

REMOVAL OF Ni(II) FROM AQUEOUS SOLUTION BY LOW-COST ADSORBENTS

ANKICA RAĐENOVIĆ, JADRANKA MALINA, ANITA ŠTRKALJ

Faculty of Metallurgy, University of Zagreb, Croatia

e-mail: radenova@simet.hr

The use of low-cost adsorbents has been investigated as a replacement for costly adsorbents and methods of removing nickel ions from aqueous solution. The purpose of this review article is to provide the scattered available information on various aspects of utilization of low-cost adsorbents derived from agricultural waste, industrial by-products and waste material or natural material. To highlight their technical applicability, selected information on initial nickel concentration, pH level, dose required, adsorption capacity, temperature, thermodynamic data, adsorption isotherm, adsorption kinetics is presented. In general, technical applicability and cost-effectiveness are the key factors in the selection of the most suitable adsorbent to treat aqueous solution contain nickel ions.

Key words: adsorption, low-cost material, Ni(II), aqueous solution.

Uklanjanje Ni(II) iz vodenih otopina jeftinim adsorbensima. Ispitivana je upotreba jeftinih adsorbensa kao zamjene skupim, te metode uklanjanja iona nikla iz vodenih otopina. Svrha ovog preglednog članka je osigurati korisne informacije o različitim aspektima korištenja jeftinih adsorbensa dobivenih iz poljoprivrednog otpada, industrijskih nusproizvoda i otpadnih ili prirodnih materijala. Prikazane su odabrane informacije o početnoj koncentraciji nikla, pH vrijednosti, koncentraciji adsorbensa, kapacitetu adsorpcije, temperaturi, termodinamici, izotermi i kinetici adsorpcije, najznačajnijima za tehničku primjenu adsorbensa. Općenito, tehnička primjena i povoljna cijena su ključni čimbenici pri odabiru većine odgovarajućih adsorbensa za obradu vodenih otopina koje sadrže nikal.

Ključne riječi: adsorpcija, jeftini materijali, Ni(II), vodena otopina.

INTRODUCTION

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. About 97% of water contamination is generated by chemicals, paper, petroleum and primarily metal sectors [1].

There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange, electrolysis, separation by membrane, adsorption, etc.,

but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment [2-11].

Adsorption is one of the more popular methods for the removal of metals ions from the aqueous solutions. Adsorption is a surface phenomenon, in which molecules of adsorbate are attracted and held to the surface of an adsorbent until an equilibrium is reached between adsorbed molecules and those still freely distributed in

the carrying gas or liquid. The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to: 1) chemical bonding; 2) hydrogen bonding; 3) hydrophobic and 4) van der Waals forces [12]. The adsorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of solute remaining in the solution at equilibrium. Langmuir and Freundlich isotherms models are frequently used isotherm models for describing adsorption of metal ions by different materials. Both the Langmuir and Freundlich isotherms can be applicable for the equilibrium data of adsorbents from many materials, suggesting that either monolayer or multilayer adsorption could occur on their surface, depending on the type of adsorbents.

The Langmuir model assumes that sorption takes place on the homogeneous surface of the adsorbent and a saturation monolayer is formed, while the Freundlich expression is an empirical equation based on the adsorption on a heterogeneous surface. However, heavy metal adsorption on heterogeneous adsorbents has been interpreted by the aid of the Langmuir isotherm on various occasions [5].

The primary requirement for an economic adsorption process is an adsorbent with selectivity, high adsorption capacity and low cost. Activated carbons, because of their high surface area, microporous character and the chemical nature of surface, have been a popular adsorbent for the removal of heavy metals from an aqueous solution. The name “activated carbon” is used denoting material with a well-developed and accessible internal pore structure. Activated carbons have internal surface areas in the range 500 to 1500 m² / g, and it is this enormous area that makes them effective adsorbents [13].

Activated carbon can be produced from various carbonaceous raw materials, each of which will impart typical qualities to the finished product. Commercial grades are normally prepared from bituminous and lignite coal, petroleum coke, sawdust, bark and wood products. Due to the different sources of raw materials, the extent of chemical activation, and the physico-chemical characteristics, each type of activated carbon has its specific application [14]. Based on its size and shape, activated carbon is classified into four types: powder (PAC), granular (GAC), fibrous (ACF), and cloth (ACC). Powdered activated carbons are often used in liquid phase applications, usually in a batch technique of adsorption. In contrast, granular activated carbons are used in both, liquid and gas phase applications.

