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ADSORPTION OF NICKEL (II) IONS FROM AQUEOUS SOLUTIONS USING ALUMINA

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Abstract: The paper presents the results achieved during the process of nickel removal from aqueous solutions by adsorption on alumina (Aluminum oxide) in continuous conditions. The continuing experiments were conducted in a glass column with diameter of 16 mm and fixed bed of adsorbent with quantity ranging from 30 to 115 g, adsorbent grains size from 1.0 to 2.0 mm, and retention time of 0.5 to 12 minutes. The quantity of nickel in the aqueous solutions was changed within the range of 0.045 up to 0.12 mg/l Ni. The analysis of the obtained experimental data defined the mutual affection of the retention time, the initial nickel concentration in the water, and the adsorbent quantity, i.e. the content of the adsorbent in the treated solution to the adsorbent capacity.

According to the achieved results, logarithmic mathematical model showed best correlation between experimental and calculated values, also maximum nickel ions adsorption uptake onto the alumina were determined as 400 mg/g.

Key words: adsorption, nickel, alumina, fixed bed operation, adsorbent capacity

Introduction

According to the WHO (World Health Organization) recommendations, the presence of nickel in the water supply system or commercially used mineral water is extremely harmful and dangerous. Based on the WHO recommendations, EU directives and domestic regulations that correspond to the abovementioned recommendations, the maximum allowed concentration of nickel is 2 μg/l (WHO, 1996; EC, 1998; Anon, 2004).

Various methods are used for removal of heavy metals from wastewater. Most of these methods involve high capital cost with recurring expenses, which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physicochemical treatment processes (Peters et al, 1985). In the last few years, adsorption has been shown to be an alternative method for removing trace metals from water and wastewater. Interest has risen recently in removing heavy metals from solutions by binding with agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust (Bin et al, 2005). Peat moss, a natural inexpensive material was also used as an adsorbent (Vengris et al., 2001). Silica gel (Filho, 1998) and activated carbon (Goyal et al., 2001) have been also used. Alumina has been also studied (Yabe, Oliveira, 2001).

The nickel removal from underground, superficial, and waste waters had not attracted any significant attention in the researches, thus resulting in no world-wide accredited procedure on nickel removal from waters. In comparison to other heavy metals and metalloids, such as Zn, Pb, Cd, As, the presence of nickel in waters is quite rarely notified. This was very important because, as a result of the occurrence of

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nickel-containing ores in Southern Macedonia and Northern Greece, there are signs of significant nickel concentrations in the underground waters in these regions (Wolkersdorfer and Bowell, 2005; Karavoltsos and Sakellari, 2008). Hence, adsorption of nickel ions from aqueous solutions was performed by applying alumina.

Adsorption And Equilibrium Isotherms

Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they desorb. The physical chemistry involved may be a complex one and no single theory of adsorption has been put forward which satisfactorily explains all systems. Most theories have been developed for gas-solid systems because the gaseous state is better understood than the liquid (Ruthven, 1984; Coulson and Richardson, 1991; Dimitrovski, 2010). Adsorption isotherm defines the functional equilibrium distribution of adsorption with different concentrations of adsorbate in solution at constant temperature. Commonly, the amount of adsorbed material per unit of adsorbent weight increases with the increasing of concentration, but not in direct proportion. Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements (Ruthven, 1984; Coulson and Richardson, 1991; Dimitrovski, 2010).

Alumina

Alumina (aluminum oxide Al_2O_3) is a fine white material similar in appearance to common salt. When an adsorbent is required which is resistant to attrition and which retains more of its adsorptive capacity at elevated temperatures than silica gel does, activated alumina may be used. Activated carbon adsorption is not nearly as effective at removing metals and inorganics as it is at removing organic compounds. This is primarily because metals often exist in solution either as ions or as hydrous ionic complexes. Neither of these forms is effectively adsorbed by carbon (Anon., 2011. Also its black colour persists and adds a gray tinge if even trace amounts are left after treatment (Anon. 2011b).

