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NI REMOVAL USING SYNTHETIC ZEOLITE

Marjana Simonič,

University of Maribor, Faculty of Chemistry and Chemical Engineering,

Smetanova 17, 2000 Maribor, Slovenia

Abstract

The aim of present work was to remove nickel from drinking water. Synthetic zeolite was chosen to reduce concentration of nickel below 0,02 mg/l, which is determined as maximum allowed value by law in drinking water. Model sample solutions were prepared. Regarding to the results of these measurements nickel removal efficiency in real drinking water samples was tested. The results showed that nickel could be removed by using NaCl modified synthetic zeolite below maximum allowed value of 0,02 mg/L. The presence of other metals has a minor impact on nickel removal.

Key words: *zeolite, drinking water, adsorption*

INTRODUCTION

Nickel is naturally occurring element. It could also be emitted into the environment through production of Ni-Cd batteries, porcelain enameling, electroplating, etc. In high concentration it poses a threat to human body. Many different methods have been developed for nickel removal from water. Adsorption is one of the cost effective methods. Particles with smaller parameter are characterized by larger surface area, and thus adsorption is enhanced (Malamis and Katsou, 2013). Studies of adsorption of nickel from the solution on mortmorillonite were extensive. The concentration range of nickel solutions were between 10 and 300 mg/L. The highest adsorption was obtained at highest concentrations, but the removal efficiency was decreasing by increasing initial concentration of nickel (Çoruh and Ergun, 2009). The highest adsorption capacity of 25 mg/g was determined if vermiculite was adopted (Abolino et al, 2008) and up to 29 mg/g in acid-activated mortmorillonite (Bhattacharyya and Sen Gupta, 2008). In the case of vermiculite Mg ions are mostly easily exchanged by other cations. It was also found that adsorption capacity could reach 50 mg/g of natural bentonite (Alandis et al, 2010), however bentonite is aluminium phyllosilicate and consists mostly of mortmorillonite. The presence of other cations has great impact on the adsorption process. The adsorption capacity determined for a metal in a single cation system could decrease considerable in mixed metal solution. The adsorption capacity depends very much on selectivity of adsorbent towards particulate cation (Malamis and Katsou, 2013). Affinity order in synthetic zeolite in mixed metal solution is presented in Table 1. If clinoptilolite is used for nickel removal, the concentration of lead could significantly reduce the adsorption capacity of Ni (Ijagbemi et al, 2010).

Table 1: Selectivity of metals

	SELECTIVITY	LITERATURE
ZEOLITE 4A	$Cu^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$	Majdan et al, 2003
	$Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} \approx Ni^{2+}$	Hui et al, 2005

In wastewater stable complexes could form which are not adsorbed on the mineral surface. The metal adsorption decrease due to capture of the metal into such complex and metal do not reach adsorption cites (Malamis and Katsou, 2013). The high content of salts could also decrease the adsorption capacities of the metal ions. The activity of the adsorbent's functional groups is strongly affected by solution pH (Çoruh and Ergun, 2009).

Nickel was effectively removed from the wastewater using synthetic zeolite (Álvarez-Ayuso et al, 2003). Almost 10 times higher sorption capacities on synthetic zeolite in comparison with natural ones were reported (Álvarez-

Ayuso et al, 2003). Therefore, in our study synthetic zeolite ZP- 4A was chosen for nickel removal from groundwater. The uptake of nickel was studied for its adsorption capacity and disturbance of other metals on adsorption on synthetic zeolite was studied. The main objective of this study was to define the effectiveness of nickel removal by using zeolite ZP- 4A. Some characteristics of the drinking water were determined. The adsorption capacity was calculated.

MATERIALS AND METHODS

Samples

Firstly, model water sample was taken for analysis. Model solutions were prepared by dissolving 1 g/L of Ni^{2+} in deionized water. Adequate working solutions were prepared by diluting this standard Ni-solution. Furthermore, experiments using drinking water were conducting. Certain amount of solution was spiked with the drinking water.

Analytical methods

The parameters were determined according to the standard methods as seen from Table 2. Conductivity meter WTW was used, pH meter MA 5470, turbidimeter Hanna 2100 and Elan 6000 was adopted for metal concentration determination.

Table 2. Standard methods

Parameter	Unit	Standard method
pH	-	DIN 38 404 – C5 (1984)
Conductivity	µS/cm	EN (DIN) 27 888 (1993)
Turbidity	NTU	DIN 38 404 (1985)
Ni^{2+}	µg/L	ISO 17294 ICP-MS
Co^{2+}	µg/L	ISO 17294 ICP-MS
Zn^{2+}	µg/L	ISO 17294 ICP-MS
Pb^{2+}	µg/L	ISO 17294 ICP-MS

Freudlich equation

Empirical Freundlich equation is determined as follows:

$$\frac{x}{m} = k \cdot Ce^{\frac{1}{n}} \quad (1)$$

x = mass of adsorbed substance [mg],

m = mass of zeolite [g],

Ce = equilibrium concentration of adsorbate in solution [mg/l],

n, k = adsorption constants [-],

The equation 2 is more appropriate:

$$log\frac{x}{m} = log\, k + \frac{1}{n} \cdot log\, Ce \quad (2)$$

MATERIALS

Zeolit ZP - 4A is a powdered material, made in Slovenia (Silkem, Kidričevo).

