



Removal of heavy metal ions by carrier magnetic separation of adsorptive particulates

D. Feng, C. Aldrich^{*}, H. Tan

Department of Chemical Engineering, University of Stellenbosch, Private Bag X1, Matieland, Stellenbosch 7602, South Africa

Received 6 July 1999; received in revised form 15 March 2000; accepted 17 March 2000

Abstract

The removal of Pb, Cu, and Cd ions from diluted solutions by sorption onto clinoptilolite, together with magnetite–Fe(OH)₃ coprecipitation and magnetic filtration, was studied at laboratory scale. Low concentrations of clinoptilolite fines were used as heavy metal ion sorbent, while low dosages of magnetite fines were used as magnetic carrier materials. In addition, hydrolyzed Fe³⁺ was used as coagulant. The magnetic clinoptilolite–magnetite–Fe(OH)₃ aggregates were removed by magnetic filtration. Experimental results showed that the process was very rapid and effective and yielded clear solutions with low residual concentrations of heavy metals. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Clinoptilolite; Ion exchange; Heavy metal ions; Magnetite; Flocculation; Carrier magnetic separation

1. Introduction

Mining and metallurgical operations handle large volumes of process water, which are invariably contaminated with fines, chemicals, metal ions, oils and other materials. Aqueous streams containing heavy metals are frequently encountered in industrial effluents and sources of Cu, Pb, Zn and Cd are very common in the electroplating

^{*} Corresponding author. Fax: +27-21-808-2059.
E-mail address: cal@maties.sun.ac.za (C. Aldrich).

facilities, electrolytic refining plants and acid mine waters, among others. For many years, the conventional approach to the removal of heavy metals consisted of the precipitation settling of the metal hydroxide, followed by thickening or filtration of the sludge. This method suffers from several drawbacks, such as incomplete precipitation, chemical instability of the precipitates and formation of large volumes of sludge that can be difficult to filter. These disadvantages can be surmounted by the use of ion exchange, especially if the concentrations of the metals are low. However, suspended solids often encountered in wastewater effluent can be a problem and for this reason, the use of magnetic resins in fluidized beds may be beneficial, as pre-clarification of the wastewater is not necessary and high levels of suspended matter can be tolerated [1].

Another approach to the removal of heavy metals is based on the use of zeolites. Most zeolites are rich in Na^+ , K^+ , and Ca^{2+} , which are usually exchangeable with metal ions [2]. Although zeolites have been known for centuries, their value as adsorbent material was only realized some 4 decades ago. This realization, as well as the discovery of abundant deposits of sedimentary zeolites has given further impetus to the use of zeolites in the treatment of recycle waste pollutants and other industrial effluents [3–5].

The sorption capacities of zeolites are dependent on their particle sizes. The cation exchange capacity rapidly decreases when zeolite size is increased above 1 mm. On the other hand, fine zeolites used in metal–ion sorption processes are very difficult to separate from treated solutions. Although flotation [6,7] can be used to remove ion-laden zeolites from solutions, the requisite flotation collectors may result in secondary pollution.

Magnetic separation of the loaded zeolites can be used to circumvent this problem. Magnetic carrier methods have been used widely in processes such as the separation of biological cells, the treatment of wastewater, coal desulphurization and mineral processing [8]. The essence of this method is to incorporate a discrete magnetic phase into the weakly or non-magnetic target particles to increase their magnetic susceptibility and to separate these agglomerates by magnetic separation. With this approach, Anand et al. [9] could remove virtually all (99.9%) the heavy metals, such as cadmium, copper, nickel and zinc by adsorption onto ferric hydroxide flocs in a pH range of 10.5–11.0. The magnetic phase was obtained from ferric sulphate, as well as a small quantity of magnetite that was added to facilitate high gradient magnetic separation. Krumm [10] described another application of carrier magnetic separation (CMS) for the purification of wastewater containing phosphate, metals, heavy metals and pigment particles with magnetite as the magnetic carrier. Magnetite has been used as a carrier in precipitation–adsorption–coagulation schemes for the treatment of wastewater containing PO_4 and Cu^{2+} [11] and Hg [12,13]. Chen [14] reported the use of magnetite carrier particles coated with ferrihydrite for the removal of Cr^{6+} and Zn from metal finishing effluents.

