

piping, water purification, gasoline additives, cable covering, ammunition and battery industries and sewage sludge [3–7].

Hydrometallurgical processes of leaching and dissolution of such raw materials under pressure or atmospheric conditions using HCl or H₂SO₄ result in leach liquors containing Co(II) and Ni(II), making their separation from aqueous solutions a challenging task. Using conventional methods such as chemical precipitation, oxidation and crystallization, it is difficult to separate in a simple and economical way. The removal of heavy metal pollutants at high concentrations from water can be readily accomplished by chemical precipitation or the electrochemical method. At low concentrations, removal of such pollutants is more effectively implemented by ion exchange or adsorption on solid sorbents such as activated carbon or coal fly ash [8,9].

The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest [10–13]. However, in order to minimize processing costs for these effluents, recent investigations have focused on the use of low-cost adsorbents [14–19]. There is an increasing demand for porous materials as adsorbents and catalyst supports. Sepiolite, which is a zeolite-like clay mineral, provides a high specific surface area. Thus, it has many industrial applications as an adsorbent.

Sepiolite is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. It owes much of its industrial applications to its molecular sized channels and large specific surface area (more than 200 m²g⁻¹) [20]. Sepiolite is used in a variety of industries including cosmetics, ceramics, detergents, paper and paint. High-capacity values were also observed for heavy metal removal and wastewater treatment using sepiolite [21,22]. The abundance and availability of sepiolite reserves together with its relatively low cost guarantee its continued utilization.

Most of the world's sepiolite reserves are found in Turkey. Thus it is important to characterize this clay mineral and evaluate how important physicochemical properties are altered during chemical and thermal treatment. Sorption depends heavily on experimental conditions such as pH, metal concentration, ligand concentration, competing ions and particle size [23,24]. Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties, and the use of sepiolitic clays is expanding [25–29].

The aim of the present investigation was to study the adsorption of Co(II) and Ni(II) ions onto natural sepiolite by measuring the effect that various parameters have on the adsorption process.

2. Materials and methods

A natural sepiolite [Mg₄Si₆O₁₅(OH).6H₂O] sample was obtained from the Mihaliccik–Eskisehir region of Turkey. The chemical composition of the sample was first identified by X-ray diffraction, differential thermal and IR spectrophotometric analysis. Chemical analysis of the sample was carried out on a GE-SPG 7, X-ray fluorescence spectrophotometer. The results are summarized in Table 1.

Sepiolite was washed thoroughly with double distilled water to remove the dirt and other foreign matter and dried at 40°C for a period of 4–5 h. The samples were 200 mesh particle size. Metal removal studies were carried out using sepiolite in two different forms: untreated and treated samples. Sample 1 is natural sepiolite; Sample 2 is treated sepiolite, which is natural sepiolite treated with 2 M HCl solution over a period of 24 h. After washing, the sample was dried at 105°C for 1 h.

Stock solutions of cobalt and nickel were prepared in bi-distilled water using the analytical reagent grade CoCl₂.6 H₂O and NiSO₄.7H₂O. The exact concentration of metal ions was verified by atomic absorption spectrophotometry (AAS).

Table 1
Chemical analysis of natural sepiolite

Component	%
SiO ₂	58.7
MgO	25.0
Al ₂ O ₃	0.5
CaO	0.5
(FeO+ Fe ₂ O ₃)	0.05
TiO ₂	0.05
Na ₂ O	0.05
MnO	Not detected
P ₂ O ₅	Not detected
Loss of ignition	14.8

The adsorption of Co(II) and Ni(II) on sepiolite samples was studied by a batch technique. The effects of factors such as pH, concentration, stirring time and sorbent amount on adsorption were investigated. The general method used for these studies is described below. The batch adsorption experiments were carried out by shaking known amounts of sepiolite with 100 ml aqueous metal solutions of 1–100 mgL⁻¹ concentration at various pHs (1–10) and at room temperature (20±2°C) in several stoppered bottles for retention times varying from 15 to 180 min at different stirring speeds (50–250 rpm). The study of adsorbent doses was carried out by varying the amount of adsorbent (0.2–1 g).

Sepiolite samples were well dispersed in aqueous metal solutions. At the end of the pre-determined time interval, the adsorbent was removed by filtration (the supernatant solution was filtered through a 0.45 µm microporous membrane filter), and the final concentration was determined in the filtrate by AAS using an air-acetylene flame. Optimum conditions were determined for both metals.

3. Results and discussion

The adsorption behavior of Co(II) and Ni(II) ions on sepiolite samples was determined at

different concentration, sepiolite amount, stirring speed, stirring time and pH of solutions. Optimum conditions were determined for sepiolite. The results are given in Figs. 1–5. The dependence of metal ion sorption on sepiolite amount was studied by varying the sorbent amount from 0.2 to 2 g while keeping the volume, 100 ml, of the metal solution constant for 30 min stirring time.

