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Advances in Environmental Research 8 (2004) 629–635

Advances in Environmental Research

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Biosorption of zinc from aqueous solutions using biosolids

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Accepted 4 April 2003

Abstract

The potential to remove zinc from aqueous solutions through biosorption using biosolids was investigated. Batch experimental results showed that the biosorptive capacity of dry, unground biosolids was 0.564 mM/(g dry biosolids). Pretreatment of the biosolids, including drying and grinding, affected the sorptive potential of the biomass. Kinetic experiments showed that dilute zinc solutions reached equilibrium within 5 h, whereas equilibrium was not reached until 24 h for more concentrated solutions. The biosorptive capacities were dependent on zinc solution pH, with pH 4 being optimal. Infrared spectra analysis suggested that carboxyl functional groups are responsible for zinc uptake.

Keywords: Biosorption; Heavy metal removal; Wastewater; Zinc; Biosolids

1. Introduction

Zinc may be found in wastewater discharges from acid mine drainage (AMD), galvanising plants, as a leachate from galvanised structures and natural ores, and from municipal wastewater treatment plant discharges. Zinc is not biodegradable and travels through the food chain via bioaccumulation. Hence, there is significant interest regarding zinc removal from wastewater streams. Traditional methods for removal of zinc ions from solution include lime precipitation and ion exchange, although these are often expensive and ineffective at low metal concentrations. Therefore, there is a need for a cost effective treatment method that is capable of removing low concentrations of zinc from solution.

Biological materials are known for their potential to adsorb heavy metals (Kratochvil and Volesky, 1998a; Chang and Hong, 1994). Biosorption is an emerging technology that uses biological materials to remove metals from solution through adsorption. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). Cheng et al. (1995) reported that metal uptake is not significantly affected by biomass viability. Therefore, any active metabolic uptake process is currently considered to be a negligible part of biosorption. Biosorbents used in previous work include marine algae (Matheickal and Yu, 1999a), peat moss (Spinti et al., 1995), waste biomass (Tobin and Roux, 1998), biosolids (Solari et al., 1996) and fungi (Kratochvil and Volesky, 1998b).

The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998a):

- Low cost;
- High efficiency of metal removal from dilute solutions;
- Minimisation of chemical and/or biological sludge;
- No additional nutrient requirements;
- Regeneration of biosorbent; and
- Possibility of metal recovery.

Both living and non-living biosorbents have been studied (Fourest et al., 1994; Veglio et al., 1997). Living

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1093-0191/04/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S1093-0191(03)00035-2

systems can be unreliable due to the many problems of maintaining active biomass populations under highly variable wastewater conditions. Non-living biosorbents provide the following advantages:

- Harsher reaction environments may be employed;
- The need for an additional nutrient supply is negated;
- Sudden death of the biomass population can be avoided;
- Regeneration with a suitable eluent allows biosorbent reuse; and
- It can be immobilised in a matrix and used in conventional ion exchange systems.

Biological wastewater treatment produces a biological sludge (biosolids), consisting of inert materials and microorganisms. Currently, there are limited reuse/disposal options for biosolids due to high concentrations of heavy metals and the risk of pathogens. Previous research has shown the ability of biosolids to remove metals from the wastewater stream. Bux and Kasan (1996) investigated return activated sludge (RAS) samples from ten different wastewater treatment plants and found that each sample displayed differing biosorptive potentials.

RAS has a solids content of $\sim$1% and consists of a variety of living microorganisms. The RAS is returned back into the wastewater treatment process to provide a constant supply of microorganisms. Waste activated sludge (WAS) consists of the non-living microorganisms which are no longer required in the wastewater treatment process and are ready for disposal. Dewatered WAS contains a solids content of $\sim$13%. In order to overcome the risk of pathogens as well as the transportation and storage issues associated with RAS, dewatered non-living WAS was chosen for this study.

The objectives of this study include identifying the maximum theoretical zinc uptake capacity of the biosolids, determining the reaction kinetics and evaluating the importance of solution pH on zinc uptake. This paper reports the results of an evaluation of the parameters important for the biosorption of zinc.

