Use of Silica Fume as Low-Cost Absorbent Material for Nickel Removal from Aqueous Solutions

EKREM KALKAN[1,*], HAYRUNNISA NADAROGLU[2] and NESLIHAN CELEBI[2]

[1]Department of Geological Engineering, Oltu Earth Science Faculty, Ataturk University, 2400 Oltu, Erzurum, Turkey
[2]Erzurum Vocational Training School, Ataturk University, 2570 Erzurum, Turkey

*Corresponding author: Fax: +90 442 8163332; Tel: +90 442 8166266; E-mail: ekalkan@atauni.edu.tr

The potential of economically low-cost cellulose containing waste materials like silica fume assessed for nickel adsorption from aqueous solutions. In this study, the potential use of silica fume in the remediation of polluted heavy metal water to remove nickel ions is presented. The effects of contact time, initial nickel concentration, pH, temperature, adsorbent dosage on the uptake of nickel were studied in batch process. The experimental investigation results show that activated silica fume has a high level of adsorption capacity for nickel ion. The adsorption data was correlated with the Langmuir and Freundlich isotherm models. It was found that the Langmuir and Freundlich isotherms fitted well to the data. Consequently, it is concluded that nickel is considerably adsorbed on silica fume and silica fume can be successfully used for the removal of the nickel ions from the aqueous solutions with heavy metals.

Keywords: Waste water, Silica fume, Aqueous solution, Nickel, Adsorption isotherms, Removal.

INTRODUCTION

The presence of heavy metals in the aquatic ecosystem causes harmful effects to living organisms and causes environmental hazards[1]. Inorganic effluents contaminate wastewater with toxic metals such as Ni, Cr, Cd, Hg, Pb and Zn[2-4]. These heavy metals are extremely toxic, non-biodegradable and accumulate in the food chain, even in relatively minute quantities. Thus, industries such as electroplating, aerospace and metal finishing are among the most hazardous from a wastewater viewpoint[5-6].

For the past several years, high levels of heavy metals in drinking water and foods have been associated with several acute and chronic illnesses in humans throughout the world[7,8]. Water pollution is the contamination of water bodies such as lakes, rivers, oceans and groundwater caused by human activities, which can be harmful to organisms and plants, present in water bodies. The presence of heavy metals in streams, lakes and groundwater reservoirs has been responsible for several health problems with plants, animals and human beings[9]. Heavy metal contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray are intensively used[10-12].

Nickel ion is one such heavy metal frequently encountered in raw wastewater streams from industries, such as non-ferrous metal, mineral processing, paint formulation, electroplating, porcelain enameling, copper sulfate manufacture and steam-electric power plants. In humans, higher concentrations of nickel can cause serious problems, such as dermatitis, allergic sensitization, lung and nervous system damage[13-18].

There is an increasing trend in searching for new heavy metal adsorbents among commercially available materials such as by-products of various industries. The examples of stabilized industrial solid wastes that were evaluated, as composite adsorbents are silica fume, fly ash, red mud, waste from electroplating industry and blast furnace slag[19-24]. One of the most promising adsorbents was found to be silica fume, a by-product of silicon material or silicon alloy metal factories. Although the silica fume is a waste material of industrial applications, it has become the most valuable by-product among the pozzolanic materials due to its very active and high pozzolanic property. Currently, it is widely used in concrete or mortar as an admixture[25-29]. In the geotechnical applications, it improves some geotechnical properties of compacted fine-grained soils[30-32].

In this research, we studied the adsorption capacities of the silica fume waste material for the removal of nickel ions from wastewater. We wish to determine whether this material might be cost-effective and are an alternative adsorbent that could replace the expensive resins now used for wastewater treatment. The nickel ions were absorbed by silica fume from polluted river water and $NiCl_2$ solution and the results shown on the adsorption behavior of nickel heavy metal in silica fume.

EXPERIMENTAL

Silica fume: It is a by-product of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. It is also collected as a byproduct in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium and calcium silicon[33]. This material has been obtained from Ferro-Chromate Factory in Antalya, Turkey. The silica fume was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200-mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling and decanting. The last suspension was filtered and the residual solid was then dried at 105 ºC, ground in a mortar and sieved through a 200-mesh sieve. Its chemical and index properties are summarized in Tables 1 and 2, respectively.

