ELSEVIER

Removal and recovery of heavy metals from electroplating wastewater by using Kyanite as an adsorbent

Mohammad Ajmal*, Rifaqat A.K. Rao, Rais Ahmad, Jameel Ahmad, Liaqat A.K. Rao[1]

Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India

Abstract

Kyanite, a commercial mineral has been utilized as an adsorbent for the removal of heavy metals, such as Ni(II), Zn(II), Cr(VI) and Cu(II) from electroplating wastewater. The effect of contact time, pH, concentration, adsorbent doses, particle size of the adsorbent, salinity and hardness, both in natural and wastewater on the adsorption of Cu(II) have been studied in detail. The adsorption of metal ions seems to be an ion exchange process. The adsorbed metals ions from electroplating wastewater were recovered by batch as well as column operation using dilute HCl solution. The column operation was found to be more effective compared to batch process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Kyanite; Desorption; Batch process

1. Introduction

Electroplating industries are one of the oldest industries concentrating on surface finishing and metal deposition. However, these processes produce metal-contaminated wastewater. Among these contaminants, copper is an important metal of industrial use and its ingestion beyond the permissible level [1] causes various types of acute and chronic disorder in man, such as hemochromatosis, gastrointestinal catarrh, cramps in the calves and a skin dermatitis brasschills, usually accompanied by high fever [2,3].

---

* Corresponding author. Tel.: +91-571-700920-23.
E-mail address: rais45@mailcity.com (M. Ajmal).
[1] Department of Geology, Aligarh Muslim University, Aligarh, India.

The industrial sources of copper in the wastewater include pulp and paper mills, fertilizers, petroleum refineries, basic steelwork foundries, non-ferrous metal works, motor vehicles, aircraft plating and finishing [4–6].

The most widely used method for removing Cu(II) is precipitation as insoluble hydroxide at alkaline pH [7–10] or as sulfides [11,12]. However, major problem with this precipitation is the disposal of the precipitated cupric hydroxide [13]. Ion-exchange treatment which is the second most widely used method for copper removal does not present a sludge disposal problem and has the advantage of reclamation of Cu(II) [14]. However, ion-exchange treatment does not appear to be economical [15].

The adsorption phenomenon has been found economically appealing for the removal of toxic metals from wastewater. Several adsorbents have been used earlier for the treatment of Cu-rich effluents at the solid–solution interface [16–19]. It has been reported that some aquatic plants [20–23], agricultural by-products [24], waste tea leaves [25], sawdust [26], natural zeolite [27], lignin [28], red mud and flyash [29], iron oxide coated sand [30], activated carbon [31,32] and recycled iron-bearing material [33,34] have the capacity to adsorb heavy metals.

The behavior of some adsorbents like silica gel, Fe(III) hydroxide, fruit peel of orange and saw dust for the removal and recovery of Hg^{2+}, Cr^{6+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Mg^{2+} from rivers and industrial wastewater have been studied in our laboratory [35–38]. In our earlier studies, the adsorption properties of pyrolusite (a manganese ore) were explored. Pyrolusite has been used for the removal of Pb(II) from wastewater [39].

Kyanite is a triclinic crystalline mineral like other aluminosilicates and closely approximates Al_2SiO_3. The color is variable ranging from colorless to blue. Kyanite, when calcined, is used in refractory products and it is the most important of the aluminosilicates [40]. Kyanite is a common constituent of the Archaean rocks of India and abundantly available in Singhbum district of Bihar, Himalayas, Andhra Pradesh and Tamil Nadu. The occurrence of Kyanites invariably in crystalline schistose rocks indicate that it is a product of metamorphism of alumina-bearing sediments most clayey materials, which have been metamorphosed under enormous pressure at a great depth in the earth's crust. It occurs extensively in commercial quantities and is used as a refractory material. It is also used in metallurgical, glass and ceramics and cement industries. Kyanite refractories are generally used in furnaces for smelting non-ferrous metals like copper, zinc and nickel alloys [41].

This paper reports the adsorption behavior of various metal ions on Kyanite.

2. Materials and methods

2.1. Preparation of adsorbent

Kyanite was ground and washed thoroughly with distilled water to clean the adhering dust. It was dried in an air at 100–105°C for 24 h. After drying, the adsorbent was sieved through different mesh size. The chemical composition of Kyanites has been reported [41] and is shown in Table 1.