2. Materials and methods

2.1. Biosorbent

Dewatered WAS from the Anglesea Wastewater Treatment Plant, Victoria, was collected for use as a biosorbent. This treatment plant was chosen because the wastewater treated is of domestic origin with low background concentrations of zinc. Biosolids with a solids content of 13.5% were collected from the belt filter press and were designated wet biosolids. Wet, dry unground and dry ground biosolids were used in preliminary investigations and showed very similar biosorptive capacities. Further work was continued only with dry unground sludge to negate the time and cost involved with the grinding of the biosolids, and also to avoid the operating issues involved with the use of wet biosolids. Wet sludge was dried at 103 °C until constant weight to form the dry unground biosolids. The initial Zn(II) concentration of the biosolids was determined by nitric acid digestion (APHA et al., 1998) and was found to be 1.24 mg/(g dry biosolids). The total cation exchange capacity of the raw biosolids was determined by titration as outlined in (Kunin (1958) and was found to be 4.12 meq CEC/(g dry biosolids).

2.2. Chemicals

Zinc solutions were prepared according to 'Standard Methods' (APHA et al., 1998) from analytical reagent grade zinc dust. Distilled water was used for all solutions. Stock zinc solutions of 15.3 mM were initially prepared and preserved with 1.5 ml of concentrated HNO_3 per litre, then diluted prior to use. Precipitation of the metal ions was not observed at the concentrations and pH values used in this study. All chemicals used were of analytical reagent grade and were used without further purification. In all cases where samples needed to be stored, they were preserved as detailed in 'Standard Methods' (APHA et al., 1998). Acid washing with a 5% (v/v) HNO_3 solution followed by a triple rinse with distilled water was conducted to avoid metal uptake onto glassware.

2.3. Experimental procedure

Batch biosorption experiments were conducted until equilibrium was reached. Equilibrium was deemed to have been reached when no further metal removal occurred. Zinc solutions were diluted to 0.076, 0.15, 0.3, 0.75 and 1.5 mM. 2.0 g (dry wt.) of dry biosolids was added to a 200 ml Zn(II) solution. All experiments were at least conducted in duplicate with the average presented in the results. The solution was placed on an orbital mixer (*Ratek OM6 Orbital Mixer*) and mixed at 200 rpm until equilibrium was reached. The biosolids were removed by filtration through a 0.45-μm membrane filter (Millipore) and the filtrates were analysed for residual zinc concentration by atomic adsorption spectrophotometry (901 AAS-GBC Scientific Equipment Pty Ltd). Absorbance was recorded in triplicate to assess the reproducibility and the mean values were used for the concentration calculations. Experiments were conducted in a temperature controlled room (20 ± 2 °C). An *Orion Research 701A Digital Ionalyzer* was used for pH measurements and was calibrated with buffer solutions at pH 4 and 7 prior to use. For experiments with controlled pH, either 0.1M NaOH or

0.1M HCl solutions were used for adjustment. Infrared analysis was conducted on a *Biorad Excalibur Series* infrared spectrophotometer.

2.4. Sorption equilibria studies

Sludge masses of 0.1, 2 and 10 g (dry wt.) were used in conjunction with solution concentrations of 0.076, 0.15, 0.3, 0.75 and 1.5 mM. Initial pH was set to 4, reaction time was 24 h and a mixing speed of 200 rpm was used. This set of experiments was conducted in triplicate, with the average reported in the results. Error bars have been included to indicate the spread of the data. This study was conducted to identify whether the sorption equilibria fitted the Langmuir model and to determine the Langmuir uptake capacity of the biosolids. The Langmuir model was chosen because, it is a common method for characterising sorption equilibria (Aderhold et al., 1996; Fourest et al., 1994; Solari et al., 1996). The use of the Langmuir model therefore, allows for comparison of the uptake capacity of biosolids with other alternative biosorbents.

2.5. Kinetic studies

Metal solution concentrations of 0.076, 0.3 and 1.5 mM were used in conjunction with 2.0 g (dry wt.) of biosolids. Reaction times of 0.25, 0.5, 1, 2, 4, 8, 10, 14, 18, 20 and 24 h were investigated. A mixing speed of 200 rpm was used for this set of experiments.