TABLE-1
CHEMICAL COMPOSITIONS OF SILICA FUME USED IN THE STUDY

Compound	Silica fume (%)
SiO_2	85-95
Al_2O_3	1-3
Fe_2O_3	0.5-1.0
CaO	0.8-1.2
MgO	1-2
TiO_2	-
Heat loss	0.5-1

TABLE-2
ENGINEERING PROPERTIES OF SILICA FUME USED IN THE STUDY

Property	Silica fume
Specific surface area (m^2/g)	20.12
Density (mg/m^3)	2-2.5
Grain size	
Gravel (> 2000 µm) %	-
Sand (2000-75 µm) %	-
Silt (2-75 µm) %	20
Clay (< 2 µm) %	80

Analytical methods: For studying metal adsorption, 1 mL of sample solution containing preferably 8×10^{-5}-8×10^{-4} mmol (4.7-47 µg) Ni was taken; 1 mL of 1.6×10^{-2} M dithizone (20-fold of maximum amount of Ni) followed by 1 mL of distilled water and 1 mL of concentrated NH_3 solution were added to yield a final volume of 4 mL. For determination of nickel, 1 mL of sample solution containing preferably 8×10^{-5} to 8×10^{-4} mmol total metal was taken; 1 mL of 1.6×10^{-2} M dithizone followed by 1 mL of distilled water and 1 mL of concentrated NH_3 solution were added to yield a 4 mL volume mixture solution[34]. The amount of nickel ions adsorbed was calculated as;

$$q_e = \frac{[(C_o + C_e)V]}{m} \tag{1}$$

where q_e(mg/g) is the amount of nickel adsorbed per gram of the adsorbent at equilibrium, C_o(mg/L) is the initial concentration of nickel, C_e(mg/L) is the concentrations of nickel at

equilibrium, V(L) is the volume of solution and m(g) is the weight of sf adsorbent.

Adsorption isotherms: Adsorption isotherms are basic requirements for the design of an adsorption system. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationships. The Langmuir and Freundlich models are the world-widely used models because of their simplicity[11,35].

RESULTS AND DISCUSSION

Effect of contact time: Fig. 1 shows the effect of contact time on the adsorption process. It can be observed that the removal of nickel increases with increasing time in the first 0.5 h and thereafter the removal is not significant, indicating that the minimum contact time necessary for a good heavy metal removal is 0.5 h. This indicates that the maximum removal of nickel is achieved within 0.5 h after which concentration of nickel in the solution become constant. This may be explained by the fact that initially for adsorption large number of vacant sides was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase[36,37]. The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy[19-38].
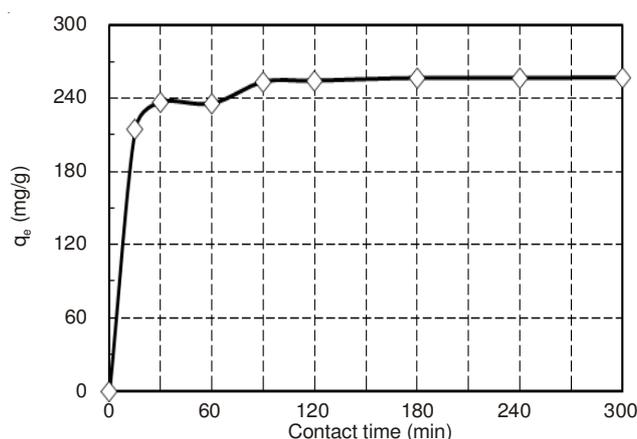
Fig. 1. Effect of contact time on the removal of nickel

Effect of initial nickel concentration: The effect of initial nickel concentration on the adsorption experiment is shown in Fig. 2. The plot showing the effect of initial concentration on the adsorption of nickel ions indicates that the total nickel ion adsorbed increases sharply in the beginning and then slowly towards the end of the run. A perusal of the results clearly indicates that adsorption of nickel increases from 30 to 200 mg/L and then become constant indicating that the maximum adsorption occurs at 200 mg/L. This trend is that of the result of the progressive increase in the electrostatic interaction between the nickel ions and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the nickel ions concentration increases[39,40].