The main difference between PAC and GAC is the smaller particle size of the powders (typically around 44 μm versus 0.6 - 4.0 mm for granules), which allows faster rates of adsorption [15]. Although a significant number of low-cost adsorbents from various materials have been found, commercial activated carbon (CAC) has still been used intensively today. A large number of researchers are still studying the use of activated carbon for removing heavy metals such as nickel [16,17]. Recently the market price of activated carbon for industrial grade is considered to be very expensive (about US\$ 2–22.00/kg), depending on the quality of activated carbon itself [18].

Due to high cost and losses of activated carbon in the application processes, there is growing interest in using low-cost alternative materials including clays, zeolites, coal, fly ash, peat, siderite, agricultural waste, charcoal etc. [19, 20]. Generally, adsorbent can be termed as “low-cost” if it requires little processing, is abundant in nature or is a by-product or waste material from industry.

The amount of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) produced from metal industry, agricultural activity, and waste disposal has increased dramatically. Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing. Nickel can cause serious health and ecological problems when released into the environment [21, 22].

The health effects of nickel include higher chances of the development of lung, nose, larynx, respiratory failure and birth defects. Certain compounds of nickel have been listed as carcinogenic. The U.S. Environmental Protection Agency (EPA) requires nickel not to exceed 0.015 mg/L in drinking water [23]. The majority of nickel compounds that are released into the

environment will adsorb onto sediment or soil particles and as result become immobile. However, in acidic soils, nickel is more mobile and often leaches out into the groundwater [24]. Nickel concentration in industrial wastewaters ranges from 3.40 to 900 mg/L [25]. Environmental regulations related to the discharge of nickel and other heavy metals make it necessary to develop methods for their removal from wastewater.

The aim of this work was to provide fundamental information in the adsorption of Ni(II) ions from aqueous solutions on different low-cost adsorbents. Many parameters including temperature, pH solution, adsorption capacity, thermodynamic data, adsorption isotherm, adsorption kinetics were studied. These parameters could be very useful in the understanding of adsorption removal of nickel ions from aqueous solutions.

SOURCES OF LOW-COST ADSORBENTS

Agricultural waste

Agricultural waste is one of the rich sources for low-cost adsorbents besides industrial by-product or natural material. Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. Agricultural waste material are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, lipids, proteins, simple sugar, starches, water, hydrocarbons. A variety of functional groups present have important role in the binding processes as for example, hydroxyl groups and carboxylic groups resulting in high affinity for metal cations[19].

Studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, apricot stone, cotton seed hulls, waste tea leaves, *Cassia fistula* leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, cotton stalks etc has been tried. These promising agricultural waste materials are used in the removal of metal ions either in their natural form or after some physical or chemical modification [8, 19, 20, 26-34].

Demirbas et al. [8] investigated Ni(II) removal from simulated solution using hazelnut shell activated carbon. Batch mode adsorption studies were carried out by varying initial metal ion concentration, agitation speed, temperature and particle

size. The equilibrium data were analysed using the Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm provided the best correlation for Ni(II) onto the activated carbon. They found that Ni(II) adsorption improved with an increasing temperature as indicated by values of the free energy changes ($\Delta G = -5.582$ kJ/mol to $\Delta G = -7.089$ kJ/mol; at 20°C to 40°C). Adsorption process is exothermic in nature ($\Delta H = -16.71$ kJ/mol). With an initial metal concentration of 15 - 200 mg/L, the optimum Ni(II) removal took place at pH 3.0 with metal adsorption capacity of 10.11 mg/g. The adsorption of Ni(II) was increasing with decreasing particle size; that is, increasing surface area of adsorbent.

Ajmal et al. [35] were employed orange peel for Ni (II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0 and that the adsorption followed the Langmuir isotherm, indicating that Ni(II) uptake might occur on a homogenous surface by monolayer adsorption. A metal adsorption capacity of 158 mg/g was achieved at 50°C. This result was significantly higher than that (6.01 mg/g) of a similar study undertaken by Annadurai et al. [36], suggesting that the adsorption capacity of an adsorbent depends on the initial concentration of adsorbate.