By adsorbing polluting metals onto zeolites and enhancing the magnetic susceptibility of these systems, the metals can be removed from wastewater effluents containing high concentrations of suspended solids, without having to pre-clarify the effluent or having to deal with the pollution problems posed by flotation reagents. In this paper, the removal of heavy metal ions in dilute solutions by use of magnetically enhanced zeolite particulates is discussed and it is shown that small dosages of zeolite and magnetite fines can lead to efficient removal of heavy metals from aqueous effluents.

2. Experimental work

2.1. Materials

A natural zeolite sample with a particle size of 100% < 74 μm was obtained from Pratley Perlite Mining. Its main phase consisted of 80–85% clinoptilolite, with formula $(\text{MgCaNa}_2\text{K}_2)_{2.5}(\text{AlO}_2)_7(\text{SiO}_2)_{30}21\text{H}_2\text{O}$, compared to the ideal of clinoptilolite, viz. $\text{CaNa}_4(\text{AlO}_2)_6(\text{SiO}_2)_{30}24\text{H}_2\text{O}$. The main features of the zeolite are summarized in Table 1.

Magnetite was used for magnetic seeding. The magnetite sample with a Fe_3O_4 content in excess of 95% was obtained from iDwala Industrial Minerals in South Africa. The sample was ground to 100% passing 15 μm .

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (analytical purity from Merck) was used as coagulant. The analytical grade reagents $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ were used for the make-up of synthetic metalliferous solutions. Analytical grade NaOH and HCl was used to make adjustments in the pH levels of the solution. Distilled water was used throughout the experiments.

2.2. Methods

All the sorption experiments were conducted at an ambient temperature of about 20°C. Batch-type bottle roll experiments with 1 L bottles were conducted for the sorption tests. The concentrations of the heavy metal ions in solution were determined both before the introduction of the clinoptilolite and after the reaction with the metals in solution. Filtration was performed in filters that did not retain the metal ions. The quantity of heavy metal ions separated from solution was determined by use of atomic absorption spectroscopy, based on the differences in the metal ion concentrations before and after introduction of the clinoptilolite.

After sorption, a known quantity of Fe^{3+} and 1 g/L magnetite were added to the clinoptilolite slurry containing the heavy metals at a pH of around 7–8. The slurry was subjected to 30 min of mechanical vibration with an amplitude of 2 mm and a frequency of 60 Hz. Magnetic separation was subsequently used to remove the solids from solution. Magnetic separation was carried out in a laboratory-scale high gradient magnetic separator with a permanent magnet assembly. The separation chamber was 20 mm long and 50 mm wide, while the separation height was 100 mm. The background magnetic field strength was 0.5 T. A magnetic stainless steel wool with a diameter of 50 μm was used as the separation matrix, with a filling factor of 5% by mass. Process efficiency was evaluated by measuring the residual metal content and turbidity (NTU

Table 1
Main properties of the Pratley clinoptilolite

Density (kg/m^3)	Bulk density (kg/m^3)	Hardness (MOH)	Pore size (nm)	Pore volume (%)	Suitable pH
2200	1920	3.5–4.0	0.35–0.60	5–10	3–12

units) in the supernatant fluid. For these turbidity measures, a nephelometer from HF Instruments was used.

3. Results and discussion

3.1. Metal sorption

At a pH of approximately 6.8, the sorption of Pb, Cu, and Cd on the clinoptilolite was around 58, 14, and 11 mg/g clinoptilolite, respectively. Experiments with mixtures of Cu, Pb, Zn and Cd ions in contact with clinoptilolite fines were performed at various clinoptilolite dosages. The initial concentration of each ion was approximately 100 mg/L, the solution pH was around 6.8 and the sorption time was 1 h. The results are shown in Fig. 1.

