

Adsorption of Ni (II) ions from aqueous solution on anode dust: Effect of pH value

Adsorbicija Ni(II) ionov iz vodne raztopine anodnega prahu: učinek pH vrednosti

ANITA ŠTRKALJ^{1,*}, ANKICA RAĐENović¹, JADRANKA MALINA¹

¹University of Zagreb, Faculty of Metallurgy, Aleja narodnih heroja 3, 44 000 Sisak, Croatia

*Corresponding author. E-mail: strkalj@simet.hr

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Abstract: In this study, the anode dust, a solid residue of aluminium production, was examined as a non-conventional and low-cost sorbent for the removal of Ni (II) from aqueous solution. The adsorption capacity was found to be pH dependent and decreased along with an increase pH. The maximum adsorption was obtained at pH 4.5. The results were analyzed by the Langmuir and Freundlich isotherm at the best pH value.

Izveček: V članku je opisan poskus z anodnim prahom, ki je trdna usedlina pri pridobivanju aluminija, za neobičajno in cenovno odstranjevanje Ni(II) iz vodne raztopine. Dokazano je bilo, da je adsorpcijska kapaciteta odvisna od pH in se zmanjšuje z naraščajočo vrednostjo pH. Največja adsorbicija je bila pri pH 0.5. Rezultati so bili analizirani z Langmuirovo in Freundlichovo izotermo pri najboljši vrednosti pH.

Key words: anode dust, adsorption, Ni (II) ions, aqueous solution, pH value

Ključne besede: anodni prah, adsorbicija, Ni (II) ioni, vodna raztopina, vrednost pH

INTRODUCTION

The removal of toxic heavy metals such as cadmium, copper, lead, nickel, mercury, and zinc from aqueous environment has received considerable attention in recent

years due to their toxicity and carcinogenicity which may cause damage to various systems of the human body.^[1]

Nickel is metal frequently encountered in raw wastewater streams from industries

such as mining, electroplating, metallurgy, electroplating, pigment and ceramics industries.^[2] This metal is non-biodegradable toxic heavy metal and may cause dermatitis, allergic sensitization and cancer.^[3,4]

It is essential to remove Ni (II) ions from industrial wastewater before being discharged. For this reason, generally are used the advanced treatment processes such as chemical reduction, ion exchange, reverse osmosis, electro dialysis, and adsorption. Since the cost of these processes is rather expensive, the use of agricultural residues or industrial by-product was received with considerable attention^[5] In recent years, a number of industrial by-product as waste mould sand,^[6] blast furnace sludge,^[7] steel slag,^[8] red mud^[9] were used for the removal of toxic metals from aqueous solutions.

For reduction of alumina in aluminium production by the electrolytic process, carbon anodes are used. The remaining parts of the anodes after use for aluminium production are called anode butts. The cleaned anode butts are crushed and reused for the production of new anodes (about 20 % of the anode is recycled). Anode dust originates from the baking process and during the transport of anodes. Owing to its granulometry and chemical composition, the anode dust is considered as a waste material.^[10,11] In this study, the anode dust, a solid residue of aluminium production, was investigated as a non-conventional and low-cost adsorbent for the removal of Ni (II) ions from aqueous solution. The influence of pH value on adsorption capacity of anode dust is examined.