Kadirvelu et al. [37] investigated activated carbon prepared from coirpith to adsorption of Ni(II) from aqueous solution. It was noted that a decreasing in the carbon concentration with constant nickel concentration, or an increase in the nickel concentration with constant carbon concentration, resulted in a higher nickel uptake per unit weight of carbon. The Langmuir and Freundlich models for dynamics of metal ion uptake proposed in this work fit the experimental data reasonably well. The adsorption capacity calculated from Langmuir isotherm was 62.5 mg Ni(II)/g at initial pH of 5.0 at 30°C for

the particle size 250–500 μm . The adsorption of Ni increased with pH from 2 to 7 and remained constant up to pH 10.

Activated carbon was prepared from almond husk by activating without and with H_2SO_4 at different temperatures [38]. The ability of the activated carbon to remove nickel (II) ions from aqueous solutions by adsorption has been investigated under several conditions such as pH, carbonisation temperature of husk, initial concentration of metal ions, contact time, and adsorbent concentration. Optimal conditions were pH 5.0, the carbonisation temperature of 700 °C, 50 min of contact time and adsorbent concentration of 5 g/L. The maximum metal removal of 37.17 mg/g occurred at pH 5.0.

The results indicate that the effective uptake of Ni(II) ions was obtained by activating the carbon, prepared from almond husk at 700 °C, through the addition of H_2SO_4 . The removal of Ni(II) were found to be 97.8% at initial concentration of 25 mg/L and the adsorbent concentration of 5 g/L. In the isotherm studies, the experimental adsorption data fitted reasonably well the Langmuir isotherm for both almond husk, activating without and with H_2SO_4 .

Balci et al. [39] conducted characterization of activated carbon produced from almond shell and hazelnut shell. Pore structure characterization and adsorption capacities of activated carbons prepared from shells of almond and hazelnut indicated that treatment with NH_4Cl increased the total surface area and improved adsorption characteristics. Chemical activation carried out at 350°C gave products with surface area values above 500 m^2/g . On the other hand, the surface area values observed for the products obtained from untreated raw materials were about half of this value. The surface area of products obtained from NH_4Cl -impregnated samples reached values of over 700 m^2/g when the carbonization temperature was increased to 700°C.

Peanut hulls were investigated for Ni(II) removal from synthetic solution. Maximum Ni(II) removal of 53.65 mg/g took place at pH ranging from 4-5 [40]. Adsorption capacity of 8.85 mg Ni/g was achieved by the use of activated carbon prepared from peat [41].

Agricultural wastes such as pecan, walnut, kenaf core, sugarcane bagasse, cotton, coconut coir in natural or modified form were utilized for metal adsorption [19].

Other agricultural wastes as coir fibers, soyabeans, corncobs have also been explored for removal of nickel. Sugarcane bagasse in its natural form showed more than 80% removal efficiency. Experiments on removal of nickel conducted on *Cassia fistula* biomass in its natural form showed 99-100% removal efficiency. Table 1 is a compilation of research work done on the removal of nickel.

Table 1. Literature data of metal removal efficiency by agricultural adsorbents

Tablica 1. Literaturni podaci o učinkovitosti uklanjanja metala jeftinim poljoprivrednim adsorbensima

Agricultural waste	Metal ion	Efficiency of removal, %	Reference
<i>Tea waste</i>	Ni(II)	86	[42]
<i>Hazelnut shell, orange peel, peanut hulls, soyabean hulls treated with NaOH, jack fruits</i>	Ni(II), Cr(III), Cu(II), Zn(II), Cd(II)	High metal adsorption	[28]
<i>Coir fiber chemically modified with H₂O₂</i>	Ni(II), Zn(II), Cu(II)	>70	[43]
<i>Maple saw dust</i>	Ni(II)	75	[44]
<i>Mustard oil cake</i>	Ni(II), Cr(III), Zn(II), Cu(II), Mn(II), Fe(II)	Up to 94	[26]

