

Waste mould sand-potential low-cost sorbent for nickel and chromium ions from aqueous solution

Potencialni niskocenovni sorbent za nikeljeve in kromove ione iz vodne raztopine odpadnega formarskega peska

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

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

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

Received: January 20, 2009

Accepted: February 25, 2009

Abstract: In the present work investigated the sorption of the metal ions on waste mould sand, which is solid residue of gray iron foundry industry. Waste mould sand can be used as a new sorption material for removing some toxic metals from aqueous solution. The system variables studied include initial concentration of Ni(II) and Cr(VI) ions and agitation time. Metal ion sorption was strongly dependent on initial concentration and agitation time. The experimental data fitted well to the Freundlich and Langmuire isotherms.

Izveček: V članku je raziskana absorpcija kovinskih ionov v odpadnem formarskem pesku, ki je odpadek v livarnah sive litine. Ta odpadni pesek je lahko uporaben kot absorpcijski material za odstranjevanje nekaterih strupenih kovin iz vodne raztopine. Kot preiskane neznanke iz sistema so vključene tudi začetne koncentracije ionov Ni(II) in Cr(VI) in čas mešanja. Absorpcija kovinskih ionov je bila močno odvisna od začetne koncentracije in časa mešanja. Pridobljeni eksperimentalni rezultati se dobro ujemajo s Freundlichovimi in Langmuirovimi izotermami.

Key words: waste mould sand, sorption, nickel ions, chromium ions

Ključne besede: odpadni formarski pesek, sorbcija, nikeljevi ioni, kromovi ioni

INTRODUCTION

People are currently exposed to the hazards of various kinds of metal pollution in wastewater and drinking water. Pollution has a harmful effect on biological systems. Therefore, the elimination of toxic metals from aqueous solutions is important for protection of public health. Heavy metals (Pb, Hg, Cd, Cr, Ni, As, etc.) are very toxic and do not undergo biodegradation^[1].

Chromium, which is on the top priority list of toxic pollutants, is present in the electro-plating, metallurgy, and chemical engineering wastewater as Cr(VI) in the form of oxides species, such as chromates (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$)^[2]. Due to its high solubility, Cr(VI) is the most hazardous, since it can accumulate in the food chain and cause several ailments^[3, 4].

Nickel is also a common toxic pollutant. Acute nickel poisoning by inhalation exposure or ingestion of nickel carbonyl or soluble nickel compounds can lead to headache, vertigo, nausea, vomiting, nephrotoxic effects, and pneumonia followed by pulmonary fibrosis^[5].

Nickel ions are frequently encountered together in industrial wastewaters (e.g. from mine drainage, plating plants, paint and ink formulation units, porcelain and metal enamellings)^[6].

The stricter environmental regulations related to the discharge of heavy metals make it necessary to develop efficient processes for Ni(II) and Cr(VI) ions removal from wastewater. Removal of hazardous metal ions especially in low concentrations from industrial effluent is of great interest due to the large quantity of material processed^[7]. The main techniques that have been used for remove heavy metals from water include chemical precipitation, membrane filtration, ion exchange, and sorption on activated carbon^[8-13]. However, these methods have limitations such as high operational cost in the case of sorption by activated carbon. Intensive studies have therefore been carried out to develop more effective and inexpensive metal sorbents^[14]. Natural materials which are available from industrial waste products or agricultural operations can be used as potential inexpensive sorbents^[15].

In foundry industry, millions tones of spent materials are disposed in the world^[16]. Over 70 % of the amount of the dumped waste materials consists of sands. For many years, the spent sands generated by foundry industry were successfully used as landfill materials. But disposal by landfill of spent sands is becoming an increasing problem as legislation is getting tighter. Also the disposal costs by current practices increases rapidly^[17]. This waste mould sand is composed of fine silica sand,

clay binder, organic carbon, and residual iron particles. Because of their potential sorptive properties, waste mould sand can be used as a low cost sorbent^[18].

In this work, waste mould sand was studied as non-conventional and low-cost sorbent for nickel and chromium ions from aqueous solution.

MATERIALS AND METHODS

Waste mould sand which is solid residue from gray iron foundry production was used as sorbent.

For analysis, a representative sample of waste mould sand was obtained by a quartering technique. It was dried at 105 °C for 4 h. The chemical composition of the sample was determined by atomic adsorption spectroscopy AA-6800, Shimadzu. Mineralogical composition was determined by XRD method using a Philips PW 1830.

Batch experiments were performed in order to evaluate the rate of Ni(II) and Cr(VI) removal in the presence of waste mould sand under different initial Ni(II) and Cr(VI) concentrations. One gram of waste mould sand was placed in contact with 50 mL solutions of different concentrations of the aqueous Ni(II) and Cr(VI) solution for a period of (0.5; 1; 1.5; 2 and 3) h on mechanical shaker. The concentration of free Ni(II) and Cr(VI) ions after

sorption was determined spectrophotometrically (model Camspec M-107) using standard procedure^[19].