Powdered zeolite in shown in Figure 1. It is a white powder. Chemical structure is $Na_{12}[Al_{12}Si_{12}O_{48}] \cdot 27H_2O$ with density 1,99 kg/dm^3. Figure 2 presents SEM image of zeolite ZP-4A. It is seen that particles diameter corresponds to 3-5 µm and pores are according to Lynd structure tipe A, small. In the center of basic cell is a hole of 1,14 nm in diameter (α cave).

Table 3 shows some characteristics of zeolite ZP-4A. The highest share represent SiO_2 and Al_2O_3. Prior to analyses the powder was degassed under vacuum at 150 ºC for 2 h.



Figure 1: Powdered zeolite ZP-4A.

Table 3: Characteristic of zeolite ZP- 4A.

Component	ZEOLITE ZP-4A
SiO_2	34,12
Al_2O_3	28,30
Na_2O	17,01
Fe_2O_3	/
TiO_2	/
CaO	/
H_2O	20,67
Specific surface area (m^2/g)	655
Pore diameter (Å)	4

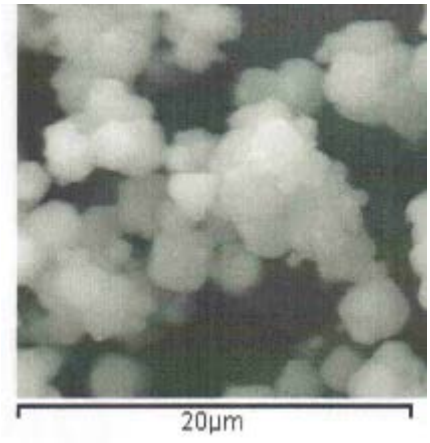


Figure 2: SEM image of powdered zeolite ZP-4A (Krečič, 2010).

RESULTS

Into the solution with 0,8 mg/L of Ni^{2+} 0,5 g of zeolite ZP-4A was added. The contact time varied from 15 minutes up to 24 hours. The results are presented in Table 4.

Table 4: Determination of contact time

t (min)	γ_{Ni} (mg/L)	η (%)
15	0,40	50,0
30	0,30	62,5
60	0,20	75,0
120	0,15	81,3
180	0,15	81,3
240	0,15	81,3
1440	0,10	87,5

Contact time was expected to be the best around 120 minutes which is comparable with the results found in literature (Purna et al, 2006).

We prepared working solutions with 10 mg/L of Ni^{2+}. Into 100 mL of working solution with the same content of Ni^{2+} different amounts of zeolite were added. These varied from 0.05g, 0.1, 1.0 up to 5.0 g of zeolite. The concentration of Ni^{2+} was measured after the equilibrium was reached. The results are presented in Table 5. It can be seen that the removal of Ni^{2+} is up to 94 %, but it can't be removed below 0.02 mg/L Ni^{2+} at initial concentration of 1mg/L Ni^{2+}.

Table 5. Determination of Ni removal with zeolite

m_{4A} (g)	η (%)
0,05	43,8
0,1	81,3
1,0	87,5
2,0	88,8
5,0	93,8

As seen from Table 5 the removal efficiency of nickel is increasing by increasing the dose of zeolite ZP-4A. The highest improvement was achieved by increasing the dose of zeolite from 0,05 to 0,1 g/L while the efficiency improved almost twice from 43 % up to 81 %.

The next experiment was direct towards generation of isotherm. For this purpose zeolite was modified by NaCl. Different amounts of zeolite were added into the solution of nickel with 2 mg/L Ni^{2+} in order to determine the Freundlich isotherm coefficients. We measured the concentration of nickel after adsorption on 0,1 up to 5 g of zeolite to plot Freundlich isotherm (Figure 3).

