DHANESH SINGH*, NARENDRA S. RAWAT**

USE OF BITUMINOUS COAL AS SORBENT FOR THE REMOVAL OF Ni^{2+} FROM WASTEWATER

The ability of powdered bituminous coal to remove Ni^{2+} from aqueous system has been investigated. The removal of Ni^{2+} on bituminous coal by sorption has been found to be concentration, pH, temperature and sorbent size dependent. The extent of removal is favourable at high temperature. Maximum sorption (71.6%) has been found at pH 6.5 and variation in sorption with pH has been explained on the basis of surface complex formation. The process of removal follows the first order kinetics.

1. INTRODUCTION

Nickel occurs mostly in the form of the oxides, silicates and sulphides and is usually associated with other sulphide, silicate or arsenide minerals. Water becomes contaminated with nickel via several sources. Elevated environmental levels of nickel may come from a variety of sources such as tableware plating [1], metal finishing [2], small parts fabrication, silver refineries, automotive plating of zinc base casting [3] and plating plants.

Nickel is a commonly occurring constituent of soil and plant [4]. Nickel has been reported to be toxic. Nickel carbonyl causes lung cancer [5]. Certain doses of nickel sulphate induce myocardial and liver damages [6]. Thus removing nickel from water is important.

Several works for the removal of Ni^{2+} have been carried out through precipitation [7], biological treatment [8] and adsorption process [9].

The aim of this work is to study the capability of bituminous coal to remove Ni^{2+} from wastewater. Bituminous coal has been found quite satisfactory to the adsorption of lead [10] and cadmium. The present investigations have been designed to explore the feasibility of Ni^{2+} removal by bituminous coal dust at different pH, temperatures, concentrations and sorbent sizes.

* Department of Chemistry, Govt. D.B. Girl's P.G. College, Raipur-492001, India.
** Department of Petroleum Engineering, Indian School of Mines, Dhanbad-826004, India.

2. EXPERIMENTAL

The adsorbent bituminous coal was obtained from Bankolla Colliery of Raniganj field. It was ground and sieved through 45 μm, 75 μm and 150 μm sieves. Physical and chemical characteristics of the samples were determined following standard method and given in table 1. The sorption experiments were carried out by shaking 1.0 g of bituminous coal with 25 cm^3 of aqueous $NiSO_4 \cdot 6H_2O$ (AR grade) solution of desired concentration in different polythene bottles. The desirable pH of solution was maintained by 0.05 M HCl or NaOH solution using pH-meter (Systronics 335). The samples were shaken in a temperature-controlled shaking machine. The progress of adsorption was determined by centrifuging the sorbate solution at certain time and analysing the supernatant for Ni^{2+} unadsorbed by Atomic Absorption Spectrophotometer (Perkin Elmer 2380).

Table 1

Chemical and physical characteristics of different coal sorbents

Constituents/coal size	45 μm	75 μm	150 μm
SiO_2	58.19	58.27	58.11
Al_2O_3	26.73	26.54	26.92
Fe_2O_3	8.89	8.81	8.82
CaO	1.56	1.56	1.52
MgO	1.13	1.17	1.17
MnO	0.01	0.28	0.24
TiO_2	1.78	1.79	1.79
Particle diameter (cm)	44×10^{-4}	71×10^{-4}	139×10^{-4}
Porosity $(cm \cdot cm^{-1})$	0.35	0.35	0.35
Surface area $(m^2 \cdot g^{-1})$	5.36	5.19	4.81
Density $(g \cdot cm^{-3})$	1.41	1.38	1.39
Moisture (%)	5.62	5.54	5.47
Volatile matter (%)	26.40	26.04	25.97
Ash (%)	20.54	20.49	20.47
Fixed carbon (%)	47.44	47.93	48.09

3. RESULTS AND DISCUSSION

Bituminous coal exhibits considerable ion-exchange property due to hydroxyl or carboxylic functional groups which were found to be present in this coal by IR study. Isomorphous replacement, broken bonds and lattice defects may contribute to cation-exchange capacity. The possibility of intraparticle transport of sorbate within the pores of bituminous coal is expected because of its porous nature.