Industrial by-products and waste material

Several studies have been conducted on the potential of industrial by-products for metal removal. Red mud, a solid byproduct from alumina production was used for Ni(II) removal from simulated wastewater. Red mud had high cation exchange capacity

(CEC) and cation exchange sites [45]. With an initial Ni(II) concentration of 400 mg/L, the maximum Ni(II) uptake of 160 mg/g occurred at pH 9.0, where chemical precipitation of Ni(II) might also occur. Among the adsorbents from industrial by-products, red mud and blast-furnace slag have high metal adsorption capacities (160

mg Ni(II)/g). Their capacities were comparable to that of orange peel (158 mg Ni(II)/g) [35].

Blast-furnace slag is a by-product in the production of pig iron and of the steel production. Dimitrova studied the adsorption of Cu(II), Ni(II) and Zn(II) ions from simulated wastewater using blast-furnace slag [46]. Converter slag can be used like an adsorbent material for wastewater treatment. The adsorption systems studied show the efficiency of nickel adsorption from solution with different initial concentration [47]. The low pH of solution and increase in temperature revealed reduced efficiency in adsorption of this metal. This effect is due to adsorbent dissolution and has to be controlled in industrial applications. Its adsorption capacities for Ni(II) was 55.76 mg/g. The metal sorption was in the form of hydro-oxo complexes and the high sorption capacity was due to the formation of soluble compounds on the internal surface of adsorbent. The Freundlich isotherm was representative for metals adsorption.

Ni(II) and Cu(II) removal from simulated wastewater using fly ash (a waste from thermal power plants) [48]. Fly ash is not effective for metal removal due to its low metal binding capacity (0.99 mg/g).

Adsorbents from industrial by-products such as iron/steel slag have some advantages for metal removal. In addition to having a wide pH range (pH 1.5–9.0) effective for metal removal, such adsorbents can be employed to treat inorganic effluent with metal concentration of less than 20 mg/L or higher than 100 mg/L. Unlike adsorbents from agricultural waste, no further work has been done on the regeneration of the spent adsorbent from industrial by-products. This could be due to the fact that adsorbents derived from agricultural waste and industrial by-products have different characteristics in nature from each other such as processing conditions, making them difficult for regeneration.

The blast furnace sludge, by-product and waste material of steelmaking industry was utilized as an adsorbent for Ni (II) ions removal from aqueous solution. Radjenovic et al [49] were compared of the experimental data for blast furnace sludge with the literature data for other types of adsorbent. It was revealed that the adsorption capacity of blast furnace sludge for nickel (90.91 mg/g) is of the same order of magnitude or greater than those found for similar adsorbents (Table 2). The maximum adsorption capacity and intensity of adsorption are enhanced at higher temperatures. The values of the free energy of adsorption (ΔG) decreased with an increase in temperature, indicating that the spontaneous nature. The positive value of enthalpy change (ΔH) indicates the endothermic nature of the adsorption, while the value of 1.93 kJ/mol undoubtedly suggests possibility of weak bonding between adsorbate and adsorbent, respectively the physical nature of sorption in this system. The positive value of entropy change (ΔS) shows the increased randomness at the solid/solution interface during the adsorption process.

The objective of study to investigate comparative adsorption characteristics for removal of Ni(II) from aqueous [50] solution was the use of low-cost abundantly available nonconventional adsorbents like calcined phosphate, red mud and clarified sludge. The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the H^+ ions with Ni(II) ions at low pH values, maximum adsorption at pH 5 and at higher pH precipitation of nickel hydroxyl species onto the adsorbents (pH 6–11). Adsorption of Ni(II) for all the adsorbents was found to follow the first-order Lagergren rate kinetics. The best adsorbent for the Ni(II) removal is the calcined phosphate. The optimum conditions were pH 5, adsorbent dosage level 10 g/L, equilibrium contact time 1 h. The highest

monolayer adsorption capacity 15.53 mg/g was obtained for calcined phosphate and the

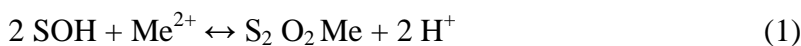
lowest 13.69 mg/g for red mud at optimum pH 5.0 (Table 2).