Effect of pH: The removal of pollutants from wastewater by adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent and the degree
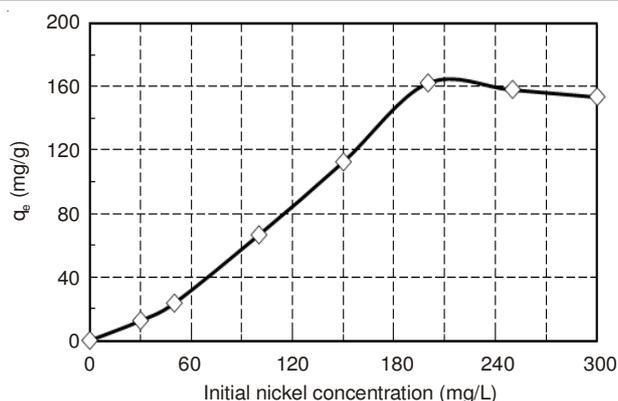
Fig. 2. Effect of initial metal ion concentration on the removal of nickel

of ionization and specification of the adsorbate[41-44]. The effect of initial pH on the equilibrium uptake of nickel ions was investigated between pH 2 and pH 10. The plot showing the effect of pH on the adsorption of nickel is presented in Fig. 3. It is shown that the absorption amount of nickel increase with increasing pH and maximum adsorption of nickel ions are obtained at pH 5 which is the initial pH of the solution. The adsorption increased from 12.1 mg/g at pH 2 to 66.7 mg/g at pH 5 and then started to decrease. An increase in pH shows a slight increase in adsorption in which the surface of the adsorbent is negatively charged and the adsorbate species are still positively charged. As the adsorbent surface is negatively charged as well, the increasing electrostatic attraction between positive adsorbate species and adsorbent particles would lead to increase adsorption of metal ions. The decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H^+ ions present in the reaction mixture. The decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes[10,11,45,46]. The removal of nickel from aqueous solution by adsorption is highly dependent on pH of the media which affects the surface charge of the solid particles and degree of ionization and speciation of adsorbate[47].
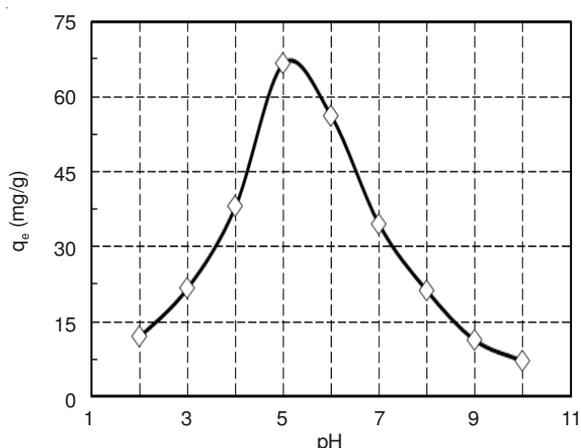
Fig. 3. Effect of pH on the removal of nickel

Effect of temperature: The temperature has a pronounced effect on the adsorption capacity of the adsorbent. The effect of temperature influencing the adsorption has been studied in the range of 20-80 °C. The effect of temperature on the adsorption capacity of silica fume is shown in Fig. 4. It is observed that the degree of adsorption increases with

increasing temperature and maximum adsorption of nickel ions are obtained at 25 °C which is the temperature of the solution. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement in the sorptive capacity of the adsorbent[48]. The temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters[49].
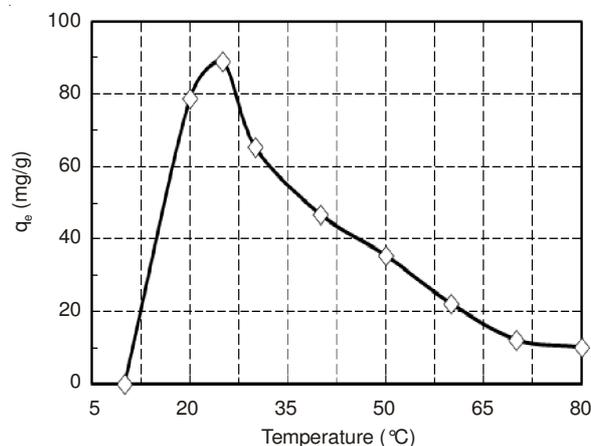
Fig. 4. Effect of temperature on the removal of nickel