As can be seen from Fig. 1, the selectivity series for the ions is $Pb \gg Zn > Cu > Cd$, with the selectivity of Cu and Zn very similar. The cation exchange behavior of the clinoptilolite depends upon the hydrated ion sizes, ion concentration, and the cation charge. The smaller the hydrated ion size, the easier the ions penetrate into the pores of the clinoptilolite. The hydrated ion size increases as follows: $Pb < Cu < Zn < Cd$ [15], which is very similar to the sorption selectivities.

Additional sorption experiments with Cu, Pb, and Cd on clinoptilolite were performed at various pH values, the results of which are shown in Fig. 2. The initial concentrations of Pb, Cu, and Cd were approximately 40, 20, and 20 mg/L, respectively, while the respective clinoptilolite dosages (1-L solution) were 0.5, 2, and 2 g.

As can be seen from Fig. 2, the sorption efficiency increased with an increase in the pH of the solution. At low pH values, the higher H^+ concentration reduced the removal of heavy metals significantly, probably because small H^+ ions competed with the divalent cations for sorption sites on clinoptilolite. At higher pH values, the hydrolyzed metal species were more amenable to sorption onto clinoptilolite. The point of zero

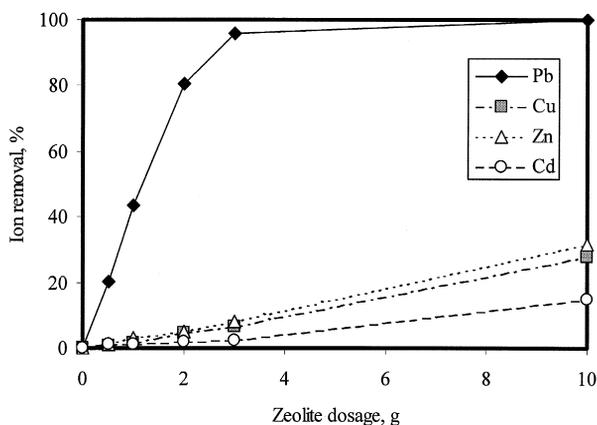


Fig. 1. Sorption selectivity of Pb, Cu, Zn and Cd on clinoptilolite.

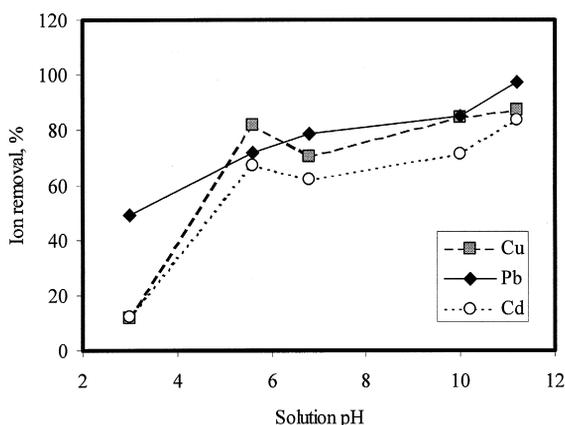


Fig. 2. Sorption of ion species on clinoptilolite as a function of pH.

charge (PZC) of clinoptilolite is around a pH value similar to that of other silicate minerals without ion addition. In the presence of cations, the PZC of clinoptilolite shifted to a pH value of around 5.6, which probably contributed to the increased sorption of Cu and Cd ions at this pH value. In neutral or basic environments, hydrogen bonding of the hydroxy–metal complex with the clinoptilolite surface, chemisorption of the hydrolyzed species and formation and adsorption of the metal hydroxide on the clinoptilolite surface are more likely similar to the adsorption of divalent cations onto quartz, previously described by Fuerstenau and Palmer [16].