Table 1
Chemical composition of Kyanite

Specific gravity	3.7
SiO_2 (%)	30.2
Al_2O_3 (%)	65.35
Fe_2O_3 (%)	3.19
TiO_2	Trace
CaO	Trace
MgO	Trace

2.2. Adsorbate solution

All chemicals used in making the adsorbate solution were of analytical grade. Stock Cu(II) solution ($1000 \, mg \, l^{-1}$) was prepared from copper nitrate and this solution was used to prepare working solution for other experiments. Solutions of the other metal ions were prepared ($1000 \, mg \, l^{-1}$) by dissolving their chlorides or nitrates in distilled water.

2.3. Batch adsorption studies

Batch adsorption experiments were carried out by shaking 0.5 g of the Kyanite (mesh 50) with 50 ml aqueous Cu(II) solution of $20–100 \, mg \, l^{-1}$ concentration at various pHs (1–12) and at temperature of $30°C$ in several stoppered bottles for retention times varying from 5 to 30 min using a temperature controlled shaker. The study of adsorbent doses was carried out by varying the amount of adsorbent (0.2–1 g). At the end of the predetermined time interval, the adsorbent was removed by the filtration and the equilibrium concentration was determined in the filtrate by atomic absorption spectrophotometry (model GBC-902, Australia) using an air acetylene flame. The amount of metal ions adsorbed on the Kyanite was calculated by subtracting final concentration in solution from initial concentration. The effect of pH on the adsorption of Cu(II) was studied as follows: 100 ml Cu(II) solution ($50 \, mg \, l^{-1}$) was placed in a beaker and the pH of the solution was adjusted by adding 0.5 M HNO_3 or 0.1 M NaOH. The concentration of Cu(II) in this solution was then determined (initial concentration). An aliquot (50 ml) of this solution was placed in a conical flask and treated with 0.5 g of adsorbent and after equilibrium, the final concentration of Cu(II) was determined.

2.4. Desorption of Cu(II)

The desorption studies were carried out by batch as well as by a column process under similar conditions. An aliquot (50 ml) of the sample containing $20 \, mg \, l^{-1}$ Cu(II) was treated with 1 g of adsorbent for 24 h. at pH 6. The solution was then filtered and filtrate was analyzed for Cu(II). The adsorbent was then transferred to another conical flask and treated with 50 ml of 0.05 M HCl solution. It was then filtered after 24 h. and the concentration of the desorbed Cu(II) was determined in the filtrate.

Column studies were conducted using 1 g of Kyanite in a glass column (0.6 cm in diameter) with glass wool support. The adsorbent was washed with distilled water and 50 ml

solution containing 20 mg l^{-1} of Cu(II) were passed through the column. The solution was recycled several time until the effluent showed an absence of Cu(II) ions. The Cu(II) adsorbed was then eluted with 0.05 M HCl solution at a flow rate of 1 ml min^{-1}. The Cu(II) eluted was collected in 10 ml fractions and the concentration was then determined by atomic absorption spectrophotometry. The same experiment was repeated and Cu(II) was eluted with increasing concentrations of HCl (0.05–0.5 M HCl).

2.5. Recovery of Cu(II) and other metal ions from electroplating wastewater

The removal and recovery of various metal ions from electroplating wastewater was carried out by batch as well as by column operations. A sample (50 ml) of the waste was placed in a conical flask. It was treated with 1 g of adsorbent. The removal and recovery was carried out as described above.

In another experiment, 50 ml of the waste was passed through the column containing 1 g of adsorbent and the desorption of Cu(II), Ni(II), Zn(II) and Cr(VI) was carried out as described above.

3. Results and discussion

The adsorption behavior of different metal ions on Kyanites at pH 4 is shown in Fig. 1. The efficiency of adsorption was in the order of Cu(II) > Ni(II) > Cr(VI) > Zn(II).