3.1. EFFECT OF CONTACT TIME AND CONCENTRATION

The removal of Ni^{2+} by bituminous coal decreases from 71.6% to 58.8% by increasing Ni^{2+} concentration from $100 \text{ mg} \cdot \text{dm}^{-3}$ to $250 \text{ mg} \cdot \text{dm}^{-3}$ at 30°C, pH 6.5 and 45 μm sorbent size. The amount of Ni^{2+} adsorbed increases with time and attains equilibrium in 120 minutes (figure 1). The time of equilibriation is independent of concentration.
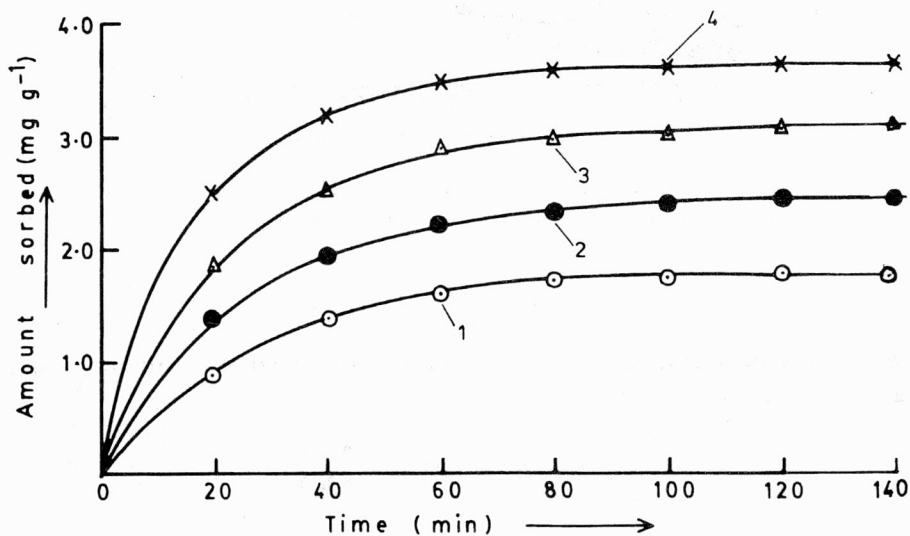

Fig. 1. Effect of concentration on the sorption of Ni^{2+} on bituminous coal dust
$1 - 100 \text{ mg} \cdot \text{dm}^{-3}$; $2 - 150 \text{ mg} \cdot \text{dm}^{-3}$; $3 - 200 \text{ mg} \cdot \text{dm}^{-3}$;
$4 - 250 \text{ mg} \cdot \text{dm}^{-3}$; pH = 6.5;
temperature = 30°C; coal dust size = 45 μm; ionic strength = 0.05M $NaClO_4$

3.2. SORPTION ISOTHERM

The equilibrium data for the sorption of Ni^{2+} on bituminous coal at 30°C, 40°C and 50°C and pH 6.5 follows the rearranged Langmuir equation [9]

$$\frac{C_e}{q_e} = \frac{1}{Q^o \cdot b} + \frac{C_e}{Q^o} \tag{1}$$

where C_e ($\text{mg} \cdot \text{dm}^{-3}$) is equilibrium concentration of Ni^{2+} and q_e is the amount of Ni^{2+} sorbed at equilibrium and Q^o ($\text{mg} \cdot \text{g}^{-1}$) and b ($\text{dm}^3 \cdot \text{mg}^{-1}$) are the Langmuir constants indicating sorption capacity and energy of sorption, respectively. The linear plot of C_e/q_e versus C_e (figure 2) suggests the applicability of the Langmuir

model and formation of monolayer coverage of Ni^{2+} on the surface of bituminous coal dust. The values of Q^o and b are calculated from the slope and intercept of the straight lines.
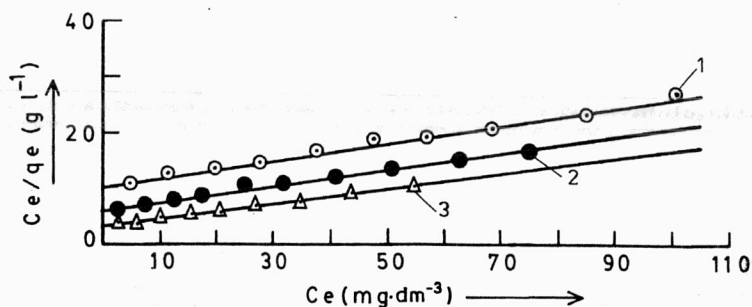