Effect of adsorbent dosage: The effect of silica fume dosage on the nickel removal was investigated by varying adsorbents dosage in the range of 30 to 200 mg/L. It was observed that the nickel removal was 73.5 at 200 mg/L (Fig. 5). It can be seen that total amount of metal ions removed from the solutions increases by the amount of adsorbent. This is an expected result because as the adsorbent concentration increases, the number of adsorbent particles surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces[50].
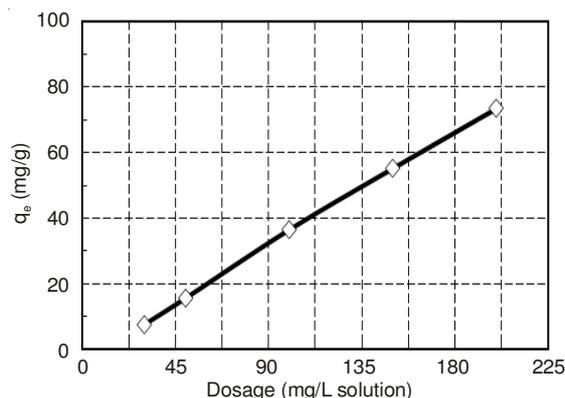
Fig. 5. Effect of silica fume dosage on the removal of nickel

The amount of nickel adsorbed on per unit weight of silica fume adsorbent decreases with the adsorbent dosage. When the adsorbent dosage is higher, there is a very fast adsorption onto the adsorbent surface, which results in a lower adsorbate concentration in the solution. However, the adsorption sites on the adsorbent surface remain unsaturated when the adsorbate concentration in the solution drops to a lower value. Thus, the amount of nickel adsorbed onto per unit weight of adsorbent gets reduced with the adsorbent dosage increasing[11,51,52].

The experimental results indicated that silica fume enhanced adsorption capacity. Without the addition of the silica fume, the leachate nickel concentration was approximately 1.262 and 11,742 mg/mL for polluted river water and $NiCl_2$ solutions, respectively. The addition of silica fume strongly inhibited the leaching of nickel in both solutions. When the silica fume was added to the aqueous solutions contaminated with nickel, the concentration of nickel in the leachate drastically reduced, whereas the adsorption capacity increased. The nickel concentration of silica fume treated leachates decreased from 1,262 to 0,436 and from 11,742 to 4,115 for the polluted river water and $NiCl_2$ solutions, respectively.

The polluted river water treated with silica fume reached their minimum point values in the nickel concentration. Because of its fine particles, large surface area and the high SiO_2 content, silica fume is a very reactive pozzolan. The nickel ions might absorb on silica fume because of its high content of silica and large surface area. The very fine silica fume particles with large surface area gave adsorbing capacity to the silica fume and they, at the pH equilibrium in the adsorption experiments, had a negative charge density in its lattice. This should be neutralized by metal adsorbed with outer-sphere bonds on the external surfaces and by the incorporation of metals in the cages and channels of fine silica fume particle framework if the hydrated ionic radius of the metals is compatible with the sizes of silica fume particle cavities[53] (Fig. 6).
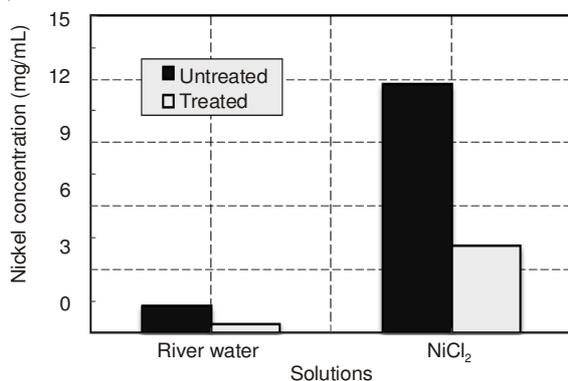
Fig. 6. Variation of nickel concentration with silica fume on the river water and $NiCl_2$

Adsorption isotherms: The Langmuir and Freundlich isotherm models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase. The Langmuir adsorption isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules[54]. The linear form of the Langmuir adsorption isotherm is represented as;

$$\frac{C_e}{q_e} = \left[\frac{1}{Q_o b} + \frac{1}{Q_o \times C_e} \right] \qquad (2)$$

where C_e (mg/L) is the equilibrium concentration of adsorbate in solution, q_e (mg/g) is the amount of nickel adsorbed per gram of the adsorbent at equilibrium, Q_o (mg/g) is the Langmuir constants related to adsorption capacity and b (L/mg) is adsor-

ption rate. Q_o and b (Table-3) were calculated from the slope and intercept of the Langmuir plot of C_e *versus* C_e/q_e (Fig. 7).