3.1. Effect of contact time

The adsorption of metal on Kyanite increases with increasing contact time. The Cu(II) uptake versus time curve Fig. 2 shows that equilibrium is attained in 30 min. The metal uptake versus time curve is single, smooth and continuous leading to saturation, suggesting
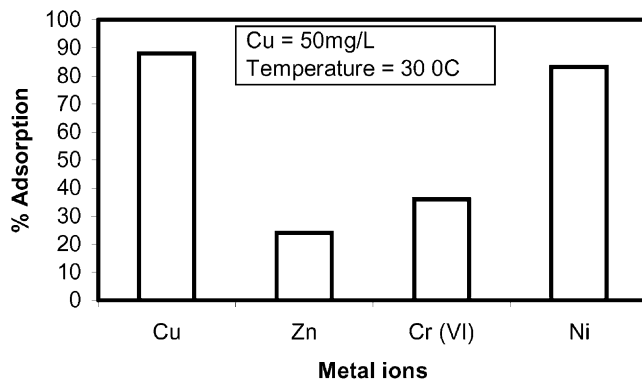

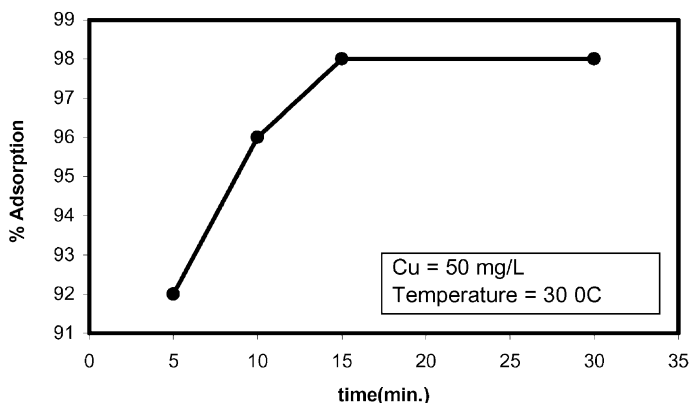Fig. 1. Adsorption of different metal ions on Kyanite.

Fig. 2. Effect of contact time on adsorption.

the possible monolayer coverage of metal ions on the surface of the adsorbent. Similar behavior was observed [42] for the adsorption of Cd(II) by Fe(III) hydroxide.

3.2. Effect of concentration

Fig. 3 shows the percentage removal of Cu(II) as a function of its increased initial concentration at pH 6. It can be concluded that maximum adsorption of Cu(II) occurs at 20 mg l^{-1} initial concentration and the minimum adsorption is observed at 100 mg l^{-1}.

3.3. Effect of pH

The effect of pH on different metal ions has been shown in Table 2 and the effect of pH on the adsorption of Cu(II) by Kyanite is presented in Fig. 4. The pH of the aqueous solution is one of the important controlling parameters in the adsorption process [16]. At lower
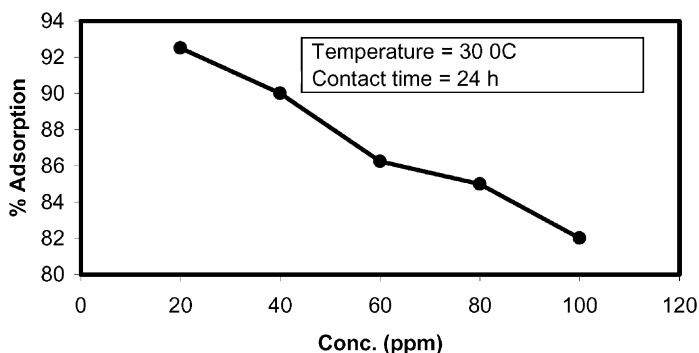

Fig. 3. Effect of concentration on adsorption.

Table 2
Effect of pH on the adsorption of different metal ions[a]

Metals	pH				
	2	4	6	8	10
Cu(II)	44	86	90	100	100
Zn(II)	60	60	73.5	91.5	94.5
Ni(II)	80	78.5	72.5	80	77.5
Cr(VI)	80	78	72	80	76.5

[a] Results are in percent adsorption.

pH values, the H^+ ions compete with metal cation for the exchange site in the system. The heavy metal cations are completely released under circumstances of extreme acidic condition [4]. The amount of adsorption increases from 44 to 88% as the pH is increased from 1 to 6. The minimum adsorption at pH 1 may be due to the high concentration and high mobility of H^+ ions, the hydrogen ions are preferentially adsorbed as compared to Cu(II) ions. The decrease in adsorption with the increase in H^+ ion concentration (low pH), indicates that the adsorption process is via ion exchange. This conclusion was further supported by the fact that 1.43 meq of Na^+ ions are desorbed from Kyanite and 1.58 meq of Cu(II) ions are introduced showing that equivalent or nearly equivalent amounts of Cu(II) ions are exchanged by Na^+ ions. Further, if the process is ion exchange then one must expect higher desorption of metal ions with increased acid concentration.