Experimental Part

The nickel sulphate ($NiSO_4 \cdot 7H_2O$) used was packed and distributed by ADWIC Company and contains a maximum limit of impurities chloride 0.01% and iron 0.02%.

The stock aqueous solution of Ni (II) containing 1000 mg/l was prepared by dissolving 4.27 mg of $NiSO_4 \cdot 7H_2O$ in 1 liter of DDW. The stock solutions were used to prepare dilute solutions of different working concentrations.

Water used for preparation of aqueous solution was tap water from "Water Supply and Sewage", Public Enterprise, Skopje with characteristics and chemical composition given in Table 1.

Working aqueous solution with different concentrations of Ni (II) ions was made with mixing at 25 ± 2 ºC on a rotary shaker at 120 rpm of tap water and prepared Ni (II) standards.

Aluminum oxide (Al_2O_3), alumina was used as an adsorbent for the removal of Ni (II) ions from aqueous solution. It is a white fine powder similar in appearance to common salt. The alumina used is packed by industrial name COMPALOX, made in USA with characteristics and chemical composition given in Table 2.

The fixed-bed experiments were carried out at 25°C in a water-jacketed glass column with an inner diameter of 16 mm and a full length of 1200 mm. Because the diameter of the column is around 10 times larger than that of the adsorbent particles, the wall effect is negligible (Korkisch, 1989). To one end of the bed, a small wooden glass was inserted, an aliquot of the fresh adsorbent was put into the bed. The aqueous solution with known concentrations of metal ions was then fed to the top of the bed at a desired flow rate driven by a micro-metering pump (Cole-Parmer, Masterflex 7518-10) until the breakthrough curve was completed. The samples in the outlet were taken at the preset time intervals. Table 3 lists the operating characteristics of the column and the fixed bed.

The treated water was sent for nickel analysis. Residual nickel concentration was determined by rather fast and less accurate colorimetric method AQUAQUANT 1.14420 provided by MERCK, while more precise results for the remaining concentration of nickel were obtained by AAS (atomic absorption spectroscopy) using an air acetylene flame conducted in AAS Model Varian Spectra AA 55 apparatus according to the ASTM D 1886 – 03 standard. Each test was duplicated and the arithmetic average result of the two tests was reported in this paper.

Table 1. Characteristics and chemical composition of the water

Characteristic	Value
Temperature (^{0}C)	18.0
pH	7.0
Turbidity (NTU)	0.34
Electroconductivity (mS/cm)	479
TRD 105^{o}C (mg/l)	275
Bicarbonates (mg/l)	398.1
m-alkalinity	61
THD^0 (^{0}D)	18.5
Calcium (mg/l)	97.95
Magnesium (mg/l)	16.6
Iron (mg/l)	0.005
Manganese (mg/l)	0.002
Sodium (mg/l)	7.17
Potassium (mg/l)	1.0
Nickel (mg/l)	0.0
Chromium (mg/l)	0.008
Chlorides (mg/l)	8.0
Sulfates (mg/l)	7.6
Silicates (mg/l)	10.0
Nitrates (mg/l)	7.4
Nitrites (mg/l)	0.0
Ammonia (mg/l)	0.0
COD (mg/l)	2.2

Table 2. Characteristics and chemical composition of the adsorbent

Characteristic	Value
Form	spherical
Color	white
Particle size (mm)	1.0 - 2.0
Specific surface area (m^2/g)	250 - 350
Total pore volume (cm^3/g)	0.35
Packed bulk density (kg/m^3)	750 - 850
Al_2O_3 (%)	90.5
Na_2O (%)	0.35
Fe_2O_3 (%)	0.01 - 0.03
SiO_2 (%)	0.02
Ignition loss 250 – 1200^{0}C (%)	9