MATERIALS AND METHODS

Preparation and characterization of anode dust

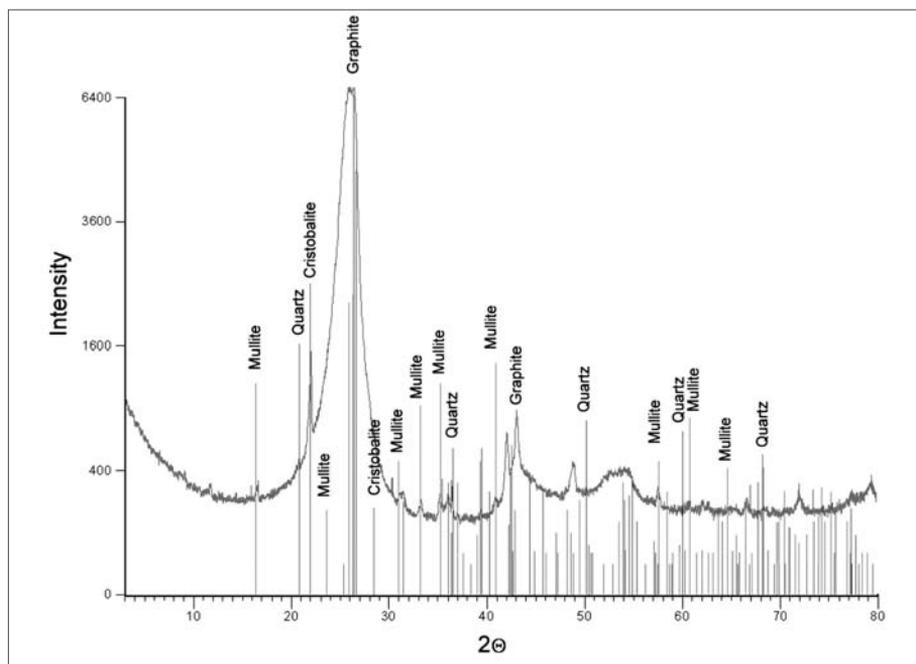
Anode dust, which is a solid residue of aluminium production, was used as the adsorbent. For analysis, a representative sample of anode dust was obtained using a quartering technique. The sample was dried at 105 °C for 4 h and sieved to particle size 0.125–0.2 mm. The chemical composition of the sample was determined by atomic absorption spectroscopy (the AAS method). The mineralogical composition of the anode dust sample was determined by the X-ray diffraction method (XRD method). The chemical composition of the examined anode dust is presented in Table 1. It was found that the anode dust was dominated by C ($w(\text{C}) = 94.49\%$), followed by Si ($w(\text{Si}) = 1.73\%$), Al ($w(\text{Al}) = 1.69\%$), S ($w(\text{S}) = 1.50\%$), and Fe ($w(\text{Fe}) = 0.34\%$). The mineralogical composition (XRD analysis) of anode dust is shown in Figure 1.

Batch experiment

A stock solution of Ni (II) ions was prepared by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1000 mL deionized water. This solution was diluted as required to obtain the standard solutions. The initial concentrations of the solutions contained 50–500 mg L^{-1} of Ni (II) ions. The batch experiments were carried out in 100 mL conical flasks by agitating 0.375 mg anode dust with 25 mL of the aqueous Ni (II) ions solution for a period of 30 min (equilibrium time) at 20 °C on a mechanical shaker. The adsorption of nickel ions by anode dust was studied in a pH range of

Table 1. Chemical composition of anode dust sample in mass fractions (w/%)

Components	C	Si	Al	S	Fe	Na	V	Ca	Ni
w/%	94.49	1.73	1.69	1.50	0.34	0.089	0.072	0.044	0.043

**Figure 1.** XRD pattern of the anode dust sample

4.5–7. Solutions of 0.5 M HCl and 0.5 M NaOH were used for pH adjustments.

$$q_e = \frac{c_0 - c_e}{m} \cdot V \quad (1)$$

The concentration of Ni (II) ions before and after the adsorption was determined spectrophotometrically with standard method.^[12]

The amount of Ni (II) ions adsorbed at equilibrium i. e. the adsorption capacity, q_e /(mg/g), was calculated according to the formula:

where,

q_e – adsorption capacity, mg/g
 c_0 – initial concentration of nickel ions, mg/L

c_e –equilibrium concentration of nickel ions, mg/L

V – volume of solution, L

m – adsorbent mass, g

RESULTS AND DISCUSSION

One of the most critical parameter in the adsorption process of metal ions from aqueous solution is the pH of medium.^[1] The capacity of Ni (II) ions removed is shown in Figure 2.