3.4. Effect of adsorbent doses

The adsorption capacity ($mg\,g^{-1}$) and percentage adsorption of Cu(II) at different doses of Kyanite is shown in Fig. 5. The degree (%) of adsorption increases as the adsorbent dose is increased. It may be concluded that by increasing the adsorbent dose, the removal efficiency
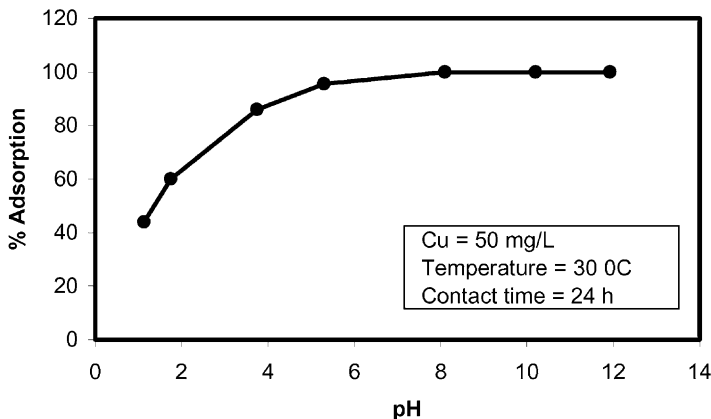
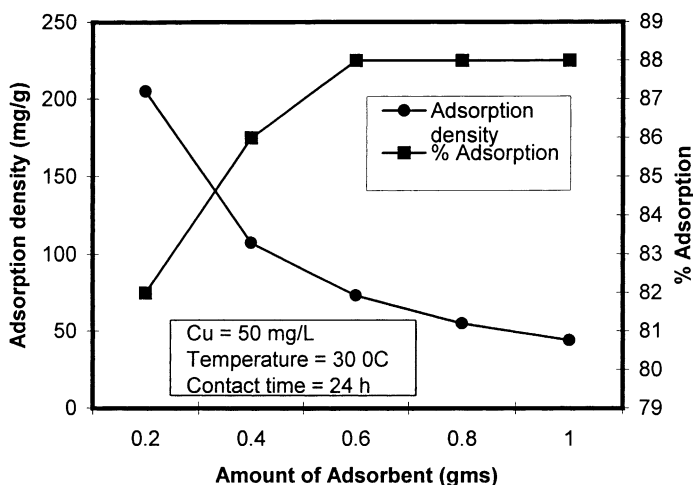

Fig. 4. Effect of pH on adsorption.

Fig. 5. Effect of adsorbent doses on adsorption.

of Kyanite increases, while adsorption density decreases with increase in adsorbent dose. The decrease in adsorption density may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process whereas the number of sites available for adsorption site increases by increasing the adsorbent doses and that results in the increase of removal efficiency [43].

3.5. Effect of particle size

The effect of particle size on Cu(II) adsorption is shown in Table 3. It is evident from the results that the adsorption of Cu(II) increases with decrease in particle size and the peak value was observed by finest particle (200 mesh size), probably because of the large surface area available.

3.6. Effect of salinity and hardness

In order to utilize Kyanite as adsorbent for the treatment of wastewater, it is important to see the effect of various ions usually present in wastewater. Therefore, the adsorption of

Table 3
Effect of particle size on the adsorption process[a]

Mesh size	Amount of Cu(II) adsorbed (mg)	Adsorption (%)
50	2.2	88
100	2.25	90
150	2.25	90
200	2.3	92

[a] Conditions: initial concentration of Cu(II) = 2.5 mg, temperature = 30°C, volume of the solution = 50 ml.

Table 4
Effect of various ions on removal of Cu(II) using Kyanite as adsorbent[a]

Salt added	Concentration $(mg\,l^{-1})$	Amount of Cu(II) adsorbed (mg)	Adsorption (%)
NaCl	100	1.85	74
Na$_2$SO$_4$	100	1.9	76
NaHCO$_3$	100	2.5	100
Tap water		2.5	100
Distilled water		2.1	84

[a] Condition: initial concentration of Cu(II) = 2.5 mg, temperature = 30°C, time = 24 h, volume of the solution = 50 ml.