Table 3. Operating characteristics of the column and fixed bed

C_o (mg Ni/l)	M_{ads} (g)	$H_{sl}\approx$ (mm)	V (ml)	V (m^3/h)	V_h (m/h)
0.045	30	121	50300	0.001937	9.637
	62	225	216850	0.000536	2.668
	115	475	255150	0.001733	8.624
0.085	30	120	31150	0.00202	10.05
	65	310	548950	0.000376	1.873
	100	430	403400	0.001767	8.791
0.12	30	122	22100	0.002053	10.215
	50	227	476590	0.000457	2.275
	115	475	670350	0.000477	2.347

Results and Discussion

Obtained experimental data is shown in Figures 1-3 as functional dependencies of amount of adsorbed nickel, adsNi from volume of treated water (aqueous solution), V. Figures are plotted with volume of treated water instead of time on x-axes and amount of adsorbed nickel instead of outlet concentrations on y-axes.

1. Because of high correlation factor ($R^2 \approx 1$) for the dependency of volume of treated water from time, an approximate uniform (plug) flow is negligible which gives a uniform outlet concentration of nickel.

2. The dependency of outlet concentration of nickel with time is not uniform because of approximate plug flow. Also high correlation factor ($R^2 \approx 1$) for dependency of volume of treated water from time, gives opportunity to plot these kind of dependency.

3. Dependency of outlet concentration of nickel with time is not uniform because of unaccomplished piston flow. Plotting this kind of dependence is possible because of high correlation factor ($R^2 \approx 1$) for dependency of volume of treated water from time.

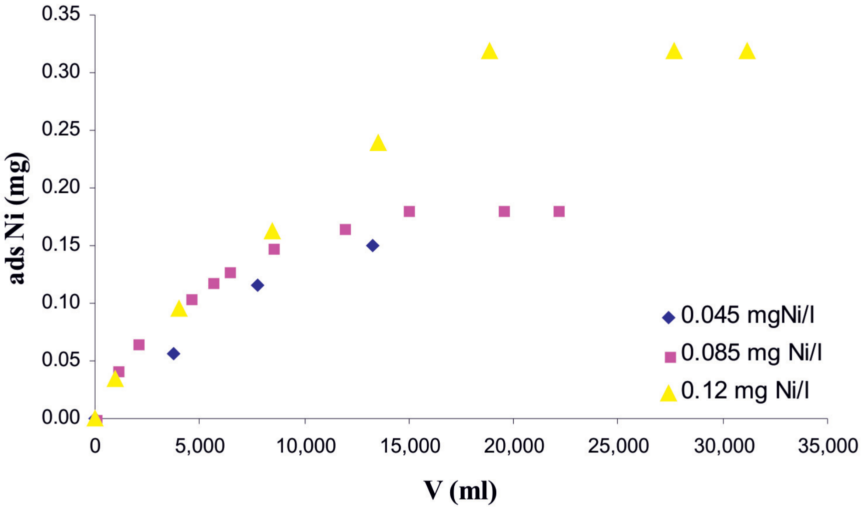

Figure 1. Dependence of amount of adsorbed nickel, adsNi(mg) from volume of treated water, V(ml) for different initial nickel concentration, C_o (mg/l) in the aqueous solution for adsorbent mass, M_{ads} = 30g