Table 2. Removal of Ni(II) by adsorption using industrial by-products and waste materials
Tablica 2. Uklanjanje Ni(II) adsorpcijom pomoću industrijskih nusproizvoda i otpadnih materijala

Adsorbent	Optimum pH	Optimum dose g/L	Adsorption capacity mg/g	Reference
<i>Magnetite</i>	5.5-6	1	18.43	[47]
<i>Fly ash</i>	8	20	0.99	[48]
<i>Activated red mud</i>	9.0		160	[45]
<i>Calcined phosphate</i>	5.0	10	15.53	[50]
<i>Red mud</i>	5.0	10	13.69	[50]
<i>Clarified sludge</i>	5.0	10	14.30	[50]
<i>Activated slag</i>	4.0	10	30	[51]
<i>Carbon anode dust</i>	4.5	15	8.64	[52]

The studies [52, 53] investigated the adsorption of Ni(II) ions on an anode dust which is industrial waste material from the aluminium production. Adsorption was pH-dependent, the low adsorption levels of nickel ions were observed at pH 4–7 and the

best results were obtained in the pH 4.5. At pH >5.0, Ni(II) ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate [38]. Adsorption of Ni(II) ions on anode dust was as follows [47, 52]:



where SOH, SOH_x and SOH_y are the corresponding surface charges of the solid anode dust surface. Me²⁺ denotes nickel ions in solution, and S₂ O₂ Me, SOMeOH and SOMe are adsorbed Ni (II) on the solid

surface. According to the value of ΔG (–12.27 kJ/mol), adsorption is the spontaneous in nature. The positive value of ΔH (22.42 kJ/mol) suggests the endothermic nature of adsorption and indicates the possibility of

weak bonding between adsorbate and adsorbents. Adsorption of Ni(II) obeys the second order rate equation [52].

Štrkalj et al [53] examined CH₃COOH-modified and KOH-modified carbon anode dust as adsorbent. After the applied modification procedure the increase of specific surface area, decrease of pore size

Natural materials

Due to its metal-binding capacity, natural materials such as zeolite and clay have been explored as low-cost adsorbents for treating metal-contaminated wastewater.

During 1970s, natural zeolites gained a significant interest due to their ion-exchange capability to remove unwanted heavy metals. Zeolite, an aluminosilicate tetrahedron connected with oxygen atom, has charge-balancing cations that counter-balance the negative charge localized on the aluminosilicate framework [54]. Sodium, calcium, potassium and other positively charged exchangeable ions occupy the channels within the structure and can be replaced with heavy metals.

Zeolite consists of a wide variety of species such as clinoptilolite and chabazite. The removal of heavy metals from wastewater using clinoptilolite was studied. The selectivity of the series of the heavy metals studied was determined to be as follows [55]:

Pb (II) > Cd (II) > Cu (II) > Co (II) > Cr (III)
> Zn (II) > Ni (II) > Hg (II).

The removal performance of clinoptilolite and chabazite was compared [56]. It was reported that both zeolites exhibited 100% removal efficiency of the investigated metal: Pb (II), Cd(II), Cu (II), Zn (II), Ni (II), Co (II) at concentration of 10 mg/L. It was also found that clinoptilolite and chabazite exhibited different selectivity for all metals studied except Pb (II). The superiority of chabazite's cation exchange capacity was due to the fact that chabazite

and pore volume, as well as the change in surface morphology in carbon anode dust samples were registered. Equilibrium results showed that CH₃COOH modification increased the carbon anode dust adsorption capacity for Ni (II) more than KOH modification.

has a higher Al substitution of Si than clinoptilolite.

It was reported that zeolites had a higher cation exchange capacity with Ni(II) and Cu(II) than that with Zn(II), Cr (III) and Fe(II) [57]. It can be explained by the fact that the Ni(II) and Cu(II) were more preferable for zeolites due to their higher concentrations. Therefore, both ions had greater opportunity to have ion exchange with the Na ions of zeolites than others.

The ion-exchange process in zeolites is influenced by several factors such as concentration and nature of cations and anions, the temperature, pH level, and crystal structure of the zeolites [58, 59].