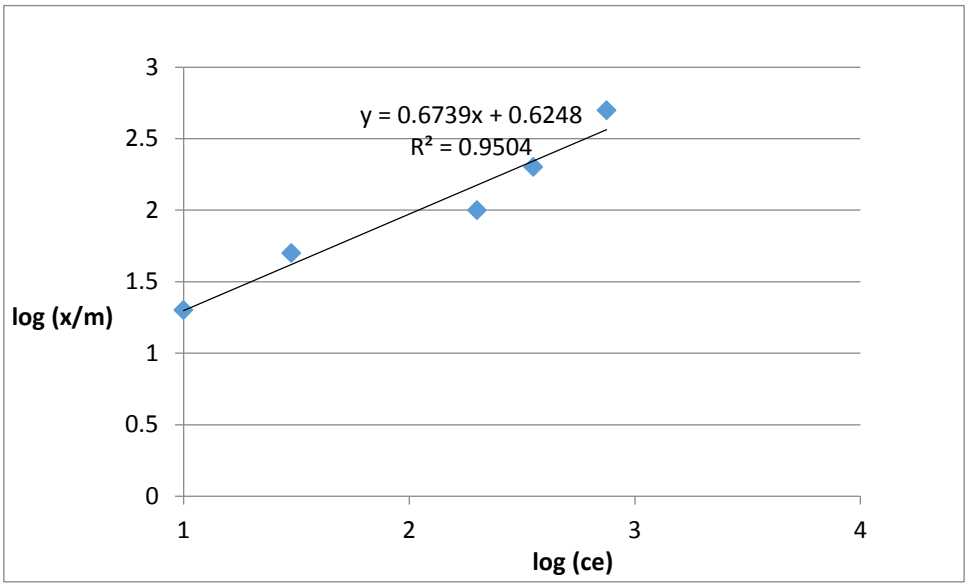


Figure 3: Freundlich adsorption isotherm

Thus, equation 2 could be re-written as:

$$log\frac{x}{m} = 0{,}6248 + 0{,}6739 \cdot log\, Ce \qquad (3)$$

According to the literature (Çoruh and Ergun, 2009) it was assumed that pH value might affect the nickel adsorption. The concentrations of nickel were measured at different pH values of solution. Results are presented in Figure 4. The highest adsorption capacity calculated at 92,5 % occurred at pH = 5. It is in accordance with other authors' results with zeolite which were modified with Na-salt (Álvarez-Ayuso et al, 2003).

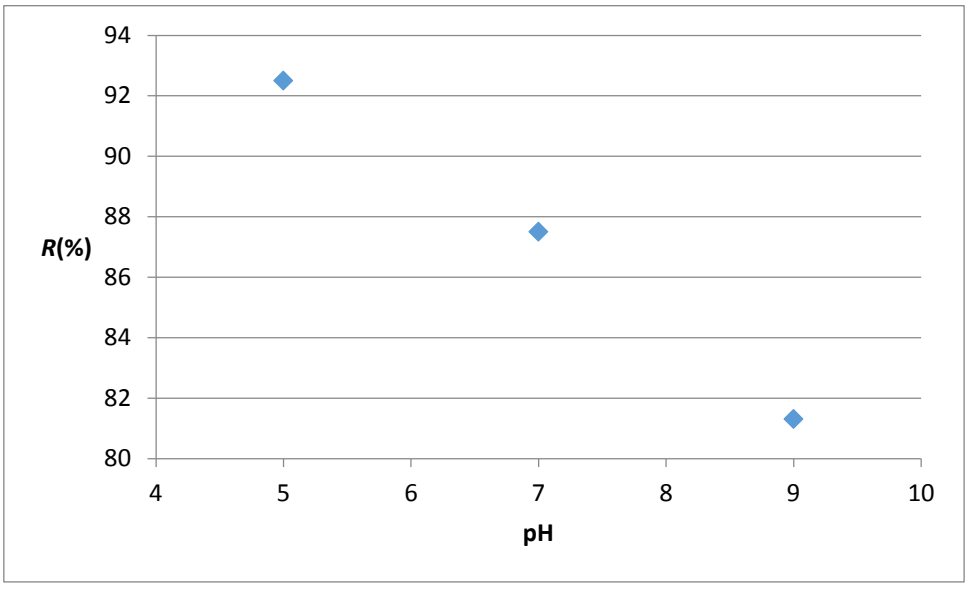


Figure 4: Initial pH value determination

The effect of other metals on nickel adsorption was studied. Into the solution of Ni^{2+}, 1 mg of Cu-, Zn-, Co- and Pb-ions were added into 100 ml nickel solution.

Table 6: Effect of other metals

Metals	m_{4A} (g)	γ_{Ni} (mg/L)	η (%)
Cu^{2+}	0,8	0,08	90,0
Zn^{2+}	0,8	0,08	90,0
Co^{2+}	0,8	0,08	90,0
Pb^{2+}	0,8	0,05	93,8

From Table 6 it is seen that other metals affect nickel adsorption only to a small extent, while the removal efficiency of nickel remained above 90 % irrespective of which metal was tested in mixed solution.

CONCLUSION

Synthetic zeolite ZP-4A could be applied for Ni removal from drinking water. The capacity of zeolite was determined to be 6,7 mg Ni^{2+} per g of Na-modified zeolite at initial concentrations of around 2 mg/L. The presence of other metals does not affect nickel removal. However, Ni^{2+} could be removed below boundary limit of 0,02 mg/L at maximum initial concentration of 0,3 mg/L Ni^{2+}.

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