The effect of pH on the adsorption capacity of anode dust may be attributed to the combination of the nature of the surface and amount of Ni (II) ions. Change of pH value causes the ionization of the acid groups (hydroxyl, carboxyl, phenol etc.) present in anode dust surface.^[13] This suggest that electrostatic interaction between divalent Ni (II) ions and anode dust nega-

tives sites could be the most prevalent mechanism of metal-binding. It is evident from Figure 2 that the capacity is higher at lower pH. The best adsorption of Ni (II) ions was obtained at the pH value of 4.5. For higher pH values, Ni (II) ions precipitate in the form of metallic hydroxides and adsorption capacity was decreased.^[14]

Adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherms at pH value of 4.5–7 with linear regression analysis.

The linear equations of Langmuir and Freundlich are represented as follows (Equations (2) and (3), respectively):^[8]

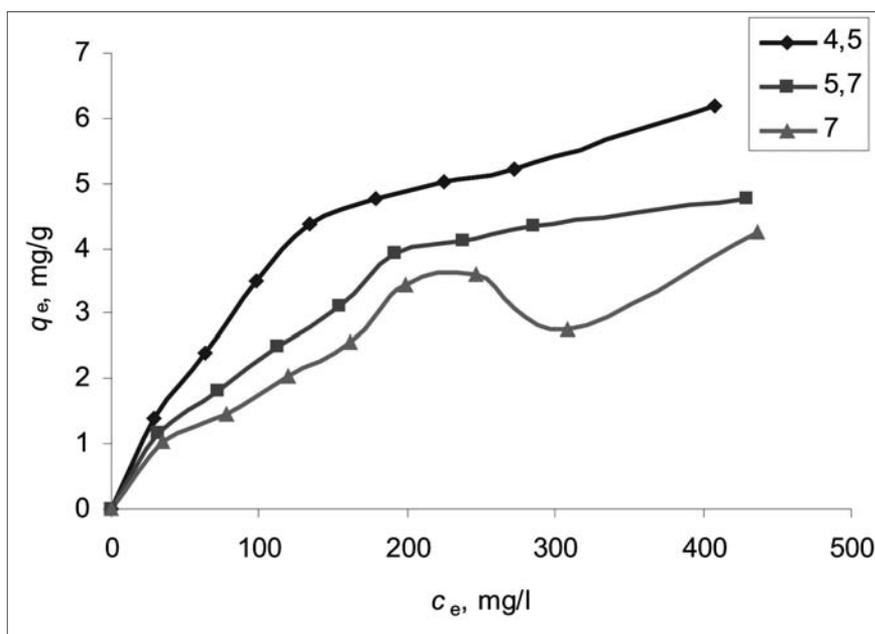


Figure 2. Effect of pH value on the adsorption capacity (q_e) of anode dust with different equilibrium concentration (c_e) of Ni (II) ions

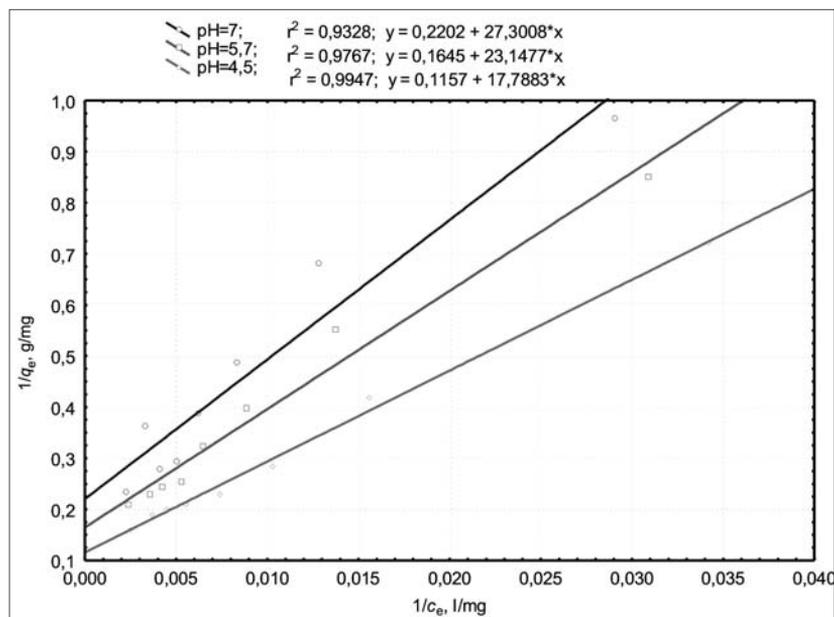


Figure 3. Langmuir isotherms for adsorption of Ni(II) ions on anode dust at pH value of 4.5–7