$$\log_{10} q_e = \log_{10} (K_F) + (1/n) \log_{10} (C_e) \qquad (3)$$

where q_e (mg/g) is the amount of nickel adsorbed per gram of the adsorbent at equilibrium, C_e (mg/L) is the equilibrium concentration of adsorbate in solution, q_e (mg/g) is the amount of nickel adsorbed per gram of the adsorbent at equilibrium. K_F and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity)[54]. K_F and n values (Table-3) were calculated from the intercept and slope of the plot (Fig. 8).
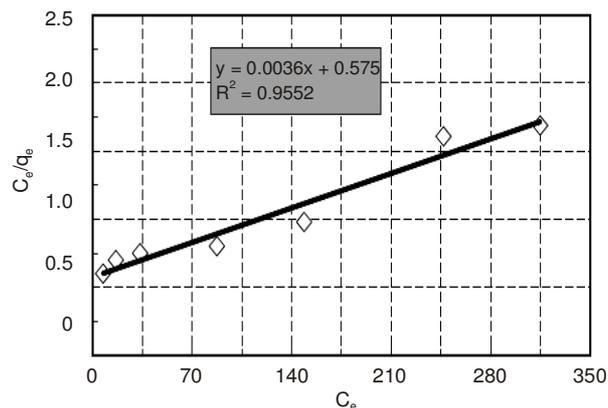
Fig. 7. Langmuir isotherm for the adsorption of nickel
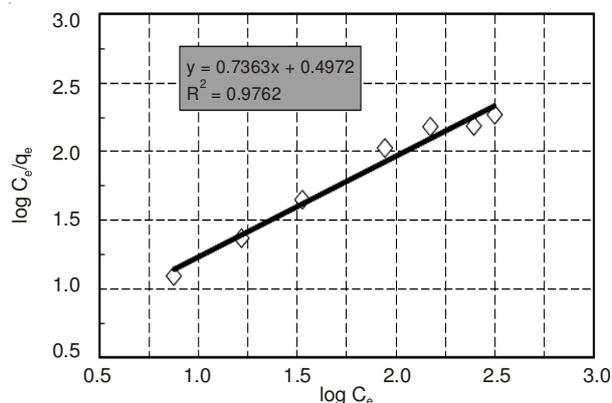
Fig. 8. Freundlich isotherm for the adsorption of nickel

TABLE 3 VALUES OF ADSORPTION ISOTHERM PARAMETERS FOR ADSORPTION OF NICKEL	
Langmuir constant	
Q_o (mg/g)	27.78
b (L/mg)	0.0063
R^2	0.9552
Freundlich constant	
K_F (mg/g)	2.1420
n (L/mg)	1.3580
R^2	0.9762

In the literature, it is pointed out that the parameters, K_F and n affect the adsorption isotherm. The larger K_F and n values, the higher the adsorption capacity. The magnitude of exponent n gives an indication of the favorability of the adsorption. The n value is 1.358 L/mg (Table-3) and it is located

to range 1-2 moderately adsorption characteristic[54,55]. Based on the correlation coefficient values, it has been deduced that Freundlich model better fitted to the experimental data (Table-3). The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of nickel ions.

Table-4 shows a comparison between the results of this work and other studies found from literature. The values of nickel specific uptake found this work were significantly higher, with two exceptions, than reported elsewhere. The comparison of adsorption capacities of silica fume used in this study with those obtained in the literature shows that silica fume is the most effective for the removal of nickel from aqueous solutions.