There are three types of clay: montmorillonite, bentonite and kaolinite. Out of the three, montmorillonite has the highest cation exchange capacity and its current market price is twenty-times cheaper than that of activated carbon [28]. Clays are hydrous aluminosilicates defined as those minerals that make up the colloid fractions of soils, sediments, rocks and water; may be composed of the minerals such as quartz, carbonate and mineral oxides. The negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as heavy metal. The large surface area of clays (up to 800 m² / g) also contributes to the high adsorption capacity.

Clay could be modified to improve its adsorption capacity. Pretreatment of clay with HCl significantly improved the removal of Ni(II), Cu(II) and Zn(II) from simulated wastewater. This could be due to the fact

that acid treatment changed the chemical composition and mineralogical structure of clay, enhancing its uptake capacity. The maximum adsorption capacities for the cations in the solution were in the order: Cu(II) > Ni(II) > Zn(II) [60].

Kaolinite is the other clay, representing a layered alumino-silicate mineral with the structure of a tetrahedral (Si center) and octahedral (Al center).

Kaolinite clay can be used to remove metal ions such as Pb(II), Cd(II), Ni(II) and Cu(II) from aqueous solution in both single and multi-metal ions [61, 62]. There are several factors affecting the adsorption of metal ions onto kaolinite clay, however, the solution pH has a significant impact on the adsorption of metal ions onto kaolinite clay. The selectivity sequence of the adsorption of tested metals was Pb(II) > Cd(II) > Ni(II) > Cu(II), and the desorption of Cd(II) and Cu(II) was much easier than that of Pb(II) and Ni(II). The maximum adsorption capacity toward Cd(II) is determined as 4.22 mg/g at an initial concentration of 80 mg/L and toward Pb(II), Cu(II), and Ni(II) as 27.7,

25.76, and 13.03 mg/g, respectively, at an initial concentrations of 800 mg/L.

In addition, the experimental data were better fitted with Freundlich equation than Langmuir model. This indicated that while the interactions were predominantly chemical in nature, the adsorption sites were non-uniform and nonspecific in nature. Furthermore, characterization of the kaolinite clays showed the low surface area what resulted from a low percentage of kaolinite components in the clay. It also was demonstrated that the kaolinite clay can be used for the removal of heavy metals in real wastewater.

Chantawong et al. [63] studied the adsorption of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II), on kaolinite and ballclay from simulated solution. Metal adsorption by kaolinite was observed as follows: Cr(III) > Zn(II) > Cu(II) ≈ Cd(II) > Ni(II) > Pb(II), and that by ballclay was: Cr(III) > Zn(II) > Cu(II) > Cd(II) > Ni(II). Ballclay has higher removal efficiency than kaolinite because illite, the major mineral in the ballclay, has a higher surface charge than kaolinite.

CONCLUSION

According to the literature data adsorption is very popular method for the removal of Ni (II) ions from aqueous solutions. In this article, the removal performance of low-cost adsorbents derived from agricultural waste, certain industrial by-products and waste material or natural material has been reviewed. It is evident from our literature survey, low-cost adsorbents have outstanding removal capabilities for Ni(II) ions. Adsorption capacity of an adsorbent (as efficiency indicator of Ni(II) uptake), depends on several parameters like dose of an adsorbents, initial concentration of Ni(II) in solution, pH value, temperature.

Most of the reported study are performed in the batch technique; this gives a platform for the relatively simple industrial application. It is important to note, adsorption capacities of the adsorbents presented in this article vary, depending on the characteristics of the individual adsorbents. High adsorption capacity has been shown for some of the metallurgical by-products and waste materials, e.g. red mud, blast furnace slag and blast furnace sludge.