Fig. 2. The Langmuir isotherm for the sorption of Ni^{2+} on bituminous coal dust
$1 - 30°C$; $2 - 40°C$; $3 - 50°C$; $pH = 6.5$; coal dust size = 45 μm; ionic strength = 0.5M $NaClO_4$

3.3. SORPTION DYNAMICS

The kinetics of sorption of Ni^{2+} on bituminous coal was studied using the Lagergren equation

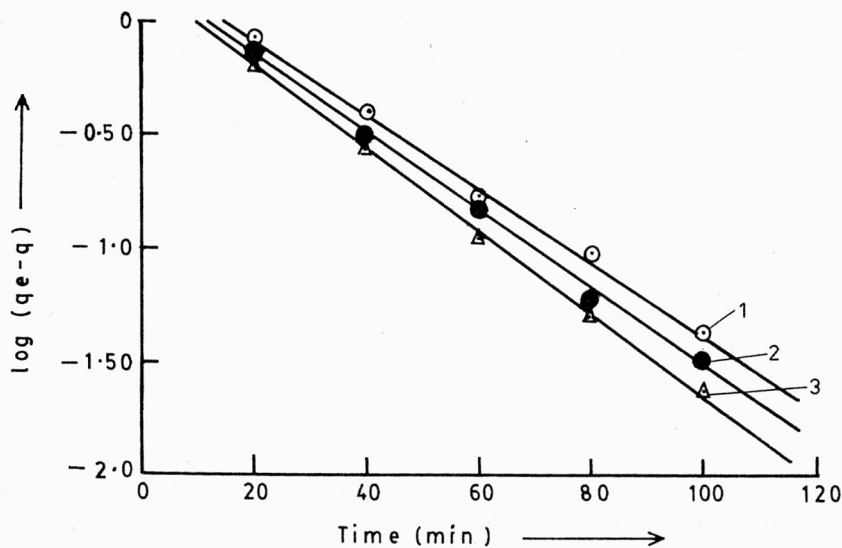$$\log(q_e - q) = \log q_e - \frac{K \cdot t}{2.303} \tag{2}$$

Fig. 3. The Lagergren plot for the sorption of Ni^{2+} on bituminous coal dust
$1 - 30°C$; $2 - 40°C$; $3 - 50°C$; $pH = 6.5$;
Ni^{2+} concentration = 100 mg·dm⁻³; coal dust size = 45 μm; ionic strength = 0.05M $NaClO_4$

where q and q_e (both in mg·g^{-1}) are the amounts of Ni^{2+} sorbed at the time t and at equilibrium, respectively. The values of rate constants K were calculated from the slope of the linear plot of log $(q_e - q)$ versus t (figure 3) and found to be 3.83×10^{-2}, 4.03×10^{-2} and 4.31×10^{-2} min^{-1} at 30°C, 40°C and 50°C, respectively. The linearity of the plots (figure 3) also indicates that the process follows the first order kinetics. The rate constants at different temperatures indicate that Ni^{2+} is sorbed on the surface of bituminous coal dust at faster rate at higher temperature.