The results indicate that adsorption percentage did not change much with increasing amounts of sepiolite. Therefore, 0.4 g of the sepiolite was used for all further studies. In the goal to deter-

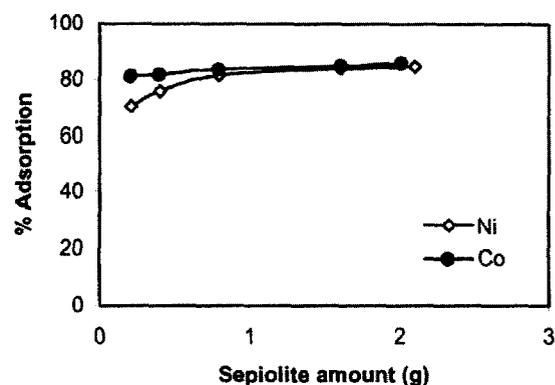


Fig. 1. Effect of sorbent amount on metal sorption (10 mgL⁻¹/100 ml, pH 5, 250 rpm).

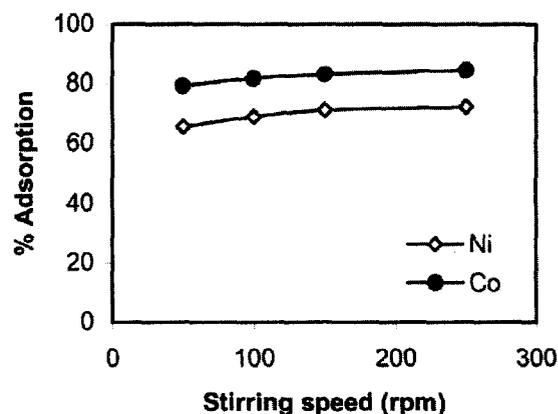


Fig. 2. Effect of stirring speed on metal sorption (0.4 g, 10 mgL⁻¹, pH 5).

mine the optimal speed of stirring, the dependence of metal sorption on stirring speed was studied by varying the stirring speed from 50 to 250 rpm for 30 min. Fig. 2 shows the effects of stirring speed on metal adsorption. The percentage of adsorption values are slowly increased with increasing stirring speed. The 250 rpm stirring speed was selected as the optimum for all metals.

Fig. 3 shows the sorption of Co(II) and Ni(II) ions of natural sepiolite (0.4 g) as a function of contact time by varying from 0 to 180 min for an initial concentration of 100 ml heavy metal ions. The percentage of adsorption values were slowly increased with increasing stirring speed and contact time. The effect of pH on the sorption of Co(II) and Ni(II) on sepiolite was studied by varying the pH of the metal aqueous solution-sepiolite suspension from 1 to 10.

The pH dependence of Co(II) and Ni(II) uptake onto natural sepiolite is shown in Fig. 4. The percentage of adsorption was increased by increasing pH values for Ni(II), but it remains almost constant up to pH 4 for Co(II), beyond which it increased sharply after this pH for both ions. For both metals a decrease in sorption is produced with a decrease in pH. In general, protons can mainly compete with metal cations

for sorption variable charge sites. Sepiolite, due to its structure and morphology, has a great number of terminal silica tetrahedrons present in its external surfaces and consistently also a great number of silanol groups. Therefore, the decrease in sorption with the decrease in pH has to be mainly associated with the suppression of sorption on these groups. Heavy metal ions tend to form a precipitate at pH higher than 6.0, and therefore adsorption by zeolite is difficult to quantify at the higher pH value of 6.0; the “true” adsorption at this pH is masked by precipitation [30].

The sorption of Co(II) and Ni(II) on modified sepiolite as a function of their concentration was studied by varying the metal concentration from 1 to 100 mgL⁻¹, while keeping all other parameters constant. When the effect of initial metal concentration was investigated, adsorption percentage for both metals decreases with increasing bulk metal concentration in the aqueous solutions until 50 mgL⁻¹ concentration value. After this concentration value adsorption percentage was a little increased for Ni(II) but adsorption percentage for Co(II) was almost stayed stable. 10 mgL⁻¹ concentration was chosen as the optimum studying concentration for Co(II)

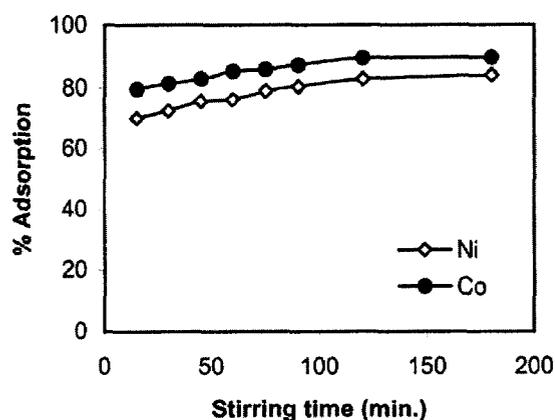


Fig. 3. Effect of stirring time on metal sorption (0.4 g, 10 mgL⁻¹, pH 5, 250 rpm).