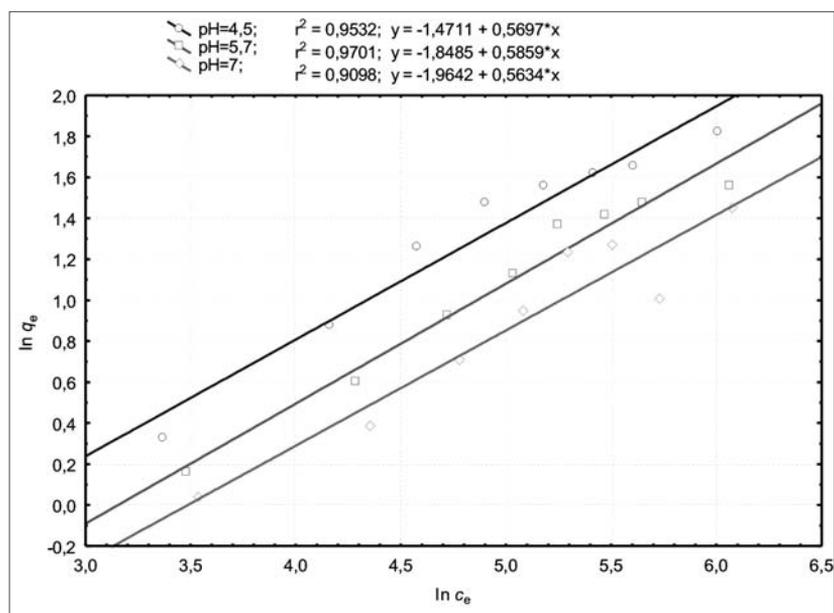


Figure 4. Freundlich isotherms for adsorption of Ni(II) ions on anode dust at pH value of 4.5–7

Table 2. Values of Langmuir/Freundlich constants and correlation coefficients

pH	Langmuir isotherm			Freundlich isotherm		
	$q_m/$ (mg/g)	$K_L/$ (L/mg)	R^2	n	K_F	R^2
7	4.54	$8.06 \cdot 10^{-3}$	0.9328	1.775	0.140	0.9098
5.7	6.08	$7.11 \cdot 10^{-3}$	0.9767	1.707	0.157	0.9701
4.5	8.64	$6.50 \cdot 10^{-3}$	0.9947	1.755	0.230	0.9532

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot c_e} + \frac{1}{q_m} \quad (2)$$

where,

q_e - adsorption capacity, mg/g

c_e - equilibrium concentration of nickel ions, mg/L

q_m - saturation adsorption capacity of the anode dust, mg/g

K_L - Langmuir constant

$$\ln q_e = K_F + \frac{1}{n} \ln c_e \quad (3)$$

where,

q_e - adsorption capacity, mg/g

c_e - equilibrium concentrations of nickel ions, mg/L

K_F and n - the Freundlich constants

The Langmuir adsorption isotherms for Ni (II) ions adsorption on anode dust are shown in Figure 3. The Freundlich adsorption isotherms for Ni (II) ions adsorption on anode dust are shown in Figure 4. The values of Langmuir and Freundlich constants and correlation coefficients were determined, and are shown in Table 2.

In general, the Langmuir model fitted the results slightly better than the Freundlich model with all R^2 values. This suggests that the adsorption of Ni (II) ions by anode dust is monolayer type.^[15] The values of maximal adsorption capacity q_m , obtained by Langmuir isotherm show that the adsorption capacity depends on pH and decreases along with an increase pH value of aqueous solution. Maximal capacity of adsorption is achieved at the pH value of 4.5.