Kinetic sorption experiments were conducted at a solution pH of 6.8 and a clinoptilolite dosage of 2 g, while the initial concentrations of Pb, Cu, and Cd were approximately 100, 20, and 20 mg/L, respectively. As indicated by Fig. 3, sorption by clinoptilolite occurs rapidly, reaching about 50% for Cd, 70% for Cu, and 90% for Pb within the first minute.

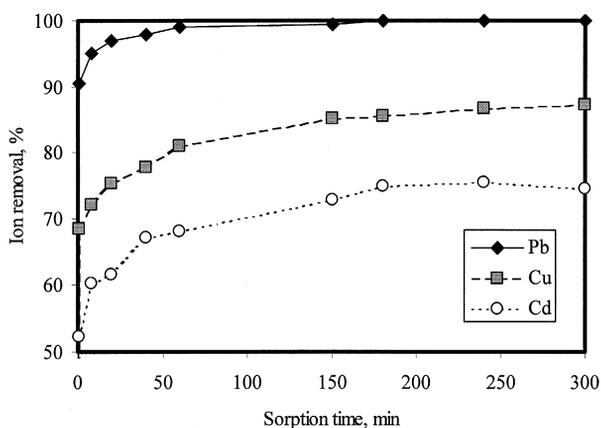


Fig. 3. Sorption kinetics of Pb, Cu, and Cd ions onto clinoptilolite.

3.2. CMS

The dramatic increase in magnetic response shown by a particle containing even small amounts (less than 1%) of a material such as magnetite arises because of the vastly greater magnetic susceptibility of ferromagnetic or ferrimagnetic materials compared with paramagnetic minerals such as siderite or most garnets. It has been calculated that a volumetric concentration of only about 0.01–0.1% of magnetite is required to render the non-magnetic materials sufficiently magnetic so that they can be recovered by conventional high-intensity magnetic separation [17].

Ultrafine magnetite particles were used as magnetic seeding, and FeCl_3 was used as coagulant when hydrolyzed. At a dosage of 0.5 g/L clinoptilolite, it was found that 0.5–1.0 g of magnetite could render all the fine clinoptilolite particles strongly magnetic. Most aggregates of loaded clinoptilolite, magnetite and $\text{Fe}(\text{OH})_3$ were large and well-structured. Although some soft, small magnetic flocs, which did not settle easily were formed, these particulates could be separated magnetically. Results of the CMS of the metal-loaded clinoptilolite–magnetite aggregates are shown in Table 2. The initial concentrations of Pb, Cu, and Cd were 3.2, 3.0, and 2.8 mg/L, respectively. The clinoptilolite dosage was 0.5 g/L, and the solution pH was 7.8.

The addition of magnetite reduced the turbidity of the solution significantly, without affecting the sorption of metal ions. The fine magnetite particles adhered to the clinoptilolite particle surfaces and could be removed by magnetic filtration. Before the addition of Fe^{3+} , Cu and Cd removal by sorption onto the clinoptilolite was less than 50%. After the addition of 100 mg/L Fe^{3+} , Cu and Pb removal increased up to 90%, while the turbidity of the solution decreased to almost that of natural water. The ion removal efficiency increased with an increase in the concentration of the Fe^{3+} . This can possibly be attributed to freshly formed clinoptilolite–magnetite– $\text{Fe}(\text{OH})_3$ aggregates that acted as new sites for ion sorption, as was also observed by Rubio and Tessele [18]. Not only could the process of clinoptilolite sorption, fine magnetite– $\text{Fe}(\text{OH})_3$ coprecipitation and magnetic filtration thus clarify the solutions containing suspensions, but it could also expedite the removal of the heavy metal ions.