TABLE-4
COMPARISON OF ADSORPTION CAPACITY
OF VARIOUS ADSORBENTS FOR NICKEL

Adsorbent	Adsorption capacity (mg/g)	Reference
Tea industry waste	11.29	50
Bassage fly ash	2.26	56
Soil shale ash	0.098	57
Coffee	6.47	58
Coarse tea	7.36	58
Zeolite	5.20	58
Iron oxide	98.00	59
Saw dust	0.005	60
Tea factory waste	18.42	61
Fly ash	0.03	62
Baker's yeast	11.40	63
Sheep manure waste	7.20	64
Sphagnum moss peat	9.18	65
Herbaceous peat	4.84	66
Bentonite	4.00	67
Bone char	100.00	68
Silica fume	27.78	This study

SEM micrographs: Figs. 9a,b show the SEM micrographs of silica fume sample before and after nickel adsorption. It is clear that the silica fume has considerable number of heterogeneous layers of pores. Thus, there is a good possibility for nickel to be adsorbed[69,70]. It is clear that, silica fume has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. Based on analysis of the images taken by SEM before and after the dye adsorption process, highly heterogeneous pores within silica fume particles were observed. After adsorption process, the pores were packed with nickel ion and this finding revealed the coverage of the modified waste material surface with molecular cloud of nickel ion[71,72].

Conclusion

It is shown that there is an approximate linear relationship between absorbance and nickel concentration in the aqueous solutions. The removal of nickel increases with increasing time in the first 0.5 h and thereafter the removal is not significant. The effect of initial concentration indicates that the total nickel ion adsorbed increases sharply in the beginning and then slowly towards the end of the run. The absorption amount of nickel increase with increasing pH and maximum adsorption of nickel
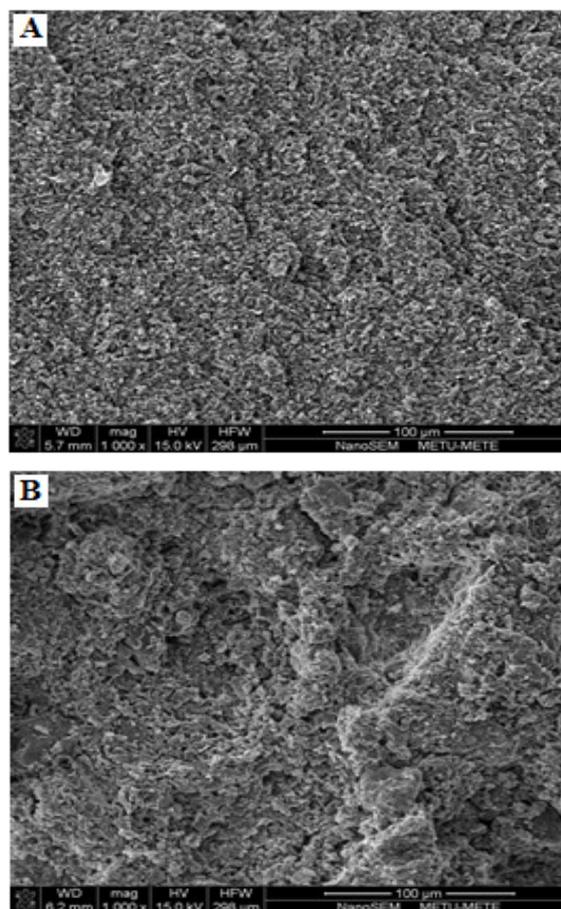
Fig. 9.   SEM images of native silica fume (a) and nickel loaded silica fume (b)

ions are obtained at pH 5. The degree of adsorption increases with increasing temperature and maximum adsorption of nickel ions are obtained at 25 °C. The adsorbent concentration increases when the number of adsorbent particles surrounding the metal ions increases. Based on the correlation coefficient values, it has been deduced that Freundlich model better fitted to the experimental data. As a result, silica fume is a valuable material for removal of nickel ions and its use for the removal of nickel ions from the aqueous solutions can potentially reduce the remediation costs.

REFERENCES

1. V.K. Gupta and A. Rastogi, *J. Hazard. Mater.*, **154**, 347 (2008).
2. S. Kalyani, P. Srinivasa Rao and A. Krishnaiah, *Chemosphere*, **57**, 1225 (2004).
3. D. Bozic, V. Stankovic, M. Gorgievski, G. Bogdanovic and R. Kovacevic, *J. Hazard. Mater.*, **171**, 684 (2009).
4. Y. Bulut and Z. Tez, *J. Environ. Sci. (China)*, **19**, 160 (2007).
5. F.V. Pereira, L.V.A. Gurgel and L.F. Gil, *J. Hazard. Mater.*, **176**, 856 (2010).
6. A.B. Albadarin, A.H. Al-Muhtaseb, N.A. Al-laqtah, G.M. Walker, S.J. Allen and M.N.M. Ahmad, *Chem. Eng. J.*, **169**, 20 (2011).
7. P.M. Choksi and V.Y. Joshi, *Desalination*, **208**, 216 (2007).