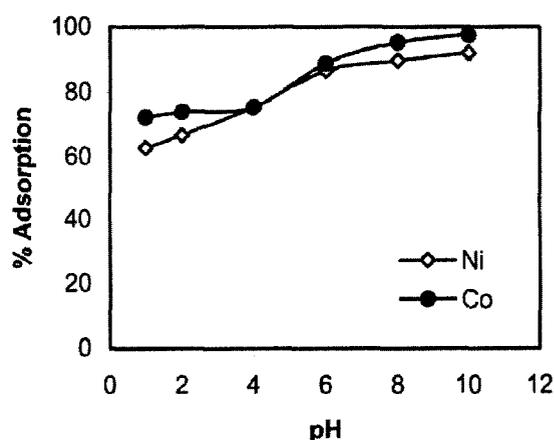


Fig. 4. Effect of pH on metal sorption (0.4 g, 10 mgL⁻¹, 250 rpm).

- [6] P.W. Zhang, T. Yokohama, O. Itabashi, T.M. Suzuki and K. Inoue, *Hydrometallurgy*, 47 (1998) 259–271.
- [7] R. Apak, E. Tütem, M. Hugül and J. Hizal, *Water Res.*, 32(2) (1998) 430–440.
- [8] B.A. Bolto and L. Pavlowski, *Wastewater Treatment by Ion Exchange*, E & FN Spon, New York, 1987.
- [9] S. Rengaraj and S.H. Moon, *Water Res.*, 36 (2002) 1783–1793.
- [10] M.O. Corapcioglu and C.P. Huang, *Water Res.*, 21 (1987) 1031–1044.
- [11] V.G. Serrano, A.M. Gorcia and A. E. Mansilla, *Water Res.*, 32 (1998) 1–4.
- [12] A. Netzer and D.E. Hughes, *Water Res.*, 18 (1984) 927–933.
- [13] C. Chang and Y. Ku, *Sep. Sci. Technol.*, 30 (1995) 899–915.
- [14] A.A. Al-Haj and R. El-Bishtawi, *J. Chem. Technol. Biotechnol.*, 69 (1997) 27–34.
- [15] M. Auboiroux, P. Baillif, J.C. Touray and F. Bergaya, *Appl. Clay Sci.*, 11 (1996) 117–126.
- [16] G. Blanchard, M. Maunaye and G. Martin, *Water Res.*, 18 (1984) 1501–1507.
- [17] H.G. Pederson, B.T. Jenson and N. Pinol, *Environ. Technol.*, 18 (1997) 807–811.
- [18] F.F.O. Orumwense, *J. Chem. Technol. Biotechnol.*, 65 (1996) 363–369.
- [19] A.G. Sanchez, E.A. Ayuso and O.J. De Blas, *Clay Minerals*, 34 (1999) 469–477.
- [20] A.R. Turker, H. Bag and B. Erdogan Fresen, *J. Anal. Chem.*, 357 (1997) 351–353.
- [21] S. Balci and Y. Dincel, *Chem. Eng. Processing*, 41 (2002) 79–85.
- [22] E. Sabah and M.S. Celik, *Sep. Sci. Technol.*, 37(13) (2002) 3081–3097.
- [23] S. Balci, *Clay Minerals*, 34 (1999) 647.
- [24] S.E. Bailey, T.J. Olin, R.M. Bricka and D. Adrian, *Water Res.*, 33(11) (1999) 2469–2479.
- [25] H.I. Unal and B. Erdogan, *Appl. Clay Sci.*, 12 (1998) 419–429.
- [26] Y. Sarikaya, N. Bicer, C. Bicer, H. Ceylan and I. Bozdogan, 3rd National Clay Symp., Ankara, 1985, pp. 221–227.
- [27] L. Daza, S. Mendioroz and J.A. Pajares, *Clays Clay Miner.*, 39(1) (1991) 1–21.
- [28] S. Inegahi, Y. Fukushima, H. Doi and O. Kamigaito, *Clay Miner.*, 25 (1990) 99–105.
- [29] E.A. Ayuso and A.G. Sanchez, *Sci. Total Environ.*, 305 (2003) 1–12.
- [30] G. McKay, M.J. Bino and A.R. Altamemi, *Water Res.*, 19(4) (1985) 491.