Cu(II) was studied in presence of various ions, such as $SO_4{}^{2-}$, $HCO_3{}^-$, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, etc. generally present in wastewater. These results are summarized in Table 4.

It can be seen that adsorption of Cu(II) is not affected in presence of Na$_2$SO$_4$ or NaCl. However, the removal of Cu(II) increases in presence of bicarbonates ions to (100%) which may be due to the fact that presence of bicarbonate ions increases the pH of water and hence is responsible for the higher uptake of copper.

3.7. Desorption studies

The adsorption of Cu(II) on Kyanite is highly pH dependent. Therefore, its desorption is possible by controlling the pH. Fig. 6 shows the desorption trend of Cu(II) in column operation. The desorption starts when a solution of 0.05 M HCl is passed through the column. It is important to note that desorption of Cu(II) increases when the concentration of HCl as eluent is increased from 0.05 to 0.1 M and 100% Cu(II) can be eluted from the column within 30 ml of effluent. The increased desorption of Cu(II) with increased acid concentration also indicates that process is via ion exchange. However, the desorption is
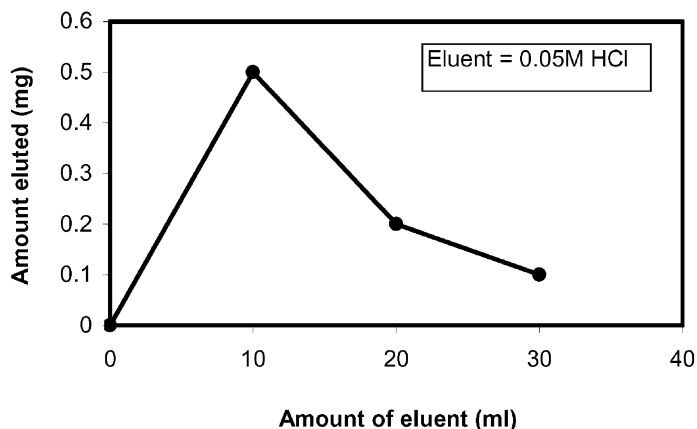

Fig. 6. Desorption of Cu(II) by column operation from Kyanite.

Table 5
Removal and recovery of Cu(II) from synthetic wastewater by batch process (volume of waste = 50 ml)[a]

Metal	Initial concentration (mg)	Amount adsorbed (mg)	Adsorption (%)	Amtount recovered (mg)	Recovery (%)
Cu(II)	1	0.8	80	0.6	75

[a] Condition: temperature = 30°C, contact time = 24 h.

slow and incomplete in a batch process. The desorption of Cu(II) from a solution containing $20 \, mg \, l^{-1}$ Cu(II) in a batch process was 75% (Table 5).

3.8. Removal and recovery of metal ions from electroplating wastewater

Kyanite was utilized for the removal and recovery of various metal ions from electroplating wastewater by batch process. The analysis of electroplating wastewater collected from a company in Aligarh (India) was carried out in our laboratory and the results are shown in Table 6. The adsorbed metal ions were recovered with 0.05 M HCl. These results are summarized in Table 7 (batch process) and in Fig. 7 (column operation). It can be seen that the removal and recovery of metal ions by column operations is much higher in the column than in the batch process. Figs. 1 and 7 indicate that adsorption of Zn(II) and Cr(VI) is very low but their recovery is high (100%). Adsorption of Ni(II) is very high but it could not be recovered with 0.05 M HCl. However, adsorption of Cu(II) was high (88%) and its recovery by column operation was also high (80%).