Low-cost, effectiveness and availability of described materials suggest that they can be used in place of expensive activated carbon for the removal of toxic Ni(II) ions 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] I. Gaballah, G. J. Kilbertus, *Geochem. Explor.*, 62 (1998) 241-286.
- [2] S. Karabulut, A. Karabakan, A. Denizili, Y. Yurum, *Sep. Purif. Technol.*, 18 (2000) 177-184.
- [3] C. Brach Papa, B. Coulomb, J. L. Boudenne, V. Cerda, F. Theraulaz, *Anal. Chem. Acta*, 457 (2002) 311-318.
- [4] P. A. Brown, S. A. Gill, S. J. Allen, *Water Res.*, 34 (2000) 3907-3916.
- [5] V. Gopal, K. P. Elango, *J. Hazard. Mater.*, 141 (2007) 98-105.
- [6] M. I. Kandah, *Sep. Purif. Technol.*, 35 (2004) 61-70.
- [7] V. K. Gupta, C. K. Jain, I. Ali, M. Sharma, V. K. Saini, *Water Res.*, 37 (2003) 4038-4044.
- [8] E. Demirbas, M. Kobya, S. Öncel, S. Sencan, *Biores. Tech.*, 84 (2002) 291-293.
- [9] H. Parab, S. Joshi, N. Shenoy, A. Lali, U. S. Sarma, M. Sudersanan, *Proc. Biochem.*, 41 (2006) 609-615.
- [10] Q. U. Jiuhui, *J. Environ. Sci.*, 20 (2008) 1-13.
- [11] T. Lee, J. Park, J. H. Lee, *Chemosphere*, 56 (2004) 571-581.
- [12] R. C. Bansal, M. Goyal, *Activated Carbon Adsorption*, Taylor and Francis Group, London, 2005.
- [13] T. Wigmans, *Carbon*, 27 (1989) 13-22.
- [14] J. W. Patrick, (Ed.), *Porosity in Carbon*, Edward Arnold, London, 1995.
- [15] Lj. Radović (Ed.), *Chemistry and Physics of Carbon*, Marcel Dekker, New York, 2001.
- [16] J. W. Shim, S. J. Park, S. K. Ryu, *Carbon*, 39 (2001) 1635-1651.
- [17] J.W. Shim, S.M. Lee, B.S. Rhee, S.K. Ryu, *Proceedings of the European Carbon Conference*, British Carbon Group, New Castle, 1996, 242-243.
- [18] www.enecon.com.au/activated.
- [19] D. Sud, G. Mahajan, M. P. Kaur, *Biores. Technol.*, 99 (2008) 6017-6027.
- [20] S. E. Bailey, T. J. Olin, R. Mark Bricka, D. Dean Adrian, *Water Res.*, 33 (1999) 2469-2479.
- [21] G. F. Nordberg, B. A. Fowler, M. Nordberg, L. Friberg, *Handbook of Toxicology of Metals*, European Environment Agency, Copenhagen, 2005.
- [22] A. H. Muhammad, N. Raziya, N. Z. Muhammad, A. Kalsoom, N. B. Haq, *J. Hazard. Mater.*, 145 (2007) 501-505.
- [23] F. Carrasco-Martin, A. Mueden, T. A. Centeno, F. Stoeckli, C. Moreno-Castilla, *J. Chem. Soc. Faraday Trans.*, 93 (1997) 2211-2215.
- [24] K. S. Sajwan, W. H. Ornes, T. V. Youngblood, A. K. Alva, *Wat. Air Soil Polution.*, 91(1996) 209-217.
- [25] J. Petterson, R. Passino, *Metal Speciation, Separation and Recovery*, Lewis Publishers. Inc., Chelsea, 1987.
- [26] M. Ajmal, R. A. K. Rao, M. A. Khan, *J. Hazard. Mater. B*, 122 (2005) 177-183.