8. E. Kalkan, H. Nadaroglu and N. Demir, *Desalination Water Treat.*, **44**, 180 (2012).

9. X. Huang, M. Sillanpëë, B. Dou and E.T. Gjessing, *Environ. Pollut.*, **156**, 270 (2008).

10. T. Aman, A.A. Kazi, M.U. Sabri and Q. Bano, *Colloid Surf. B*, **63**, 116 (2008).

11. Y. Jiang, H. Pang and B. Liao, *J. Hazard. Mater.*, **164**, 1 (2009).

12. H. Cho, D. Oh and K. Kim, *J. Hazard. Mater.*, **127**, 187 (2005).

13. P.X. Sheng, Y.P. Ting, J.P. Chen and L. Hong, *J. Colloid Interf. Sci.*, **275**, 131 (2004).

14. V. Padmavathy, P. Vasudevan and S.C. Dhingra, *Process Biochem.*, **38**, 1389 (2003).

15. H. Hasar, *J. Hazard. Mater.*, **97**, 49 (2003).

16. I. Villaescusa, N. Fiol, M. Martinez, N. Miralles, J. Poch and J. Serarols, *Water Res.*, **38**, 992 (2004).

17. Z. Aksu, *Process Biochem.*, **38**, 89 (2002).

18. E. Malkoc and Y. Nuhoglu, *J. Hazard. Mater.*, **127**, 120 (2005).

19. B. Tansel, *Recent Pat. Chem. Eng.*, **1**, 17 (2008).

20. T.A. Kurniawan, G.Y.S. Chan, W.H. Lo and S. Babel, *Sci. Total Environ.*, **366**, 409 (2006).

21. A.F. Bertocchi, M. Ghiani, R. Peretti and A. Zucca, *J. Hazard. Mater.*, **134**, 112 (2006).

22. A. Bhatnagar, A.K. Jain, A.K. Minocha and S. Singh, *Sep. Sci. Technol.*, **41**, 1881 (2006).

23. S.V. Dimitrova and D.R. Mehanjiev, *Water Res.*, **34**, 1957 (2000).

24. E. Kalkan, H. Nadaroglu, N. Dikbas, E. Tasgin and N. Çelebi, *Pol. J. Environ. Stud.*, **22**, 105 (2013).

25. R.D. Hooton, *ACI Mater. J.*, **90**, 143 (1993).

26. C.D. Atis, F. Ozcan, A. Kilic, O. Karahan, C. Bilim and M.H. Severcan, *Build. Environ.*, **40**, 1678 (2005).

27. A.H. Toutanji and Z. Bayasi, *Cement Concr. Res.*, **29**, 497 (1999).

28. E. Kalkan, *Eng. Geol.*, **87**, 220 (2006).

29. E. Kalkan, *Appl. Clay Sci.*, **52**, 345 (2011).

30. E. Kalkan and S. Akbulut, *Eng. Geol.*, **73**, 145 (2004).

31. E. Kalkan, *Appl. Clay Sci.*, **43**, 296 (2009).

32. E. Kalkan, *Cold Reg. Sci. Technol.*, **58**, 130 (2009).

33. E. Kalkan, *Appl. Clay Sci.*, **80-81**, 117 (2013).

34. B.D. Ozturk, H. Filik, E. Tutem and R. Apak, *Talanta*, **53**, 263 (2000).

35. J.D. Seader and E.J. Henly, Separation Process Principles, John Wiley & Sons Inc. (2006).

36. R. Saravanane, T. Sundararajan and S. Sivamurthyreddy, *Indian J. Environ. Health*, **44**, 78 (2002).

37. M. Bansal, D. Singh, V.K. Garg and P. Rose, *World Acad. Sci. Eng. Technol.*, **51**, 431 (2009).

38. N. Celebi, H. Nadaroglu and E. Kalkan, *Fresenius Environ. Bull.*, **21**, 1982 (2012).

39. V.K. Gupta, C.K. Jain, I. Ali, M. Sharma and V.K. Saini, *Water Res.*, **37**, 4038 (2003).

40. P.S. Kumar, K. Ramakrishnan and R. Gayathri, *J. Eng. Sci. Technol.*, **5**, 232 (2010).

41. H.A. Elliott and C.P. Huang, *Water Res.*, **15**, 849 (1981).

42. C.H. Weng and C.P. Huang, Proceedings of the 1990 Environmental Engineering Speciality Conference, ASCE, New York, NY, USA, p. 923 (1990).