Table 2
Effect of Fe^{3+} concentration on ion removal by carrier magnetic separation of the metal-loaded clinoptilolite

$[\text{Fe}^{3+}]$ (mg/L)		0	0	10	40	80
Magnetite (g/L)		0	1	1	1	1
Pb	Final [Pb] (mg/L)	0	0	0	0	0
	Removal (Pb%)	100	100	100	100	100
	Turbidity (NTU)	88.00	42.85	35.46	6.24	1.25
Cu	Final [Cu] (mg/L)	1049	1.48	1.16	0.26	0.02
	Removal (Cu%)	50.33	50.67	61.33	91.33	99.33
	Turbidity (NTU)	87.68	40.74	34.50	6.08	1.16
Cd	Final [Cd] (mg/L)	1.60	1.59	1.21	0.39	0.16
	Removal (Cd%)	42.86	43.21	56.79	86.07	94.29
	Turbidity (NTU)	88.25	41.25	35.60	6.20	1.34

3.3. Regeneration of clinoptilolite

After magnetic filtration, the magnetic flocs were washed off the magnetic matrix. Regeneration took 3 days to be completed in a neutral environment, with a 5% sodium chloride solution used as regenerant. After regeneration, the magnetic clinoptilolite–magnetite– $\text{Fe}(\text{OH})_3$ flocs could again be used for the removal of the heavy metal ions. The ferric flocs and magnetite could be separated from the clinoptilolite by adding HCl at pH levels of approximately 3.0–3.5.

3.4. Mechanism

The attachment of the fine magnetite particles to the clinoptilolite can be considered in terms of the energy equilibria associated with the formation of the aggregates. In a simplified form, the total interaction energy (V_T) is mainly the sum of the energies of van der Waals (V_A) and electrical interactions (V_R), i.e. $V_T = V_A + V_R$. Van der Waals interactions are attractive forces associated with dipoles, induced dipoles, and London forces. Schenkel and Kitchener [19] have expressed the magnitude of these interactions by $V_A = AR_1R_2/[6(R_1 + R_2)X]$, where A is complex Hamaker constant of the particles, measured in joules, R_1 and R_2 are particle radii and X is the distance separating the particles, which are assumed to be spherical.

The critical parameter determining the magnitude of the van der Waals interaction is the Hamaker constant. A method for calculating the Hamaker constant from adsorption data has been described by Hough and White [20], while Fowkes and Paul [21] have proposed methods for calculating the Hamaker constant. As clinoptilolite is a porous adsorbent with a high surface area, these simple models suggest that the attractive van der Waals forces may play an important role for the adsorption of magnetite fines onto the clinoptilolite particle surfaces.

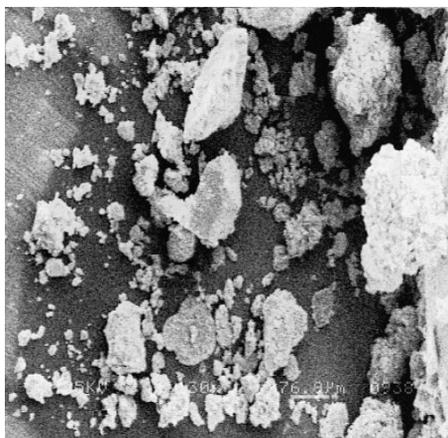


Fig. 4. Structure of the clinoptilolite–magnetite aggregates in the absence of Fe^{3+} .

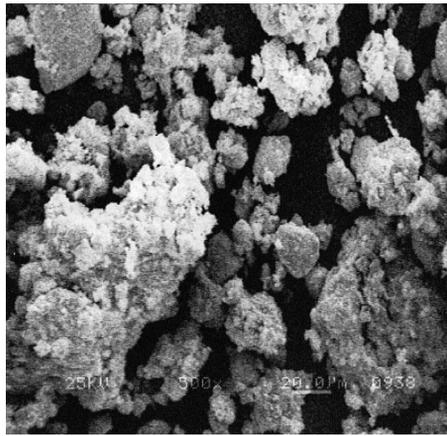


Fig. 5. Structure of magnetite–clinoptilolite–Fe(OH)₃ aggregates at 40 mg/L [Fe³⁺].