The mass of metal ions solute sorbed per 1 g of sorbent, sorption capacity (q (mg/g)) was calculated using equation (1):

$$q = \frac{\Delta c}{m} \cdot V \quad (1)$$

where is:

Δc – mass concentration of metal ions, mg/L

V - volume of solution, L

m - sorbent mass, g

The Langmuir and Freundlich isotherms are used to interpret sorption equilibrium data^[20]. Their equations are commonly used for describing different sorption systems. The linear equation of Langmuir and Freundlich are represented as follows (equations (2) and (3), respectively):

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

where is:

q_e - the mass of metal ions solute sorbed per 1 g of sorbent, sorption capacity, mg/g

c_e - the equilibrium concentration of metal ions, mg/L

q_m - saturation sorption capacity of the waste mould sand, mg/g

K_L - Langmuir constant

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

where is:

q_e - the mass of metal ions solute sorbed per 1 g of sorbent, sorption capacity, mg/g

c_e - the equilibrium concentrations of metal ions, mg/L

K_F and n - Freundlich constants

The free energy of sorption (ΔG°) can be related to the equilibrium constants K_L (L/mg) corresponding to the reciprocal of the Langmuir constant q_m , by the van't Hoff equation:

$$\Delta G^\circ = -RT \ln K_L \quad (4)$$

The removal efficiency (E , %) was calculated using the following relation:

$$E = \frac{c_0 - c_e}{c_0} \cdot 100 \quad (5)$$

where is:

c_0 - the initial concentrations of metal ions, mg/L

c_e - the equilibrium concentrations of metal ions, mg/L

RESULTS AND DISCUSSION

Characterization of the waste mould sand

Table 1 and Figure 1 present chemical

and mineralogical composition of examined waste mould sand. The waste mould sand is dominated by the mass fraction of SiO_2 (96.1 %).

Table 1. Chemical composition of waste mould sand

Composition	w/%
SiO_2	96.1
Fe	2.57
Al_2O_3	0.85
Ca	0.31
C	0.12
Mg	0.03
Cr	0.009
Mn	0.008

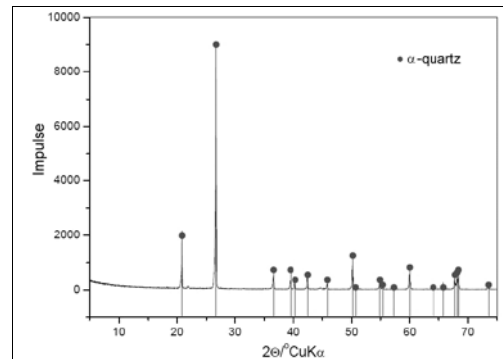


Figure 1. XRD diffractogram analysis of waste mould sand

Effect of contact time

The effect of contact time on the uptake of Ni(II) and Cr(VI) ions was studied in single solutions using differential concentrations ((50, 100, 200, 300 and 500) mg/L). The results obtained can be presented as curves $q = f(t)$. Their char-

acteristic form is shown in Figure 2 for initial concentration of 300 mg/L.

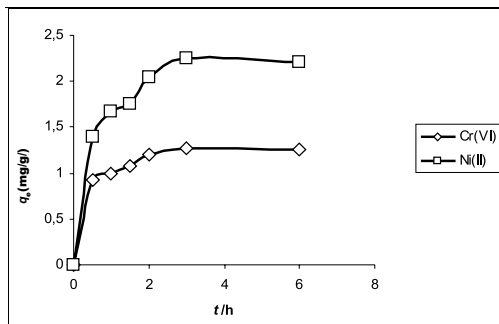


Figure 2. Adsorption capacity, q_e versus contact time for an initial concentration of 300 mg/L

The results show that the removal process was rapid and the equilibrium agitation time for the sorption of Ni(II) and Cr(VI) is 3 h. Such results can be related by theory from which: a) diffusion across the liquid film surrounding the solid particles, b) diffusion within the particle itself assuming a pore diffusion mechanism, and c) physical or chemical sorption at a site^[21].

Effect of initial concentration

The effect of initial concentration of Ni(II) and Cr(VI) is shown in Figure 3. Results from this plot indicate that removal efficiency E decreases from 18.2 % to 9.4 % for Ni(II) and from 9.6 % to 4.6 % for Cr(VI) as the initial concentration is increased from 50–500 mg/L.