CONCLUSIONS

- The adsorption capacity of anode dust for the removal of Ni (II) ions was found to be pH dependent and decreased along with an increase of solution pH.
- The best adsorption of Ni (II) ions was obtained at the pH value of 4.5.
- Equilibrium data can be fitted by Langmuir and Freundlich adsorption isotherms, and the Langmuir

model fitted the results slightly better than the Freundlich model.

- The obtained adsorption capacity value is promising in the use of anode dust as an efficient low-cost and nonconventional adsorbent for the removal of Ni (II) ions from solutions.

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REFERENCES

- [1] LIN, S. H., LAI, S. L., LEU, H. G. Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process. *Journal of Hazardous Materials*, B76 (2000), 139–153.
- [2] PARAB, H., JOSHI, S., SHENOY, N., LALI, A., SARMA, U. S., SUDERSANAN, M., Determination of kinetics and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. *Process Biochemistry*, 41 (2006), 609–615.
- [3] ABU AL-RUB, F. A., KANDAH, M., AL-DABAYBEH N., Nickel removal from aqueous solutions using sheep manure wastes. *Engineering in Life Sciences*, 2 (2002), 111–116.
- [4] ABU AL-RUB, F.A., KANDAH, M., AL-DABAYBEH, N. (2003): Competitive adsorption of nickel and cadmium on sheep manure wastes; experimental and prediction studies. *Separation and Science Technology*, 38 (2003), 483–497.
- [5] HASAR, H., Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk. *Journal of Hazardous Materials*, B97 (2003), 49–57.
- [6] ŠTRKALJ, A., MALINA, J., RAĐENović, A.: Waste mould sand-potential low-cost sorbent for nickel and chromium ions from aqueous solution. *RMZ-Materials and geoenvironment*, 56 (2009), 118–125.
- [7] RAĐENović, A., MALINA, J., ŠTRKALJ, A.: Distribucijski koeficijent uklanjanja Ni²⁺ iona iz vodenih otopina pomoću visokopećnog mulja. Proc. of 13 Int. Conf. MATRIB 08/Grilec, K. (ed.), Vela Luka, (2007), 180–184.
- [8] ĆURKOVIĆ, L., CERJAN-ŠTEFANOVIĆ, Š., RASTOVČAN - MIOČ, A. (2001): Batch Pb²⁺ and Cu²⁺ removal by electric furnace slag. *Water Research*, 35 (2001), 3436–3440.
- [9] ZUBOULIS, A., KYDROS, K. A.: Use of red mud for toxic metals removal: the case of nickel. *Journal of Chemical Technology and Biotechnology*, 58 (1993), 95–101.

- [10] THONSTAD, J., FELLNER, P., HAARBERG, G. M., HIVEŠ, J., KVANDE, H., STERTEN, A. (2001): *Aluminium Electrolysis*, Aluminium-Verlag, Düsseldorf.
- [11] GRJOTHEIM, K., KVANDE, H. (1993): *Introduction to Aluminium Electrolysis*, Aluminium-Verlag, Düsseldorf.
- [12] FRIES J., GETROS, H. (1977): *Organic Reagents for Trace Analysis*. E. Merck Darmstadt.
- [13] ŠTRKALJ, A. (2009): *Sorpcija Cr (VI) i Ni (II) iona iz vodenih otopina na ugljičnoj anodnoj prašini*, Ph. D. Thesis. Sisak: University of Zagreb, Faculty of Metallurgy, Sisak; 201 p.
- [14] RADOVIĆ, L.J. R. (2001): *Chemistry and Physics of Carbon*, Marcel Dekker, New York.
- [15] PIMENTEL, P. M., MELO, M. A. F., MELO, D. M. A., ASSUNCAO, A. L. C., HENRIQUE, D. M., SILVA JR., C. N., GONZALEZ, G.: Kinetics and thermodynamics of Cu(II) adsorption on oil shale wastes. *Fuel Processing and Technology*, 89 (2008), 62–67.