

# PARA-MAGNETIC COMPOSITE MICROPARTICLES AS HEAVY METAL ION-EXCHANGERS

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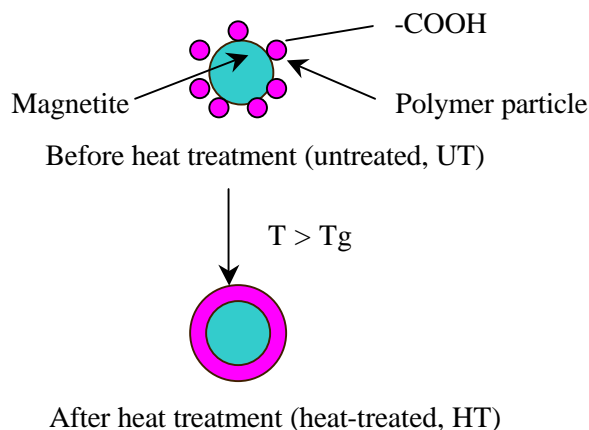
**INTRODUCTION:** Considerable work on the use of magnetic composite particles in the area of biosciences, medicine, and wastewater treatment has been published. However, the report on their use as ion-exchangers to remove metal cations from wastewater has been limited [1, 2]. In this work, composite particles (CP) have been made by combining functionalised polymer nanoparticles with microparticles of magnetite using an encapsulation process [3]. The advantage of these particles is that they provide a very large area per unit volume. The polymer was mainly of acrylic composition and was designed to include components that would give the particles colloidal stability. The polymer particles carried carboxylic groups to function as ion-exchange entities; they were made from solution-polymer by replacing the solvent phase with water. The derived composite particles included a magnetite core to facilitate separation from the aqueous phase applying a magnetic field. Association between the polymer particles and the magnetite particles was achieved by mixing at a pH range in which the former particles carried a net negative surface charge whilst the other particles carried a net positive charge [3]. To enhance this electrostatic, opposite charge attraction, the magnetite particles were coated with a cationic polymeric surfactant before they were mixed with the polymer particles. The dispersion of composite particles was heated to a temperature in excess of the glassy transition temperature of the polymer which was found to be around 70 °C, anticipating that the polymer particles should spread over the magnetite to form a polymeric layer. The process is schematically illustrated Figure 1. The performance of the composite particles as ion-exchangers was investigated in the separation and recovery of selected heavy metal cations (e.g.  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$ ) in a batch reactor at laboratory scale.

## METHODS:

### Chemical and Reagents

Azo-bis (4 cyanovaleric acid), azo-bis (2-2 methyl propionamide dihydrochloride), methacryloyloxy ethyl trimethyl ammonium chloride (QMa, 75% in water), N-vinyl pyrrolidone (VP), vinyl acetate (VA), methyl methacrylate (Mma), butyl acrylate (Ba), acrylic acid (AA), and

magnetite ( $Fe_3O_4$  with particles sizes  $< 5 \mu m$ ) were obtained from Aldrich Chemical Company. Methoxy poly(ethylene glycol) methacrylate (MeOPEGMA) was kindly supplied as a 50 % solution in water by International Speciality Chemicals Limited. Ethyl acetate and ethanol (96%) were purchased from BDH. The general purpose grade metal salts used (BDH) were  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $ZnSO_4 \cdot 7H_2O$ ,  $CrCl_3 \cdot 6H_2O$ , and  $Ni(NO_3)_2 \cdot 6H_2O$ . HCl (1N) and NaOH (1N) were used to adjust pH. Distilled water was used throughout.



*Fig. 1: Schematic representation of the encapsulation of composite particles.*

## Experimental

### Preparation of cationic polymeric surfactant

Cationic polymeric surfactant was produced by solution terpolymerisation of vinyl acetate, vinyl pyrrolidone, and methacryloyloxy ethyl trimethyl ammonium chloride using azobismethylpropionamide dihydrochloride as an initiator. The proportions of monomers used in the preparation (by solution polymerisation) of the cationic surfactant were VA/VP/QMa 34/21/45 (%wt). A mixture of ethanol and water was used as a solvent.

### Preparation of anionic polymer particles

The polymer was made by solution tetrapolymerisation of MeOPEGMA, Mma, Ba, AA in the proportions 15/69/34/5 (%wt) respectively. A mixture of ethyl acetate and ethanol was used as a solvent. The solution

polymer was converted into colloiddally-stable particles by a two-step process: the ethyl acetate was displaced by distillation during addition of further ethanol; the ethanol was subsequently substantially displaced by addition of water and distillation. The particles exhibited steric, colloidal stability arising from the MeOPEGMA components.