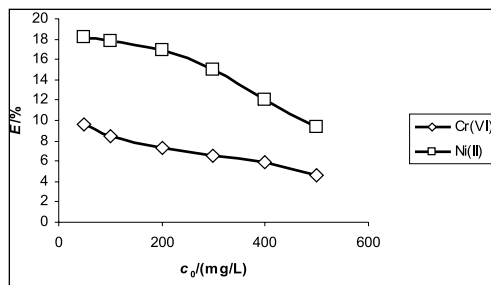


Figure 3. Influence of initial concentration of Ni(II) and Cr(VI) on the fraction of removal metal ions

The percentage of sorption metal ions to the waste mould sand decreased as the initial concentration of metal ions was increased from 50 mg/L to 500 mg/L. This appears to be due to increase in the number of ions competing for the available binding sites in the sorbent.

Sorption isotherms

The sorption isotherms are regular, positive, and concave to the concentration axis. Initial sorption is quite rapid, which is followed by a slow approach to equilibrium at higher metal ion concentrations (Figure 4).

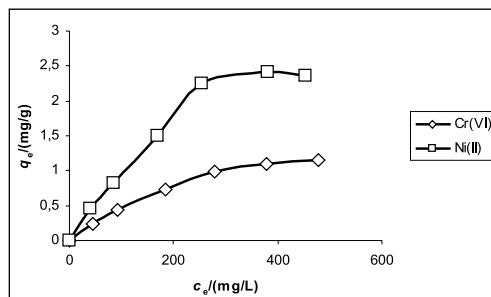


Figure 4. Adsorption capacity, q_e versus equilibrium concentrations of Ni(II) and Cr(VI) ions

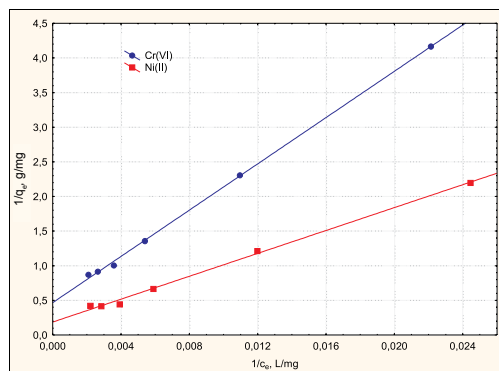


Figure 5. Langmuire isotherms for sorption of Ni(II) and Cr(VI) on 20 °C

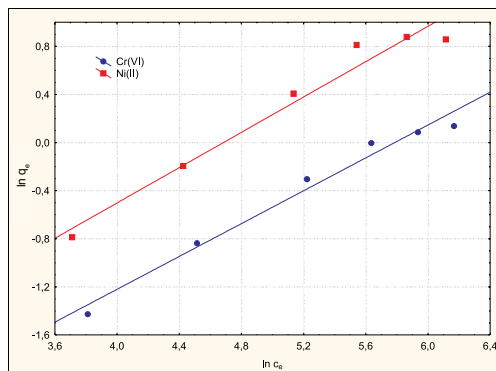


Figure 6. Freundlich isotherms for sorption of Ni(II) and Cr(VI) on 20 °C

Table 2. The values of Langmuir and Freundlich constants and correlation coefficients

	LAI				FAI		
	$K_L/(L/mg)$	$q_m/(mg/g)$	R^2	$-\Delta G/(kJ/mol)$	K_F	$1/n$	R^2
Ni(II)	$2.266 \cdot 10^{-3}$	5.340	0.9982	14.83	$32.055 \cdot 10^{-3}$	1.360	0.9651
Cr(VI)	$2.796 \cdot 10^{-3}$	2.141	0.9996	14.32	$19.197 \cdot 10^{-3}$	1.464	0.9899

Figures 5 and 6 show the Langmuire and Freundlich sorption isotherms for Ni(II) and Cr(VI) sorption on waste mould sand. The values of Langmuir and Freundlich constants and correlation coefficients were determined and are shown in Table 2.

The correlation coefficients (R^2) values (Table 2) indicate that, generally, experimental data were better fitted to the Langmuir equation. Langmuir's isotherm model is valid for monolayer sorption onto the homogenous sorbent surface. Once a sorbate molecule occupies a site, no further sorption can take

place at that site. The Freundlich expression is an empirical based on sorption on a heterogenous surface^[22]. Negative values of ΔG° indicating that the spontaneous nature of sorption.

CONCLUSION

The equilibrium agitation time for the sorption of Ni(II) and Cr(VI) is 3 h. Results indicate that removal efficiency E decreases as the initial concentration is increased from 50–500 mg/L. The sorption data fit in both Freundlich and Langmuir isotherms. Langmuire iso-

therm model shows a better agreement with equilibrium data. Negative values of ΔG° indicating that the spontaneous nature of sorption. Waste mould sand indicate better sorption properties for Ni(II) than for Cr(VI) ions. The obtained sorption capacity value is promising in the waste mould sand use as efficient low-cost sorbent in Ni(II) and Cr(VI) removal from solutions.

Acknowledgement

This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia, under the project 124-1241565-1524.