Table 6
Analysis of electroplating wastewater

TDS	74.1
Conductivity ($uscm^{-1}$)	1140
Cu ($mg \, l^{-1}$)	8
Ni ($mg \, l^{-1}$)	14
Zn ($mg \, l^{-1}$)	3.2
Cr(VI) ($mg \, l^{-1}$)	42
Na ($mg \, l^{-1}$)	182
K ($mg \, l^{-1}$)	10
Ca ($mg \, l^{-1}$)	78
pH	2.2

Table 7
Removal and recovery of metal ions from electroplating wastewater (50 ml) by a batch process

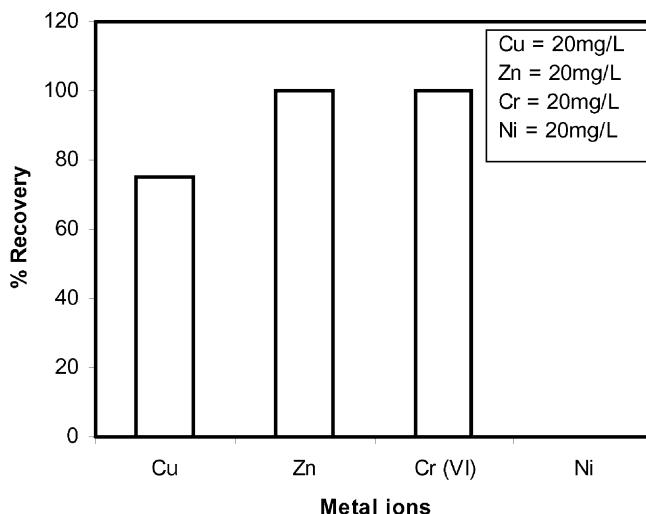| Metal	Initial concentration (mg)	Amount adsorbed (mg)	Adsorption (%)	Amount recovered (mg)	Recovery (%)
Cu(II)	0.4	0.325	81.25	0.125	38.4
Zn(II)	0.16	0.025	15.6	0.015	60
Ni(II)	0.7	0.5	71	0.15	30
Cr(VI)	2.1	0.3	5.5	0.105	35

Fig. 7. Recovery of different metal ions on Kyanite.

4. Conclusions

1. Adsorption studies of Cu(II), Zn(II), Ni(II) and Cr(VI) using Kyanite as an adsorbent have shown the percent adsorption in the order of Cu(II) > Ni(II) > Cr(VI) > Zn(II).
2. Equilibrium was attained in 30 min and the maximum adsorption of Cu(II) was observed at initial concentration of $20\,mg\,l^{-1}$.
3. Complete adsorption is possible at pH 8. The degree (%) of adsorption increases with increase in adsorbent dose (0.2–1 g) and decrease in particle size of Kyanite.
4. The efficiency of adsorbent for copper removal in presence of other ions (usually present in electroplating wastewater) has been studied and it can be concluded that total (100%) adsorption is possible in presence of $100\,mg\,l^{-1}$ $NaHCO_3$ in $50\,mg\,l^{-1}$ of Cu(II) solution.
5. The utility of Kyanite has been demonstrated by removing Cu(II) along with other metal ions present in electroplating wastewater. A concentration of Cu(II) ions as high as $8\,mg\,l^{-1}$ in the waste can be reduced to $1.5\,mg\,l^{-1}$. The adsorbed Cu(II) ions could be recovered with 0.05 M HCl. However, the percent recovery of Cu(II) is increased by column operation (80%) under similar conditions of elution.

References

[1] Indian Standard Institution, Indian Standard for Trace Metal in Drinking Water, 1983, pp. 15–10500.

[2] T.R. Comp, Water and its Impurities, Reinhold, New York, 1964.

[3] A.G. Mukherjee, Environmental Pollution and Health Hazards Causes and Control, Galgotia Publication, New Delhi, 1986.

[4] U. Forstner, C.T.W. Wittman, Metal Pollution in the Aquatic Environment, Springer, New York, 1981.

[5] F. Dalang, J. Buffle, W. Haerdle, Study of the influence of fulvic substances on the adsorption of Cu(II) ions at the kaolinite surface, Environ. Sci. Technol. 18 (3) (1984) 134–140.

[6] D.W. Jenkins, Flow of toxic metals in the environment, in: Proceedings of the International Conference on Environmental Sensing and Assessment, Vol. 1, Willey/Interscience, New York, 1976.

[7] R.F. Weiner, Plating 54 (1967) 1354–1356.

[8] G.L. Culp, R.L. Culp, New Concepts in Water Purification, Van Nostrand Reinhold, New York, 1974.

[9] H. Schilling, P. Schilling, K. Fshwasser, M. Mildner (VEB Projektierung Wasserwirt Schaft Halla), Germany (East), AD 236720 (C1 C02FI/G), Appl. 275 (1986) 738; 30 April 1985, p. 4 (Chem. Abstr 105:231932h).