#### Preparation of composite particles

Ten g of magnetite was initially mixed with 300 mL of a 20% wt cationic surfactant solution for 16 hours at pH 8 using ball-milling. A ceramic pot containing different sizes of stainless steel beads was used for this purpose. The coated particles were washed several times with water. The particles were magnetically separated from an aqueous phase after each wash by placing a strong magnet under the container. Any nonmagnetic particles were removed with the wash liquid. The particles were dried overnight in a fume cupboard. The dried surfactant coated particles were added to a dispersion of the polymer particles (3% weight content) at pH 8. The resulting composite particles were stored and used as slurry whose solid content was found to be 0.03 g/L. To prepare composite particles as ion exchangers in the form of  $H^+$  and  $H^+Na^+$ , they were further treated with 5 % HCl solution to remove ionised impurities. The particles were then converted into  $H^+Na^+$  -form by treatment with 5% NaOH solution and washed with distilled water until pH 10 was reached. Under this condition, it was found that only 20%  $Na^+$  displacement was achieved. The slurry of composite particles was heat-treated at 80 °C, which was above the Tg of the polymer particles.

#### Particle Characterisation

The zeta-potential of surfactant coated magnetite, polymer particles, and composite particles was determined by using a Malvern Zetamaster at room temperature. The pH of a range of samples was altered by adding a very small amount of acid and alkaline solutions containing 2 mmoles of HCl with 3 mmoles of NaCl and 2 mmoles of NaOH with 3 mmoles of NaCl.

The size distribution of polymer particles was measured by photon correlation spectroscopy (Malvern Autosizer S4700); laser diffraction (Malvern Mastersizer 2000) was used for the composite particles.

The glass-transition temperature of polymer particles was measured by a differential scanning calorimeter (Perkin Elmer DSC pyris1) at a heating rate of 10 °C/min. The samples of polymer particle dispersions had been cast on a dish and dried at room temperature in a dessicator for 2 weeks.

The morphology of surfactant-coated magnetite and composite particles was observed with a scanning electron microscope (SEM, JEOL T-220A). The samples for SEM work were dried at room temperature under an air flow and then ground with a mortar to break up agglomerations.

#### Metal ions sorption experiments:

The characteristics of composite particles are presented in Table 1.

*Table 1. Properties of composite particles.*

Physical form	Aggregates (~7µm diameter) in slurry
Exchange characteristics	
Functional group	-COO <sup>-</sup>
Counter ion	H <sup>+</sup> , H <sup>+</sup> +Na <sup>+</sup>
Carboxylic groups content* (mmol/g dry composite particles)	0.217
Operating condition	
pH	5-7
Temperature (°C)	20
Regenerant (strong acid)	1 N. aq.

\* The polymer carboxylic groups content was measured by gas chromatography.

These experiments were carried out with composite particles which had not been heat-treated.

#### *Capacity studies*

Metal cations sorption from the single-metal aqueous solutions was investigated in batch sorption-equilibrium experiments. Selected metal cations were Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>. In sorption isotherm studies, aqueous metal cation solutions with different concentrations in the range 0-25 mmol/L were mixed with 10 mL of the slurry of the particles in 500 mL conical flasks at pH 5.5. The solutions were made up to 50 mL for each concentration. The flakes were shaken for 30 minutes at 400 osc./min using a flask shaker. This sorption time was expected to be more than sufficient for the system to reach equilibrium, because the separate experiments had indicated that the process was almost instantaneous. After sedimentation of the particles had been induced by applying a magnetic field, the supernatant was filtered through 0.45 µm membrane filters. The quantity of metal cations sorbed on the particles was determined by atomic absorption spectroscopy, based on the differences in the metal cation concentrations before and after introduction of the particles.

Competitive sorption of metal cations from their mixture was also investigated in a batchwise form. A solution (500mL) containing different amounts of each metal cation was mixed with 2.5 mL slurry of the particles in a 2L beaker. The mixture was agitated by a three-blade impeller driven by a variable speed motor at 250 rev./min, at pH 5. Initial concentrations of metal cations were 0.078 mmol/L for  $\text{Cu}^{2+}$ , 0.076 mmol/L for  $\text{Zn}^{2+}$ , 0.096mmol/L for  $\text{Cr}^{3+}$ , and 0.088 mmol/L for  $\text{Ni}^{2+}$ .