Electrical interactions arise from the charges of the fine particles in the magnetite–clinoptilolite suspension and the overlap of the electrical double layers of these particles. The stability of the suspension can be controlled by adjusting the zeta potentials of the fine particles by use of suitable reagents. The principal parameters for determining the magnitudes of the electrical interactions are the relevant potentials at the particle surfaces and the electrolyte concentration in the suspension. In the range of experimental conditions considered in this investigation, the electrical interactions were more or less invariant and future studies would have to consider this factor.

Fig. 4 shows a typical scanning electron microscope (SEM) image of the structure of the magnetite–clinoptilolite aggregates in the absence of Fe³⁺. On this image, the large clinoptilolite particle surface (grey background), as well as an adsorbed layer of

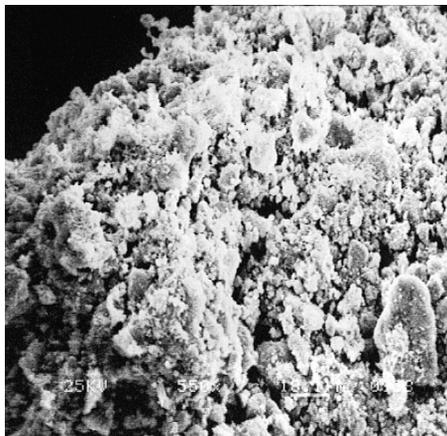


Fig. 6. Structure of magnetite–clinoptilolite–Fe(OH)₃ aggregates at 100 mg/L [Fe³⁺].

magnetite fines (white) are clearly visible. Aggregation is not complete, hence, the free fine particles are also visible on the clinoptilolite surface.

On the other hand, the net attractive energy raised by the bridging effect of the hydrolyzed Fe^{3+} enhances the agglomeration of magnetite and clinoptilolite particles, as indicated in Fig. 5. This figure shows a clinoptilolite–magnetite agglomerate after addition of 40 mg/L Fe^{3+} . Very few fines are visible, since most of the magnetite and clinoptilolite have combined to form magnetic aggregates of moderate size, covered by spongy $\text{Fe}(\text{OH})_3$. These aggregates are magnetically sensitive, and easily removed by magnetic filtration. These porous magnetite–clinoptilolite– $\text{Fe}(\text{OH})_3$ aggregates act as secondary sorption sites for the heavy metal ions, leading to the improved removal of heavy metals observed experimentally.

The average size of the magnetite–clinoptilolite– $\text{Fe}(\text{OH})_3$ aggregates increased with an increase in the concentration of the Fe^{3+} . Fig. 6 shows a SEM image of the aggregates at an Fe^{3+} concentration of 100 mg/L. These aggregates are large and dense compared to those shown in Fig. 5, associated with an Fe^{3+} concentration of 40 mg/L, which may contribute to better process efficiency.

4. Conclusions

The experimental results showed that CMS of particulates using clinoptilolite, a natural zeolite, is particularly suitable for the removal of heavy metal ions from aqueous solutions similar to those found in industrial effluent streams. Clinoptilolite sorption, with magnetite– $\text{Fe}(\text{OH})_3$ coprecipitation and magnetic filtration was found to be highly efficient at removing heavy metals such as Pb, Cu, and Cd, and also produced solutions with very low turbidities. In dilute solutions, the amount of clinoptilolite required to remove the metal ions efficiently was found to be very low (around 0.5 g/L). In addition, the Fe^{3+} concentration affected the process efficiency significantly by forming magnetite–clinoptilolite– $\text{Fe}(\text{OH})_3$ aggregates via the bridging effect of $\text{Fe}(\text{OH})_3$. Moreover, these adsorbents could be regenerated and as such, the system could form the basis of more efficient industrial operations.