3.4. EFFECT OF TEMPERATURE

The rate of sorption of Ni^{2+} on bituminous coal increases by increasing temperature (figure 4). The amount of Ni^{2+} sorbed increases from 7.16% to 89.6% by increasing temperature from 30°C to 50°C, respectively, indicating that the process is endothermic. Sorption capacity Q^o and sorption energy b also increase (table 2) by increasing temperature, suggesting that the active centres available for sorption of Ni^{2+} increase with temperature [12]. The increase in the uptake of Ni^{2+} with temperature may also be due to the enhanced rate of interparticle diffusion of sorbate [13].
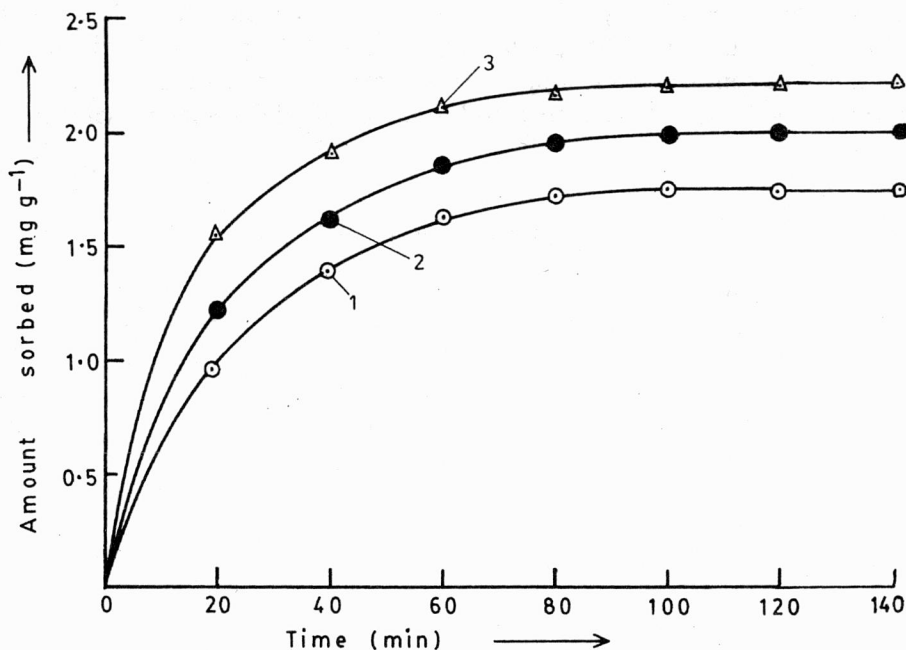

Fig. 4. Effect of temperature on the sorption of Ni^{2+} on bituminous coal dust
1 – 30°C; *2* – 40°C; *3* – 50°C; pH=6.5; Ni^{2+} concentration=100 mg·dm^{-3};
coal dust size=45 μm; ionic strength=0.5M NaClO$_4$

Table 2

Values of Q^o and b at different temperatures

Temperature (°C)	Q^o (mg·g^{-1})	b (dm^3·mg^{-1})
30	6.4705	0.0154
40	7.2998	0.0228
50	8.3333	0.0400

The changes in free energy G^o, enthalpy H^o and entropy S^o of sorption (table 3) were calculated using the following equations:

$$G^o = RT_1 \ln K_1,$$

$$H^o = R\frac{T_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1},$$

$$S^o = \frac{H^o - G^o}{T_1}$$

where K_1 and K_2 are the equilibrium constants at the temperatures T_1 and T_2, respectively. The values of equilibrium constants at each temperature were obtained from the limiting slope of sorption isotherm at zero concentration. The negative value of G^o (table 4) indicates the spontaneous nature of the process. Positive values of H^o at different temperatures support endothermic nature of the process. The positive values of S^o may be due to dissolution of soluble species present in coal.

Table 3

Thermodynamic parameters

Temperature (°C)	G^o (Kcal·mol^{-1})	H^o (Kcal·mol^{-1})	S^o (Kcal·mol^{-1})
30	−0.75	11.37	41.32
40	−1.15	18.40	61.18
50	−1.78	−	−

Table 4

Values of Q^o and b at different pH

pH	Q^o (mg·g^{-1})	b (dm^3·mg^{-1})
2.0	4.5163	0.0092
4.0	4.742	0.0117
6.5	6.4705	0.0154