REFERENCES

- [1] PEHLIVAN, E., ARSLAN, G. (2007): Removal of metal ions using lignite in aqueous solution-Low cost biosorbents. *Fuel Processing Technology*; Vol. 88, pp. 99–106.
- [2] BABEL, S., KURNIAWAN, T. A. (2004): Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents. *Chemosphere*; Vol. 54, pp. 951–996.
- [3] AGGARWAL, D., GOYAL, M., BANSAL, R. C. (1999): Adsorption of chromium by activated carbon from aqueous solution. *Carbon*; Vol. 37, pp. 1989–1997.
- [4] LEE, T., LIM, H., LEE, Y., PARK, J. (2003): Use of waste iron metal for removal of Cr(VI) from water. *Chemosphere*; Vol. 53, pp. 479–485.
- [5] SAJWAN, K. S., ORNES, W. H., YOUNGBLOOD, T. V., ALVA, A. K. (1996): Uptake of soil applied cadmium, nickel and selenium by bush beans. *Water, Air and Soil Pollution*; Vol. 91, pp. 209–217.
- [6] SRIVASTAVA, V. C., MALL, I. D., MISHRA, I. M. (2008): Competitive adsorption of cadmium (II) and nickel (II) metal ions from aqueous solution onto rice husk ash. *Chemical Engineering and Processing: Process Intensification*; Vol. 48, pp. 370–379.
- [7] LIU, S. X., CHEN, X., CHEN, X. Y., LIU, Z. F., WANG, H. L. (2007): Activated carbon with excellent chromium (VI) adsorption performance prepared by acid-base surface modification. *Journal of Hazardous Materials*; Vol. 141, pp. 315–319.
- [8] GABALDON, G., MARZAL, P., FERRER, A. (1996): Single and competitive adsorption of Cd and Zn onto granular activated carbon. *Water Research*; Vol. 30, pp. 3050–3060.
- [9] KADIRVELU, K., FAUR-BRASQUET, C., CLOIREC, P. LE. (2000): Removal of Cu(II), Pb(II) and Ni(II) by adsorption onto activated carbon cloths. *Langmuir*; Vol. 16, pp. 8404–8409.
- [10] MOHAN, D., PITTMAN, C. U. (2006): Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of Hazardous Materials*; Vol. 137B, pp. 762–811.
- [11] MOHAN, D., SINGH, K. P., SINGH, V. K. (2006): Trivalent chromium removal from wastewater using low cost acti-

- vated carbon derived from agricultural waste material and activated carbon fabric cloth. *Journal of Hazardous Materials*; Vol. 135, pp. 280–295.
- [12] MOHAN, D., SINGH, K. P. (2002): Single-multi component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. *Water Research*; Vol. 36, pp. 2304–2318.
- [13] ATKINSON, B. W., BUX, F., KASAN, H. C. (1998): Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents. *Water SA*; Vol. 24, pp. 129–135.
- [14] GUO, X., ZHANG, S., SHAN, X. (2007): Adsorption of metal ions on lignin. *Journal of Hazardous Materials*; Vol. 151, pp. 134–142.
- [15] ÜNLÜ, N., ERSOZ, M. (2007): Removal of heavy metal ions by using dithiocarbamated-sporopollenin. *Separation and Purification Technology*; Vol. 52, pp. 461–469.
- [16] DUNGAN, R. S., DEES, N. H. (2007): The characterization of total and leachable metals in foundry molding sands. *Journal of Environmental Management*; Vol. 90, pp. 1–10.
- [17] JL. S., WAN, L., FAN, Z. (2001): The toxic compounds and leaching characteristics of spent foundry sands. *Water, Air, and Soil Pollution*; Vol. 132, pp. 347–364.
- [18] LEE, T., PARK, J., LEE, J. (2004): Waste green sands as reactive media for the removal of zinc from water. *Chemosphere*; Vol. 56, pp. 571–581.
- [19] FRIES, J., GETROS, H. (1977): Organic Reagents for Trace Analysis. E. Merck Darmstadt.
- [20] MOHAPATRA, D., MISHRA, M. D., MISHRA, S. P., CHAUDHURY, G. R., DAS, R. P. (2004): Use of oxide minerals to abdate fluoride from water. *Journal of Colloid Interface Science*; Vol. 275, pp. 355–359.
- [21] ZELEDON-TORUNO, Z., LAO-LUQUE, C., SOLE-SARDANS, M. (2005): Nickel and copper removal from aqueous solution by an immature coal (leonardite): effect of pH, contact time and water hardness. *Journal of Chemical Technology and Biotechnology*; Vol. 80, pp. 649–656.
- [22] GOPAL, V., ELANGO, K. P. (2007): Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaste of Paris. *Journal of Hazardous Materials*; Vol. 141, pp. 98–105.