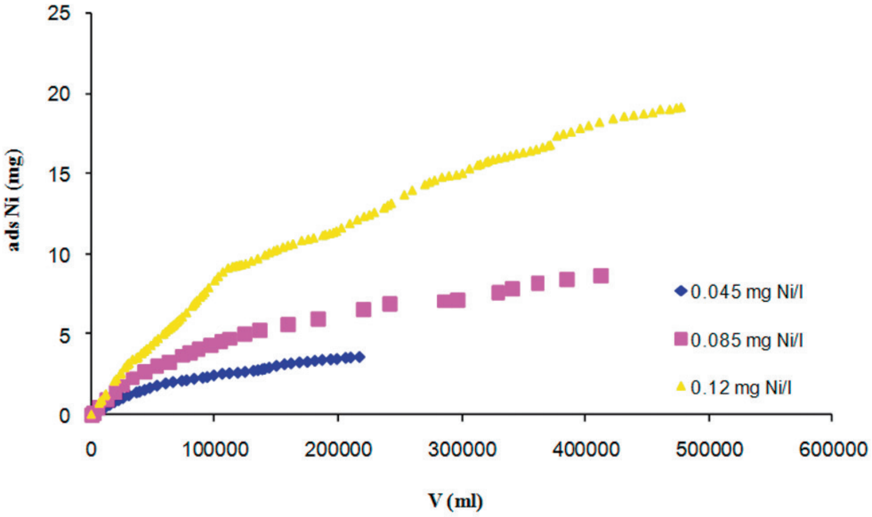

Figure 2. Dependence of amount of adsorbed nickel, adsNi(mg) from volume of treated water, V(ml) for different initial nickel concentration, C_o (mg/l) in the aqueous solution for adsorbent mass, M_{ads} = 60g

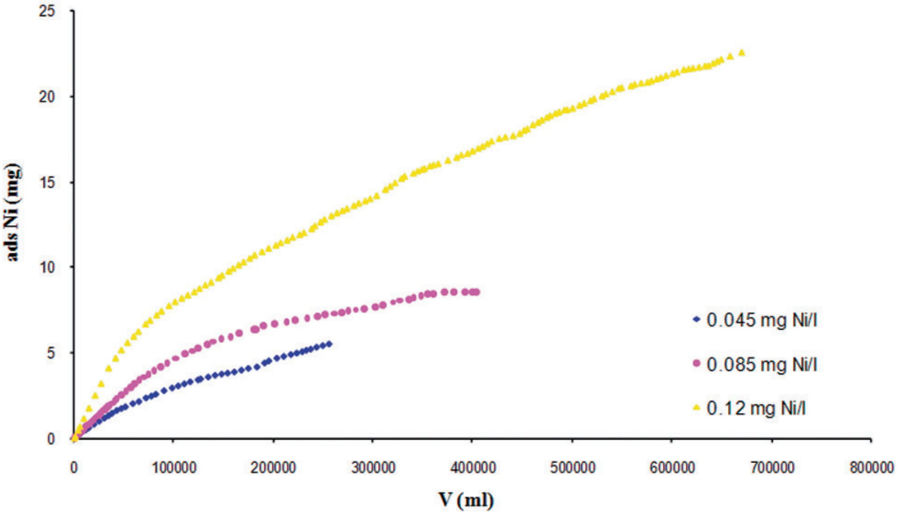

Figure 3. Dependence of amount of adsorbed nickel, adsNi(mg) from volume of treated water, V(ml) for different initial nickel concentration, C_o (mg/l) in the aqueous solution for adsorbent mass, M_{ads} = 115g

The simplest method to determine isotherm constants for two parameter isotherms is to transform the isotherm variables so that the equation is converted to a linear form and then to apply linear regression. The accuracy of the fit of an isotherm model to experimental equilibrium data was typically assessed based on the magnitude of the coefficient of determination for the linear regression i.e., the isotherm giving a correlation coefficient, R^2 value closest to unity was deemed to provide the best fit (Ho et al., 2002).

However, we will concurrently have to consider that equilibrium nickel concentrations in aqueous solutions for the largest number of experimental measurements are very low. Hence, even the smallest mistakes for the third decimal figure may lead to some deviations when experimental data is evaluated, especially when determining the sum linearization for all experimental results for various nickel contents and different adsorbent content in the aqueous solution. An attempt was made to linearize the experimental data in various functions like step, semi-logarithmic, logarithmic, reciprocal, exponential, square polynomial, etc. Experimental results were used to obtain equation which will appropriate explained adsorption process. When mathematical description was obtained for each particular variable (initial nickel concentration, C_o, or adsorbent mass, M_{ads} in the aqueous solution), then is called individual. When mathematical description was obtained for all variables together (initial nickel concentration, C_o, and adsorbent mass, M_{ads} in the aqueous solution), then is called summary (Dimitrovski et al., 2011).