3.5. EFFECT OF pH

The removal of pollutants from wastewater by sorption is highly pH-dependent which affects the surface charge of sorbent, the degree of ionisation and speciation of sorbate.
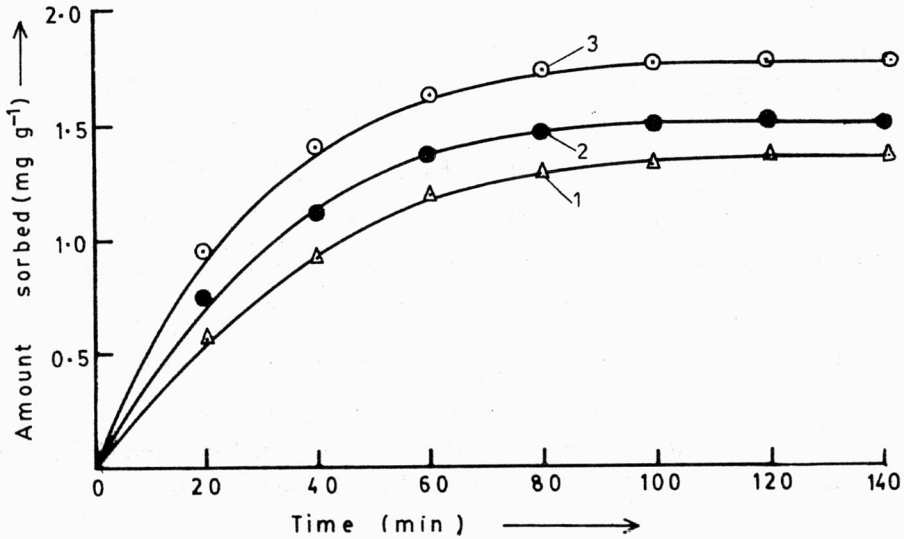

Fig. 5. Effect of pH on the sorption of Ni^{2+} on bituminous coal dust
1 – pH = 2.0; *2* – pH = 4.0; *3* – pH = 6.5; temperature = 30°C; Ni^{2+} concentration = 100 mg·dm^{-3}; coal dust size = 45 μm; ionic strength = 0.05M $NaClO_4$
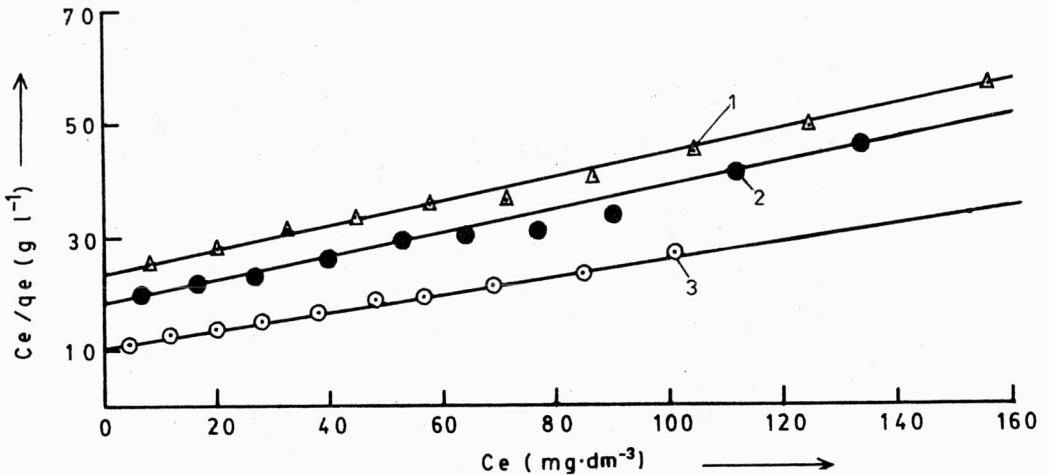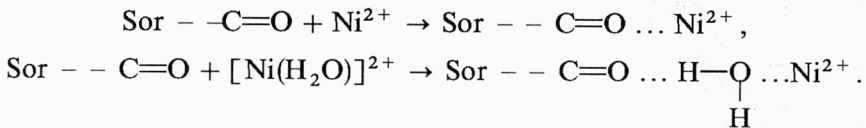

Fig. 6. The Langmuir isotherm for the sorption of Ni^{2+} on bituminous coal dust
1 – pH = 2.0; *2* – pH = 4.0; *3* – pH = 6.5; temperature = 30°C;
Ni^{2+} concentration = 100 mg·dm^{-3}; coal dust size = 4.5 μm; ionic strength = 0.05M $NaClO_4$

The rate of sorption increases with increasing pH of solution (figure 5). The amount of Ni^{2+} sorbed increases from 54.4% to 71.6% by increasing pH from 2.0 to 6.5, respectively, at 30°C, 45 μm sorbent size and Ni^{2+} concentration of 100 mg dm^{-3}. The capacity of sorbent (table 4) also increases with the increase of pH. These capacities were also calculated applying linear Langmuir equation (1) (figure 6). The sorption of Ni^{2+} on bituminous coal may be explained based on the ion-exchange mechanism. Over most of pH range, Ni^{2+} and $NiSO_4$ are the predominant species and $Ni(OH)_2$ and $[Ni(OH)_3]^-$ appear only when pH is highly basic [14].

