. The values of the constants which results from these two graphical representations were compared in between them.

The Langmuir equation is valid for monolayer adsorption on a mineral surface containing a finite number of sites. The model assumes uniform energies of sorption on the surface and no transmigration of anionic species in the surface plane has place. Generally, there are a lot of properties (particle size, temperature, pH, ionic strength etc.) which have a large influence on the adsorption capacity of minerals, but these properties were not study in this paper. For Langmuir equation a plot of (c_e / Γ) versus (c_e) is liniar and fig 3 gives the Langmuir isotherms for NO_2^- anion adsorption onto different quantities of alumina.

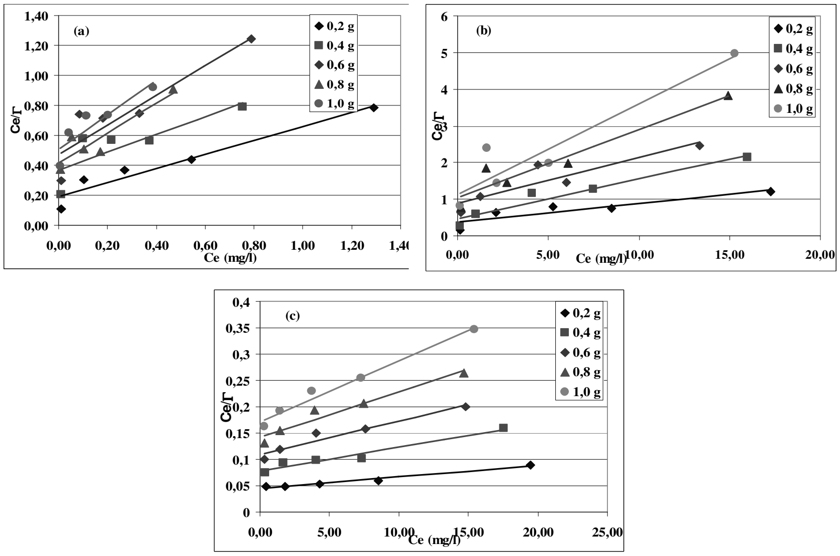

Fig. 3. Langmuir plots for NO_2^- adsorption onto different amounts of Al_2O_3 (0.2-1.0 g) (a) 10^{-3} M $NaNO_2$ solution; (b) 10^{-2} M $NaNO_2$ solution; (c) 10^{-1} M $NaNO_2$ solution

These graphs have the $(\text{intercept})^{-1} = k \cdot \Gamma_{max}$ and the $(\text{slope})^{-1} = \Gamma_{max}$. The values of the individual constants (Γ_{max} and k) obtained by evaluating of Langmuir plots are given in tab. 2. As we expect, the amplitude of the adsorption (Γ_{max}) indicated the amount of NO_2^- anion per unit of weight of adsorbent increase from diluted solution (10^{-3} M) to the concentrated solution (10^{-1} M) with almost two orders of magnitude.

Tab. 2. Values of Langmuir and Freundlich constants obtained from the plots for the adsorption of each $NaNO_2$ solution onto aluminium oxide

$NaNO_2$ solution	Adsorbant amount [g]	LANGMUIR isotherm		FREUNDLICH isotherm	
		Γ_{max}	k	K_F	n
10^{-3} M solution	0,2	2,139	2,446	2,454	3,584
	0,4	1,696	1,595	1,03	2,962
	0,6	1,011	2,097	0,71	2,964
	0,8	0,989	2,458	0,494	2,509
	1,0	0,872	2,262	0,416	2,556

10^{-2} M solution	0,2	29,069	0,178	65,659	40,322
	0,4	9,233	0,189	35,686	39,215
	0,6	6,293	0,183	22,516	2,816
	0,8	5,390	0,179	18,595	36,63
	1,0	4,033	0,22	15,739	42,49
10^{-1} M solution	0,2	454,54	0,048	684,699	2,365
	0,4	222,201	0,057	365,931	2,417
	0,6	156,25	0,058	253,863	2,435
	0,8	116,279	0,06	192,087	2,434
	1,0	86,956	0,066	154,703	2,461

Also, we can see an exception for Γ_{max} value at 10^{-2} M solution, where a large value is present (Γ_{max} = 29.069 mg/g adsorbant), which can be a measurement error. Although the differences in Γmax values are evidently, overall an increasing trend of adsorption can be observed, from the diluted to concentrated solutions. Concerning the other parameter which represent the adsorption constant of the process, the value of *k* parameter indicates a decreased of adsorption from the concentrated to the diluted solution. The parameter varied from k=0.066 for 10^{-1} M $NaNO_2$ solution and 1 g mineral substratum to k=2.446 for 10^{-3} M $NaNO_2$ solution and 0.2 g mineral substratum. As we expect, the mineral oxide present o higher adsorption affinity in the diluted solution comparable with the adsorption affinity in the concentrated solution for the analyzed chemical specie (McKay et al., 1989).

The adsorption capacity of mineral substratum can be explain using the Freundlich equation. In the figure 4 are presented the graphical representations obtained with the linearized Freundlich equations. The values of non-competitive constants evaluated from graphical representations are presented in tab. 2. The values of Freundlich constants are indicators for adsorption capacity (K_F) and adsorption intensity (n), respectively. As we expect, the magnitude of the adsorption increases from the diluted solution (10^{-3} M) to the concentrated solution (10^{-1} M) of studied anion, in the same direction like Langmuir isotherm does for the above case. Some unexpected values were found for the smallest amounts of mineral oxide in the diluted solution (10^{-3} M $NaNO_2$): K_F=2.454 for 0.2 g Al_2O_3 and K_F = 1.03 for 0.4 g Al_2O_3, respectively.