Analysis of the experimental data showed that the most successful linearization for each particular variable was logarithmic and reciprocal function and these obtained coefficients are given in Table 4.

Table 4. Logarithmic and reciprocal function coefficients

		Logarithmic f.			Reciprocal f.		
	M (g)	a	b	R^2	a	b	R^2
C_0 = 0.045 mg Ni/l	30	0.8167	-9.5824	0.9808	61792	1.2024	0.9906
	62	0.7607	-7.8648	0.9697	22066	0.1423	0.9998
	115	0.7927	-8.0867	0.9900	21957	0.1088	0.9999
C_0 = 0.085 mg Ni/l	30	0.6714	-7.9263	0.9804	26379	2.5182	0.9939
	65	0.6485	-6.1393	0.9669	12331	0.0838	0.9998
	100	0.8083	-7.9757	0.9719	26797	-0.3677	0.9696
C_0 = 0.120 mg Ni/l	30	0.4854	-6.4046	0.9574	20522	4.5583	0.9973
	50	0.7247	-6.3815	0.9847	8987.2	0.0362	0.9982
	115	0.6943	-6.1002	0.9728	8283.4	0.0371	0.9999

The resulting arithmetic expressions for summary variables are presented by Equations 1-12, while one example of graphic expression for obtained experimental and calculated values is given in Figure 4.

4.1. Summary arithmetical expressions (mathematical models) for amount of adsorbed nickel, adsNi(mg) dependencies from volume of treated water, V(ml) for different initial nickel concentration, C_o (mg/l) in the aqueous solution

Logarithmic function

$$\ln Ni_V = (-0.0002\ M_{ads} + 0.8034) \ln V + (0.0154\ M_{ads} – 9.5742) \qquad C_o=0.045\ mg/l \qquad (1)$$

$$\ln Ni_V = (0.002\ M_{ads} + 0.5823) \ln V + (-0.0007\ M_{ads} - 7.3012) \qquad C_o=0.085\ mg/l \qquad (2)$$

$$\ln Ni_V = (0.0017\ M_{ads} + 0.522)\ \ln V + (0.0038\ M_{ads} - 6.5402) \qquad C_o=0.12\ mg/l \qquad (3)$$

Reciprocal function

$$Ni_V = V/[(-\ 0.0116\ M_{ads} + 1.2873)\ V + (-421.68\ M_{ads} + 64368)] \qquad C_o = 0.045\ mg/l \qquad (4)$$

$$Ni_V = V/[(-\ 0.0412\ M_{ads} + 3.4245)\ V + (5.9714\ M_{ads} + 21448)] \qquad C_o = 0.085\ mg/l \qquad (5)$$

$$Ni_V = V/[(-\ 0.0401\ M_{ads} + 4.1476)\ V + (-111.12\ M_{ads} + 19820)] \qquad C_o = 0.12\ mg/l \qquad (6)$$

4.2. Summary arithmetical expressions (mathematical models) for amount of adsorbed nickel dependencies from volume of treated water for different adsorbent mass, M_{ads} in the aqueous solution

Logarithmic function

$$\ln Ni_V = (-\ 4.3988\ C_o + 1.0244)\ \ln V + (42.348\ Co - 11.5) \qquad M_{ads} = 30\ g \qquad (7)$$

$$\ln Ni_V = (-\ 0.535\ C_o + 0.7559)\ \ln V + (20.33\ Co - 8.4894) \qquad M_{ads} = 60\ g \qquad (8)$$

$$\ln Ni_V = (-\ 1.2717\ C_o + 0.8711)\ \ln V + (25.925\ Co - 9.548) \qquad M_{ads} = 115\ g \qquad (9)$$