In coal there are hydroxyl or carboxylic groups which can interact with Ni^{2+} as follows [14]:

$$Sor - - OH + Ni^{2+} \rightarrow Sor - - ONi^+ + H^+,$$

$$Sor - - COOH + Ni^{2+} \rightarrow Sor - - COONi^+ + H^+.$$
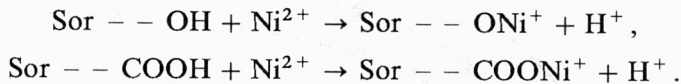
There may be polar interaction between ketone groups [15] and Ni^{2+}

$$Sor - -C{=}O + Ni^{2+} \rightarrow Sor - - C{=}O \ldots Ni^{2+},$$

$$Sor - - C{=}O + [Ni(H_2O)]^{2+} \rightarrow Sor - - C{=}O \ldots H-\underset{H}{\overset{|}{O}} \ldots Ni^{2+}.$$

Thus, positive charge developed on sorbate surface repel Ni^{2+}, thereby decreasing sorption in acidic medium. In alkaline medium, nickel gets precipitated.

3.6. EFFECT OF PARTICLE SIZE

The rate of sorption of Ni^{2+} on bituminous coal increases by decreasing sorbent size (figure 7). The amount of Ni^{2+} sorbed increases from 56.8% to 71.6% by
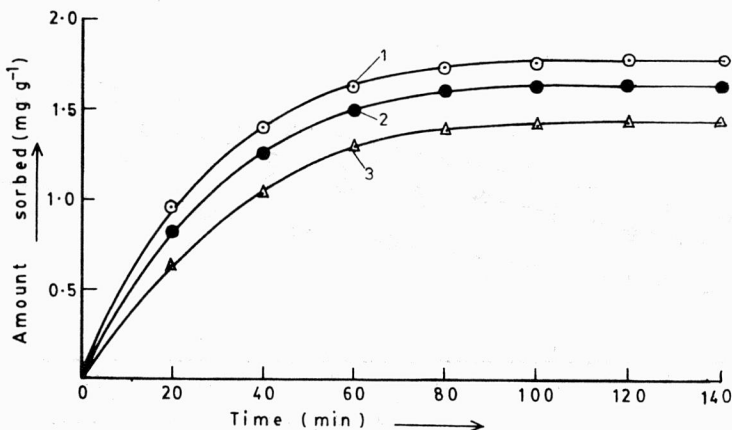

Fig. 7. Effect of particle size on the sorption of Ni^{2+} on bituminous coal dust
1 – 45 μm; 2 – 75 μm; 3 – 150 μm; pH = 6.5; temperature = 30°C;
Ni^{2+} concentration = 100 mg·dm^{-3}; ionic strength = 0.05M $NaClO_4$

decreasing the size of coal particles from 150 μm to 45 μm, respectively, at 30°C, pH 6.5 and Ni^{2+} concentration of 100 mg·dm^{-3}. The capacity Q^o and adsorption energy b also increase by decreasing sorbent size (table 5). The values of Q^o and b for different fractions of coal were determined using the linear Langmuir equation (figure 8). The increase in the amount of Ni^{2+} sorbed by the sorbent particles of decreasing size may be due to large surface area of smaller size sorbent.
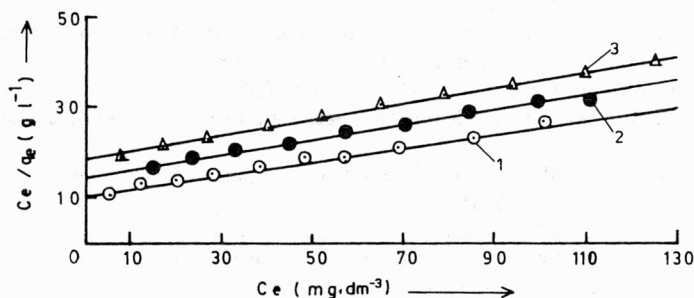