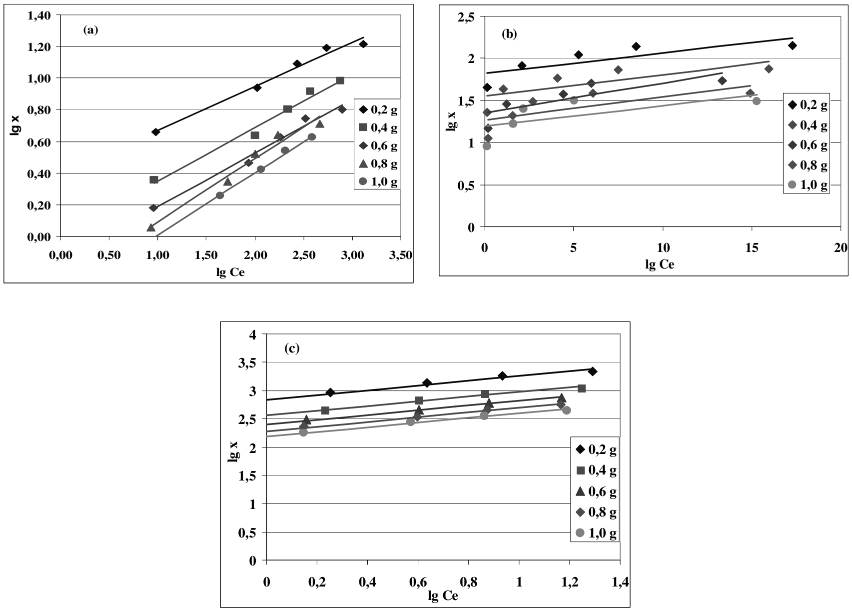

Fig. 4. Freundlich plots for NO_2^- adsorption onto different amounts of Al_2O_3 (0.2-1.0 g) (a) 10^{-3} M $NaNO_2$ solution; (b) 10^{-2} M $NaNO_2$ solution; (c) 10^{-1} M $NaNO_2$ solution

The value of n constant from Freundlich equation show (with one exception) the better affinity for medium concentration of analyzed anion (10^{-2} M), comparable with the other solutions. If for 10^{-1} M and 10^{-3} M $NaNO_2$ solutions the values for n constants are almost the same, for this solution (10^{-2} M), the values of n constant are higher with one order of magnitude comparable with the values obtained with the other two solutions. An exception for 0.6 g of Al_2O_3 mineral oxide is also present.

Both models of equations are developed to describe a single specie adsorption. However, the Freundlich model provides a more realistic description of the process, because it does not involve a complete monolayer of anion on the oxide surface; by contrary the Langmuir equation involves this condition.

Conclusions

Due to these difficulties associated in predicting the nature of adsorption process, empirical procedures based on adsorption equilibrium conditions have been commonly used to predict the adsorber size and performance (McKay et al., 1989). The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of sorbent. The most commonly used equilibrium models are Freundlich, Langmuir beside Redlich Peterson, Dubinin Raduskevich, Temkin and Sips isotherm models etc. (White, 2001, Harris, 1998). Equilibrium data well representing the Freundlich isotherm represents the expectation of multilayer sorption. Similarly the equilibrium representing the Langmuir confirms the monolayer coverage of solute particles onto sorbent particles. Apart from Freundlich and Langmuir isotherm model, the most often-used equilibrium model is Redlich Peterson model, which incorporates both the advantageous significance of both the Freundlich and Langmuir model. Redlich Peterson isotherm equation represents the equilibrium curve to follow Henrys law and the curve behavior follows Freundlich isotherm equation at higher initial solute concentrations. Another equilibrium model derived from the limiting behavior of Freundlich and Langmuir equilibrium model is Sips or Langmuir-Freundlich model. This model suggests equilibrium data follow Freundlich curve at lower initial solute concentration and follow Langmuir pattern at higher solute concentrations. Another most commonly used equilibrium model to predict the sorption nature is Dubinin Raduskevich model and it is used to calculate the mean free energy of sorption as it is transferred to the surface of solid from infinite distance in the solution. Also the results were mainly used to identify whether chemisorption is involved. The dependence of temperature on equilibrium capacity can be identified based on the heat of adsorption value using Temkin isotherm equation. The best fit of equilibrium data in Temkin isotherm equation indicates the heat of adsorption is liner rather than logarithmic.

In this paper the adsorption of NO_2^- anion by aluminium oxide dust was studied. The test solutions were prepared by dilution of 10^{-1} M to 10^{-2} M and 10^{-3} M, respectively, from the stock solution. In experiment were used different volumes (20 to 100 mL) of the above concentrations and the pH was mentioned at constant value ($pH \approx 4$). For adsorption studies 0.2 to 1.0 g of aluminium oxides ($d=0.3-0.6$ mm) was suspended in different volumes of NO_2^- solution All the flasks were agitated on a magnetic stirrer for 10 - 15 min, until o chemical equilibrium was attained. After mixing, the solutions were filtered, and the content of NO_2^- anion at equilibrium was measurement through ionic chromatography. The results show that the maximum adsorption appears in the case of the more concentrated solution of $NaNO_2$ (10^{-1} M) and to small quantities of mineral oxide, both for Langmuir and for Freundlich isotherms (with some exceptions). The value of k constant from Langmuir equation shows a better affinity of mineral substratum for NO_2^- in diluted solutions comparable with the concentrated solutions of analyzed anion. In the same time, the value of n constant from Freundlich equation shows (with one exception) a better affinity for medium concentration of analyzed anion, comparable with the other solutions.

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