*Influence of the counter ions on the exchange with  $\text{Zn}^{2+}$  at different pH.*

A ratio (R) was defined as follows.

$$R = \frac{\text{Zn}^{2+} \text{ in the solution (mmol)}}{\text{COOH or COOH+Na (mmol)}}$$

The R ratios were 1/4, 1/8, 1/16 for both forms. The experiments were conducted in the same manner as in the sorption isotherm section. The initial  $\text{Zn}^{2+}$  concentration was kept constant at 0.076 mmol/L. The pH ranged from 5 to 7.

*Recovery and re-use of the composite particles*

In an extraction experiment, 0.3 g of the composite particles were loaded into a solution of  $\text{Zn}^{2+}$ , initial concentration = 0.31 mmol/L, with  $R = 1/4$  at pH 7. After extraction, the composite particles were recovered by treatment with 50 mL of 1M. HCl aq. Kinetics studies indicated that 3 hours contact was in excess of the required time to reach equilibrium. At the end of the experiment, the amount of  $\text{Zn}^{2+}$  in the solution was measured. 10 cycles of consecutive extraction and stripping were carried out.

## RESULTS AND DISCUSSION:

### Particle characterisation

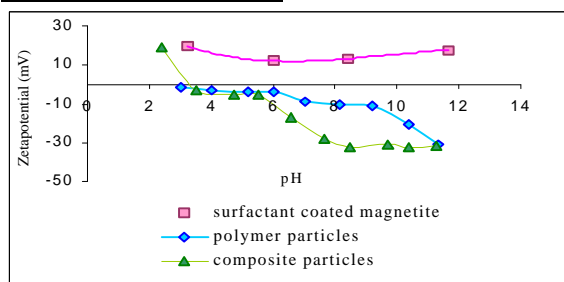


Fig. 2: Variation of surface charge with pH.

Figure 2 shows the result of the zeta-potential examination of cationic surfactant-coated magnetite, polymer particles, and composite particles at different pH values. As anticipated the presence of cationic surfactant on magnetite whose isoelectric point is around 6.5 shifted the surface charge of magnetite into the positively-charged

region at alkaline pH. The charge of polymer particles tended to lie in the negatively charged region at all pHs. The negative charge of polymer particles increased with pH values due to ionisation of the carboxylic groups from both the initiator and acrylic acid. The zeta-potential characteristics of the composite particles resembled those of polymer particles rather than those of surfactant-coated magnetite. This confirmed that surfactant-coated magnetite was covered with the polymer particles.

The sizes of the polymer particles were found to be in the range of 50 to 70 nm. The particle size analyser gave the sizes of aggregates of composite particles to be less than 7  $\mu\text{m}$ .

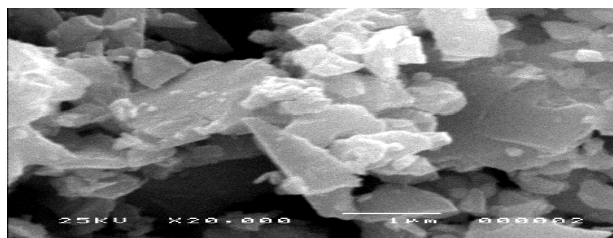


Fig. 3a: SEM micrograph of surfactant-coated magnetite.

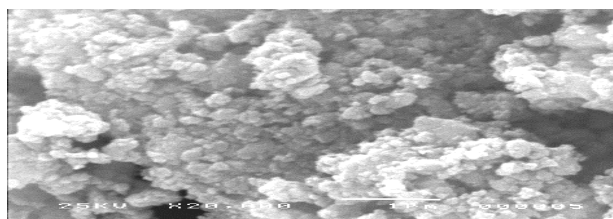


Fig. 3b: SEM micrograph of UT composite particles.

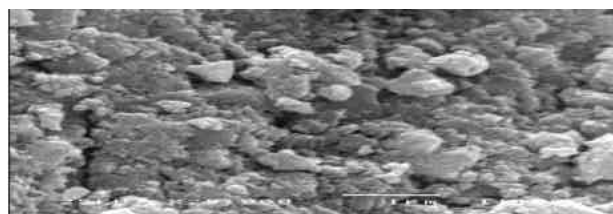


Fig. 3c: SEM micrograph of HT composite particles.