Fig. 8. The Langmuir isotherm for the sorption of Ni^{2+} on bituminous coal dust
1 – 45 μm; 2 – 75 μm; 3 – 150 μm; pH = 6.5; temperature = 30°C;
ionic strength = 0.05M NaClO$_4$

Table 5

Values of Q^o and b for different particle sizes

Coal size (μm)	Q^o (mg·g^{-1})	b (dm^3·mg^{-1})
45	6.4705	0.0154
75	5.8749	0.0113
150	5.6248	0.0093

4. CONCLUSIONS

The use of bituminous coal as a sorbent for the removal of Ni^{2+} from aqueous solution was investigated. It was observed that:

(i) Sorption increased with the increase of temperature and pH of medium.

(ii) Sorption increased with the decrease in sorbent size.

(iii) Maximum sorption was at pH 6.5, sorbent size of 45 μm and Ni^{2+} concentration equal to 100 mg·dm^{-3}.

From the above observations it is clear that bituminous coal dust may be effectively used as a sorbent for the removal of Ni^{2+} from wastewater under suitable conditions. Similar work on activated bituminous coal and fly ash as a sorbent is also in progress.

REFERENCES

[1] NEMEROW N.L., *Theories and Practices of Industrial Waste*, Wesley Publishing Co. Inc., 1963.
[2] ADERSON J.S., LOBST E.H., Water Poll. Cont. Fed., 1968, 40, 1786.
[3] LOWE W., Water Poll. Cont. Fed., 1970, London, 2780.
[4] *Geobotany and Biochemistry in Mineral Exploration by Brooks*, R.P. Harper and Row (ed.), 1972, New York.
[5] BAILEY R.A., CLARK H.M., FERRIS J.P., KRANSE S., STRONG R.L., *Chemistry of the Environment*, Academic Press, 1981, New York.
[6] [In:] *Cassarett and Doull's Toxicology – The Basic Science of Poison*, 2nd ed., Hammond B.P., Belides R.P. (ed.), McMillan Publishing Co., 1980, New York.
[7] NILSON R., Water Res., Pergamon Press, 1971, 5, 51.
[8] NIELBOER E., RICHARDSON H.S., Env. Poll., 1980, B1, 3.
[9] VISHWAKARM P.P., SINGH V.N., Asian Env., 1989, 11, 49.
[10] SINGH D., RAWAT N.S., Ind. J. of Chem. Technology, 1994, 1, 266–270.
[11] RAWAT N.S., RANJANA, SINGH D., Ind. J. of Environ. Prot., 1993, 13, 193–197.
[12] MCKAY G., OTTERBURNS M.S., SWEENEY A.G., Water Res., 1980, 14, 21.
[13] BYE G.S., MCTROY M., MALATI M.A., Can. J. 1972, 50, 1642.
[14] BODEK I., LYMAN W.J., REEHI W.F., ROSENBLATT D.H., *Environmental Inorganic Chemistry*, publication of SETAC, Pergamon Press, Inc., 1988, New York.
[15] PARFITT R.L., MORTL M.M., Soil Sci. Soc. Am. Proc., 1968, 32, 355.

UŻYCIE WĘGLA KAMIENNEGO JAKO SORBENTA DO USUWANIA Ni²⁺ ZE ŚCIEKÓW

Badano zdolność sproszkowanego węgla kamiennego do usuwania Ni^{2+} z roztworów wodnych. Stwierdzono, że usuwanie Ni^{2+} w wyniku sorpcji na węglu kamiennym zależy od stężenia, pH, temperatury i wielkości sorbenta. Wysoka temperatura korzystnie wpływa na usuwanie Ni^{2+}. Sorpcja była najbardziej efektywna dla pH = 6,5, a jej zmiany wraz z pH wytłumaczono powstawaniem kompleksów powierzchniowych. Proces usuwania Ni^{2+} przebiega zgodnie z kinetyką pierwszego rzędu.