[10] Z. Zhou, Y. Xue, Kuangye Gongcheng 7 (4) (1987) 24–28.

[11] H.P. Larsen, J.K.P. Shou, L.W. Ross, JWPCF 45 (8) (1973) 1682–1695.

[12] E. Mann, A. Denne, Korresp. Abwasser 33 (10) (1986) 942–943.

[13] D.V. Jackson, Metal Finish. J. 18 (1972) 235–242.

[14] G.H. Botham, W.R.J. Bryson, Dairy Res. 20 (1953) 154–155.

[15] R. Pinner, V. Crowle, Electropl. Met. Finish. 3 (1971) 13–31.

[16] H.A. Elliot, C.P. Huang, Water Res. 15 (1981) 849.

[17] G.C. Gupta, F.L. Harrison, Pollut. Res. 1 (1983) 1.

[18] G.C. Bye, M. McEvoy, M.A. Malati, J. Chem. Tech. Biotechnol. 32 (1982) 781.

[19] K.K. Panday, G. Prasad, V.N. Singh, Water Air Soil Pollut. 27 (1986) 287–296.

[20] G.L. Layon, P.J. Peterson, R.R. Brooks, G.W. Butler, J. Ecol. 59 (1971) 421.

[21] S. Trideeh, A.J. Englande, M.J. Hebert, R.F. Wilkinson, in: W.J. Cooper (Ed.), Chemistry in Water Reuse, Vol. 2, Ann Arbor Science, Ann Arbor, MI, 1981, p. 521.

[22] A.K. De, A.K. Sen, D.P. Modak, S. Jana, Water Air Soil Pollut. 24 (1985) 351.

[23] G. Fajardo, C. Alberto, Rev. Colomb. Quim. 14 (1-2) (1987) 89–97.

[24] P. Kumar, S.S. Dara, Water Sci. Technol. 13 (7) (1981) 353–361.

[25] T. Tanwee, K.R. Majid, Environ. Technol. Lett. 9 (1988) 1223–1232.

[26] D.S. Bhargava, M.S. Gupta, B.S. Varshney, Asian Environ. 9 (4) (1987) 29–37.

[27] G. Yuan, H. Seyama, M. Soma, B.K.G. Theug, A. Tanaka, J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng. A 34 (3) (1999) 625–648.

[28] S.B. Lalvani, A. Hubner, T.S. Wiltowski, Energy Sources 22 (1) (2000) 45–46.

[29] R. Apak, E. Tutem, M. Hugul, J. Hizal, Water Res. 32 (2) (1998) 430.

[30] M.M. Benjamin, R.S. Sletten, R.P. Bailey, T. Bennett, Water Res. 30 (11) (1996) 2609.

[31] Vaughan Jr., B.E. Reed, R.C. Viadero Jr., M. Jamil, M. Berg, Adv. Environ. Res. 3(3) (1999) 29.

[32] K. Rinkus, B.E. Reed, W. Lin, Sep. Sci. Tech. 32 (14) (1997) 2367.

[33] E.H. Smith, Water Res. 30 (10) (1996) 2424.

[34] E.H. Smith, A. Amini, J. Environ. Eng. 126 (1) (2000) 58.

[35] M. Ajmal, A. Mohammad, N. Fatima, A.H. Khan, Microchem. J. 39 (1989) 361–371.

[36] M. Ajmal, A.M. Sulaiman, A.H. Khan, Water Air Soil Pollut. 68 (1993) 485–492.

[37] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Water Res. 30 (1996) 1478–1482.

[38] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, J. Haz. Mat. 79/1-2 (2000) 117–131.

[39] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Environ. Monit. Assess. 38 (1995) 25–35.

[40] W.A. Deer, R.A. Howie, J. Zussmau, An Introduction to the Rock Forming Minerals, Wiley, New York, 1966.

[41] S. Deb, Industrial Minerals and Rocks of India, Allied Publishers Private Ltd., New Delhi, India, 1980, p. 365.

[42] C. Namasivayam, K. Ranganathan, Water Res. 29 (1995) 1737.

[43] D.C. Sharma, C.F. Forster, Water Res. 27 (7) (1993) 1201–1208.