- [27] K. Kadirvelu, P. Senthilkumar, K. Thamaraiselvi, V. Subburam, *Biores. Technol.*, 81 (2002) 87-90.
- [28] T. A. Kurniawan, G. Y. S. Chan, W. Lo, S. Babel, *Sci. Total. Environ.*, 366(2006) 409-426.
- [29] U. Kumar, M. Bandyopadhyay, *Biores. Technol.*, 97 (2006) 104-109.
- [30] S. J. T. Pollard, G. D. Fowler, C. J. Sollars, R. Perry, *Sci. Total. Environ.*, 116 (1992) 31-52.
- [31] S. Qaiser, A. R. Saleemi, M. M. Ahmad, *Environ. Biotechnol.*, 10 (2007) 409-416.
- [32] Z. Reddad, C. Gerente, Y. Andres, M. C. Ralet, J. F. Thibault, P. L. Cloirec, *Carbohydr. Polym.*, 49 (2002) 23-31.
- [33] M. Kobya, E. Demirbas, E. Senturk, M. Ince, *Biores. Technol.*, 96 (2005) 1518-1521.
- [34] S. Srivastava, A. H. Ahmed, I. S. Thakur, *Biores. Technol.*, 98 (2007) 1128-1132.
- [35] M. Ajmal, R. A. K. Rao, R. Ahmad, J. Ahmad, *J Hazard Mater* 79, (2000) 117-131.
- [36] A. Annadurai, R. S. Juang, D. J. Lee, *Water Sci. Technol.* 47 (2002) 185-190.
- [37] K. Kadirvelu, K. K. Thamaraiselv, C. C. Namasivayam, *Sep. Purif. Technol.*, 24 (2001) 497-505.
- [38] H. Hasar, *J. Hazard. Mater.*, 97 (2003) 49-57.
- [39] S. Balci, T. Doğu, H. Yücel, *J. Chem. Biochem. Technol.*, 60 (1994) 419-426.
- [40] K. Periasamy, C. Namasivayam, *Waste Manage.*, 15 (1995) 63-68.
- [41] Y. S. Ho, G. McKay, *Water Res.*, 34 (2000) 735-742.
- [42] F. Malkoc, Y. Nuhoglu, *J. Hazard. Mater. B*, 127 (2005) 120-128.
- [43] S. R. Shukla, R. S. Pai, *Biores. Technol.* 96, (2005) 1430-1438.
- [44] U. K. Garg, M. P. Kaur, V. K. Garg, D. Sud, *Biores. Technol.*, 99 (2008) 1325-1331.
- [45] A. I. Zoubulis, K. A. Kydros, *J. Chem. Technol. Biotechnol.*, 38 (1993) 95-101.
- [46] S. V. Dimitrova, *Water Res.*, 30 (1996) 228-232.
- [47] N. Ortiz, M. A. F. Pires, J. C. Bressiani, *Waste Manage.*, 21 (2001) 631-635.
- [48] B. Bayat, *J. Hazard. Mater. B*, 95 (2002) 251-273.
- [49] A. Radjenovic, J. Malina, A. Štrkalj, *Desal. Water Treat.*, 21 (2010) 286-294.
- [50] Y. Hannachi, N. A. Shapovalov, A. Hannachi, *Korean J. Chem. Eng.*, 27 (2010) 152-158.
- [51] D. Feng, J. S. J. Van Deventer, C. Aldrich, *Sep. Purif. Technol.*, 40 (2004) 61-67.
- [52] A. Štrkalj, A. Rađenović, J. Malina, *Can. Metall. Q.*, 50 (2011) 3-9.
- [53] A. Štrkalj, A. Rađenović, J. Malina, *J. Min. Sect. B-Metall.*, 46 (2010) 33-40.
- [54] S. Babel, T. A. Kurniawan, *J. Hazard Mater.*, B 97 (2003) 219-243.
- [55] M. J. Zamzow, B. R. Eichbaum, *Sep. Sci. Tech.*, 25 (1990), 1555-1569.
- [56] S. K. Ouki, M. Kavanagh, *Waste Manage. Res.*, 15 (1997) 383-394.
- [57] K. M. Ibrahim, T. NasserEd-Deen, H. Khoury, *Environ. Geol.*, 41 (2002) 547-551.
- [58] E. Erdem, N. Karapinar, R. Donat, *J. Colloid Interface Sci.*, 280 (2004) 309-314.
- [59] M. K. Doula., A. Ioannou, *Micropor. Mesopor. Mater.*, 58 (2003) 115-130.

[60] T. Vengris, R. Binkiene, A. Sveikauskaite, *Appl. Clay Sci.*, 18 (2001) 183-190.

[61] M. Jiang, X. Jin, X. Lu, Z. Chen, *Desalination*, 252 (2010) 33-39.

[62] M. Sprynskyy, B. Buszewski, A. P. Terzyk, J. Namieśnik, *J. Colloid and Interf. Sci.*, 304 (2006) 21-28.

[63] V. Chantawong, N. V. Harvey, V. N. Bashkin, *Water Air Soil Pollut.*, 148 (2003) 111-125.