Reciprocal function

$$Ni_V = V/[(44.465\ C_o - 0.9458)\ V + (-558197\ C_o + 82747)] \qquad M_{ads} = 30\ g \qquad (10)$$

$$Ni_V = V/[(-\ 1.4158\ C_o + 0.2054)\ V + (-\ 176017\ C_o + 29129)] \qquad M_{ads} = 60\ g \qquad (11)$$

$$Ni_V = V/[(-\ 1.2153\ C_o + 0.0273)\ V + (-175136\ C_o + 33607)] \qquad M_{ads} = 115\ g \qquad (12)$$

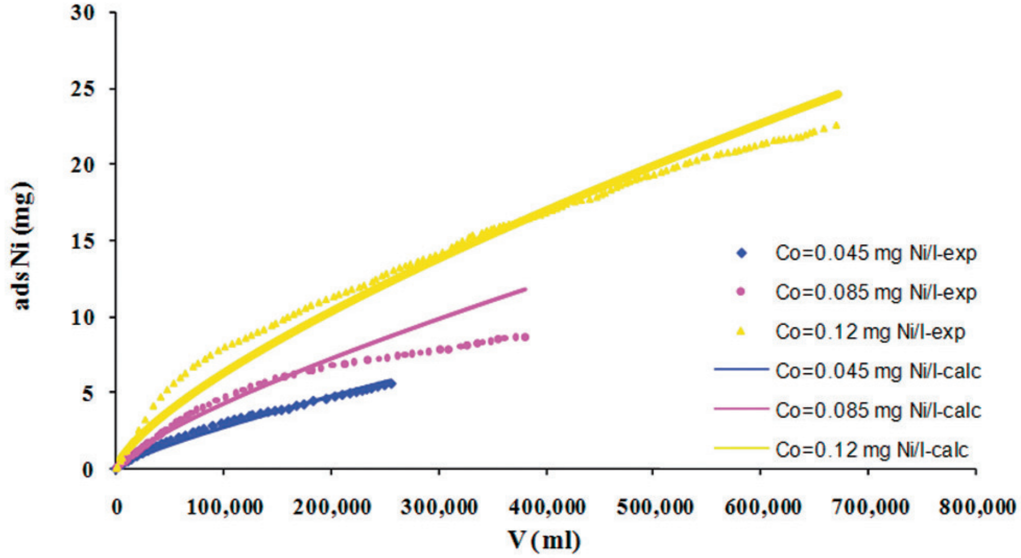

Figure 4. Logarithmic dependence of amount of adsorbed nickel from volume of treated water for different initial nickel concentration in the aqueous solution for M_{ads}=115g

4.3. Adsorbent capacity at saturation was calculated as the amount of adsorbed nickel (II) ions on unit quantity of adsorbent (alumina) for different initial concentration and different adsorbent mass.

Table 5. Retention time and adsorbent capacity

C_o (mg Ni/l)	M_{ads} (g)	$\square_{ret}$ (min)	q_{ads} (mg Ni/g ads)
0.045	30	0.75	17.483
	62	5.74	58.887
	115	3.57	48.248
0.085	30	0.72	10.600
	65	9.38	160.815
	100	2.95	86.340
0.12	30	0.72	6.017
	50	8.94	383.424
	115	12.06	196.530

Conclusions

This paper demonstrated the results of a detailed study of the adsorption process that removed Ni (II) ions from aqueous solution using alumina. The experimental data indicates that the lower initial metal ion concentration is, and the adsorbent dose is higher, more Nickel is adsorbed on alumina. The experimental data was evaluated by step, semi-logarithmic, logarithmic, reciprocal, exponential, square polynomial etc. functions and equilibrium adsorption fitted well in logarithmic and reciprocal functions. The kinetics of sorption seems to be controlled by diffusion of nickel ions into the micropores. Analysis of the experimental data showed that the maximum nickel ions adsorption uptake onto the alumina was 400 mg/g. The results of the study indicated that alumina has great potential to remove Ni(II) ions from aqueous solution and that such adsorbent can very well be recommended for water and wastewater treatment and for the control of the level of Ni pollution.

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