Scanning electron micrographs (Fig. 3a, 3b, 3c) show that the particles were not uniform and were aggregated. Surfactant coated magnetite exhibited a smooth surface (Fig. 3a). The composite particles (Fig. 3b) had a rough surface due to the presence of the polymer particles. The composite particles after heat treatment (Fig. 3c) provided a smoother and less nodular surface than those before heat treatment, as expected.

### Capacity studies

Experimental results showed that the process was almost instantaneous, yielding complete removal when the initial concentrations of heavy metals were very low (0.015-0.076 mmol/L). Considering the ratio of mmoles of metal extracted to the mmoles of carboxylic groups in the amount of particles used, the maximum values were found in using single metal solutions: 4.42 for  $\text{Cu}^{2+}$ , 3.87 for  $\text{Cr}^{3+}$ , 2.12 for  $\text{Ni}^{2+}$ , and 1.94 for  $\text{Zn}^{2+}$ . These ratios are higher than the stoichiometric ratio, suggesting that ion exchange is not the only mechanism of metal extraction. With the multicomponent solution, the relative amount of the different cations extracted was consistent with the above results, i.e.  $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Ni}^{2+} \sim \text{Zn}^{2+}$ .

### Influence of the counter ions on the exchange with $\text{Zn}^{2+}$ at different pH values.

Table 2 shows the removal percentages of  $\text{Zn}^{2+}$  as a function of the R ratio. It showed that the choice of counter ions had an influence on the exchange capacities at all investigated pH values, especially in acidic solution.  $\text{H}^+$ + $\text{Na}^+$ -form tended to have higher affinity for  $\text{Zn}^{2+}$ . This finding could be explained in terms of the degree of dissociation of carboxylate group, which is heavily dependent on pH and counter ions. Decreasing the R ratio value (increasing in the number of active groups) led to an increase in  $\text{Zn}^{2+}$  removal. Nevertheless, complete removal could not be achieved even with a relatively large excess of counter ions ( $R=1/16$ ,  $\text{pH}=7$ ). In terms of the surface complexation model, one part of  $\text{H}^+$  counter ions is situated in the diffuse layer where the exchange occurs and the other is specifically connected to the surface (in the Stern layer) where it is difficult for  $\text{Zn}^{2+}$  to reach, in the case of weak acid exchangers. This led to a decrease in available active sites [4].

Table 2. Removal percentages of  $\text{Zn}^{2+}$  as a function of the R ratio (initial  $\text{Zn}^{2+}$  concentration kept constant at 0.076 mmol/L,  $T=20^\circ\text{C}$ ).

pH	Particles	% removal		
		R=1/16	R=1/8	R=1/4
5	$\text{H}^+$ form	6	3	1
5	$\text{H}^+$ + $\text{Na}^+$ form	17	8	6
6	$\text{H}^+$ form	52	36	27
6	$\text{H}^+$ + $\text{Na}^+$ form	62	39	23
7	$\text{H}^+$ form	92	92	84
7	$\text{H}^+$ + $\text{Na}^+$ form	93	93	87

### Recovery and Reuse

Figure 5 clearly indicates that heavy metals could be repeatedly adsorbed and stripped without

significant loss in the loading capacity of the composite particles.

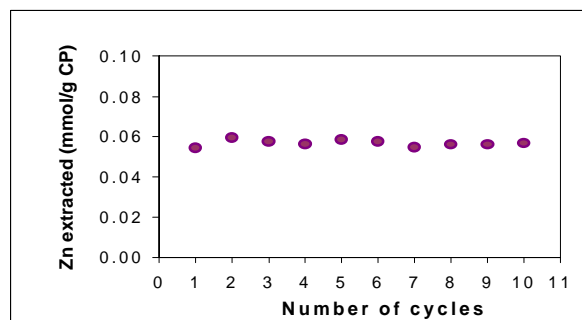


Fig. 5: The extraction performance of the composite particles as a function of the number of cycles (initial  $\text{Zn}^{2+}$  concentration for each cycle was 0.31 mmol/L, at pH 7).

### CONCLUSIONS:

The metal cations sorption process on composite particles is almost instantaneous, yielding complete removal when the initial concentrations of heavy metals are very low.  $\text{H}^+$ -form composite particles appeared to be less efficient than  $\text{H}^+$ + $\text{Na}^+$ -form ones under the experimental conditions studied. Consecutive loading and stripping showed the feasibility of the composite particles for metal cation extraction.

### REFERENCES:

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