43. B. Bayat, *J. Hazard. Mater.*, **95**, 251 (2002).

44. M. Imamoglu and O. Tekir, *Desalination*, **228**, 108 (2008).

45. S.S. Shukla, L.J. Yu, K.L. Dorris and A. Shukla, *J. Hazard. Mater.*, **121**, 243 (2005).

46. A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, *J. Colloid Interf. Sci.*, **282**, 320 (2005).

47. M.M. Rashad, M.M. Hessien, E.A. Abdel-Aal, K. El-Barawy and R.K. Singh, *Powder Technol.*, **205**, 149 (2011).

48. Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi and A. Montiel, *J. Hazard. Mater.*, **156**, 412 (2008).

49. J. Das, B.S. Patra, N. Baliarsingh and K.M. Parida, *Appl. Clay Sci.*, **32**, 252 (2006).

50. S. Cay, A. Uyanik and A. Ozasik, *Sep. Purif. Technol.*, **38**, 273 (2004).

51. B.M.W.P.K. Amarasinghe and R.A. Williams, *Chem. Eng. J.*, **132**, 299 (2007).

52. J. Nouri, I. Ghodbane, O. Hamdaoui and M. Chiha, *J. Hazard. Mater.*, **149**, 115 (2007).

53. H. Nadaroglu, E. Kalkan and N. Demir, *Desalination*, **251**, 90 (2010).

54. V. Bansal, A.P. O'Mullane and S.K. Bhargava, *Electrochem. Commun.*, **11**, 1639 (2009).

55. R.E. Treybal, Mass Transfer Operations, McGraw Hill, New York, p. 447 (1980).

56. V.K. Gupta and I. Ali, *Sep. Purif. Technol.*, **18**, 131 (2000).

57. R. Shawabkeh, A. Al-Harahsheh and A. Al-Otoom, *Sep. Purif. Technol.*, **40**, 251 (2004).

58. M. Minamisawa, H. Minamisawa, S. Yoshida and N. Takai, *J. Agric. Food Chem.*, **52**, 5606 (2004).

59. S.K. Srivastava, G. Bhattacharjee, R. Tyagi, N. Pant and N. Pal, *Environ. Technol. Lett.*, **9**, 1173 (1988).

60. M. Ajmal, A. Hussain Khan, S. Ahmad and A. Ahmad, *Water Res.*, **32**, 3085 (1998).

61. F.P. Padilha, F.P. de França and A.C.A. da Costa, *Bioresour. Technol.*, **96**, 1511 (2005).

62. M. Rao, A.V. Parwate and A.G. Bhole, *Waste Manage.*, **22**, 821 (2002).

63. V. Padmavathy, P. Vasudevan and S.C. Dhingra, *Process Biochem.*, **38**, 1389 (2003).

64. F.A.A. Al-Rub, M. Kandah and N. Al-Dabaybeh, *Eng. Life Sci.*, **2**, 111 (2002).

65. Y.S. Ho, D.A. John Wase and C.F. Forster, *Water Res.*, **29**, 1327 (1995).

66. R. Gundogan, B. Acemioglu and M.H. Alma, *J. Colloid Interf. Sci.*, **269**, 303 (2004).

67. E.G. Pradas, M.V. Sanchez, E.C. Cruz, M.S. Viciana and M.E. Perez, *J. Chem. Technol. Biotechnol.*, **59**, 289 (1994).

68. G. McKay, Use of Adsorbents for the Removal of Pollutants from Waste Water, CRC Press, Bocca Baton, FL (1985).

69. M. Arami, N. Limaee and N. Mahmoodi, *Chem. Eng. J.*, **139**, 2 (2008).

70. M.C.S. Reddy, V. Nirmala, C. Ashwini, *Arab. J. Chem.*, (2013) doi:10.1016/j.arabjc.2013.09.029.

71. Mahmoodi, R. Salehi, M. Arami and H. Bahrami, *Desalination*, **267**, 64 (2011).

72. H. Nadaroglu, N. Celebi, E. Kalkan and G. Tozsin, *Jokull J.*, **63**, 87 (2013).