References

- [1] D.R. Dixon, D.B. Hawthorne, Continuous ion exchange using magnetic shell resins: III. Treatment of effluents containing heavy metal ions, *J. Appl. Chem. Biotechnol.* 28 (1978) 10–16.
- [2] D.W. Breck, *Mineral zeolites, Zeolite Molecular Sieves (Structure, Chemistry, and Use)*, Wiley-Interscience, Wiley, New York, 1974, pp. 186–244, Chapter 3.
- [3] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, *Water Res.* 18 (12) (1984) 1501–1507.
- [4] M.A. Jama, H. Yucel, Equilibrium studies of sodium–ammonium, potassium–ammonium and calcium–ammonium exchanges on clinoptilolite zeolite, *Sep. Sci. Technol.* 24 (15) (1990) 1393–1416.
- [5] M.F. Brigatti, G. Franchini, P. Frigieri, C. Gardinali, L. Medici, L. Poppi, Treatment of industrial wastewater using zeolite and sepiolite, natural microporous materials, *Can. J. Chem. Eng.* 77 (1999) 163–168.
- [6] J. Rubio, I.A.H. Schneider, W. Aliaga, New processes for heavy metals separations from waste water

- streams in the mining industry, Proc. Clean Technologies for the Mining Industry, Santiago, 1996, pp. 85–98.
- [7] A.I. Zouboulis, D. Zamboulis, K.A. Matis, Foam separation of zeolites: applications for zinc ion removal, Sep. Sci. Technol. 26 (3) (1991) 355–365.
- [8] P. Parsonage, Coating and carrier methods for enhancing magnetic and flotation separations, in: J.S. Laskowski, J. Ralston (Eds.), Colloid Chem. Miner. Process., Elsevier, Amsterdam, 1992, pp. 331–360, Chap. 11.
- [9] P. Anand, J.E. Etzel, F.J. Friedlaender, Heavy metals removal by high gradient magnetic separation, IEEE Trans. Magn. Mag-21 (5) (1985) 2062–2064.
- [10] E. Krumm, Waste water treatment with magnetic separators, Chem. Tech. (Heidelberg) 20 (5) (1991) .
- [11] C. De Latour, H. Kolm, High gradient magnetic separation: a water treatment alternative, J. Aust. Water Works Assoc. 68 (1976) 327.
- [12] B.A. Bolto, D.R. Dixon, R.J. Eldridge, Graft polymerisation on magnetic polymer substrates, J. Appl. Polym. Sci. 22 (1978) 1977.
- [13] M. Benjamin et al., Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation, J. Water Pollut. Control Fed. 54 (1982) 1472.
- [14] W.Y. Chen, P.R. Anderson, T.W. Holsen, Recovery and recycle of metals from waste water with magnetite bases adsorption process, Res. J. Water Pollut. Control Fed. 63 (7) (1991) 958.
- [15] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, pp. 95–242.
- [16] M.C. Fuerstenau, B.R. Palmer, Anionic flotation of oxides and silicates, Flotation — A.M. Gaudin Memorial, 1976, pp. 148–196, Chap. 7.
- [17] P. Parsonage, Selective magnetic coating for mineral separation, Trans. Inst. Min. Metall., Sect. C., Miner. Process. Extr. Metall. 93 (1984) C37–C44.
- [18] J. Rubio, F. Tessele, Removal of heavy metal ions by adsorptive particulate flotation, Miner. Eng. 10 (7) (1997) 671–679.
- [19] J.H. Schenkel, J.A. Kitchener, A test of the Derjaguin–Verwey–Overbeek theory with a colloidal suspension, Trans. Faraday Soc. 56 (1) (1960) 161–173.
- [20] D.B. Hough, L.R. White, The calculation of Hamaker constants from Lifshitz theory with applications to wetting phenomena, Adv. Colloid Interface Sci. 14 (1980) 3–41.
- [21] F.M. Fowkes, R.J. Paul, in: E.D. Goddard, B. Vincent (Eds.), Polymer Adsorption and Dispersion Stability, American Chemical Society, Washington, DC, 1984, p. 331.