2.6. pH studies

When investigating the effect of initial pH value, metal solution concentrations of 0.076 and 0.3 mM were used in conjunction with 2.0 g (dry wt.) of biosolids. Initial solution pH was adjusted to 2, 3, 4 and 6. Many wastewaters, including AMD and industrial effluents, fall within this pH range. These pH values were also chosen to avoid metal precipitation at higher pH values, and to investigate the effect of low pH for metal elution from the biosolids. The reaction time was 24 h and a mixing speed of 200 rpm was used.

3. Results and discussion

3.1. Sorption equilibria studies

The zinc uptake capacity of the biosolids was evaluated using the Langmuir adsorption isotherm (Fig. 1). This isotherm represents the equilibrium distribution of metal ions between the aqueous and solid phases. Eq. (1) can be used to model the adsorption isotherm.

$$q = q_{\max}\frac{bC_{\mathrm{eq}}}{1+bC_{\mathrm{eq}}} \tag{1}$$

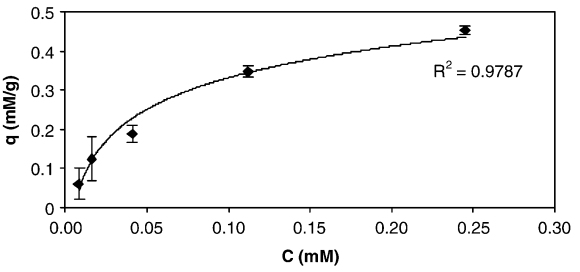

Fig. 1. Equilibrium isotherm of zinc adsorption onto unground biosolids with pH adjustment to 4.

where

- C_{eq} is the equilibrium zinc solution concentration (mM),
- q is the amount of zinc adsorbed onto the biosolids at equilibrium (mM/g),
- $q_{\max}$ is a Langmuir constant of the maximum zinc uptake (mM/g), and
- b is also a Langmuir constant of the ratio of the adsorption rate constant to the desorption rate constant, which is related to the energy of adsorption through the Arrhenius equation (Chong and Volesky, 1995).

The Langmuir isotherm is based on these assumptions (Fourest and Roux, 1992):

- metal ions are chemically adsorbed at a fixed number of well-defined sites;
- each site can only hold one ion;
- all sites are energetically equivalent; and
- there is no interaction between the ions.

When the initial metal concentration rises, adsorption increases whilst the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is equated by Eq. (2)

$$\frac{C_{\mathrm{eq}}}{q} = \frac{1}{q_{\max}b} + \frac{C_{\mathrm{eq}}}{q_{\max}} \tag{2}$$

The average equilibrium zinc concentrations ranged from 0.008 to 0.25 mM and the solution pH was initially set to pH 4. The adsorption capacity was determined to be 0.564 mM/g with a Langmuir constant of 12.05. These values compare well with other data reported in the literature. Aderhold et al. (1996) reported a maximum zinc uptake capacity of 0.299 mM/g using the seaweed *Durvillea potatorum*, although the pH was not reported. Puranik and Paknikar (1997) and Fourest et al. (1994) both investigated the use of mycelial waste biomass and found maximum uptake capacities of 0.231

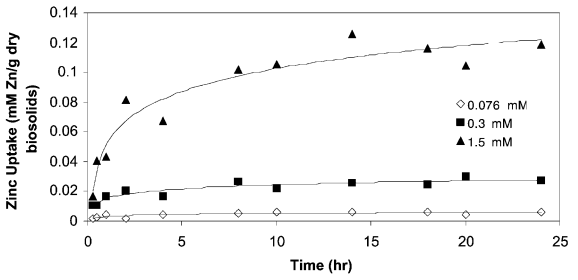

Fig. 2. Kinetic profile of zinc biosorption onto unground biosolids with 10 g/l biosolids addition and no pH adjustment.

mM/g at a pH of 5.5 and 0.33 mM/g at a pH of 5, respectively. Ouki and Kavannagh (1999) used the natural zeolite chabazite for zinc adsorption and determined the maximum uptake capacity to be 0.08 mM/g at pH 5. Solari et al. (1996) investigated the use of non-living digested sewage sludge as a biosorbent. A maximum zinc uptake capacity of 0.392 mM/g at pH 7 was reported, which compares favourably with the value of 0.564 mM/g obtained in this study.

Kratochvil and Volesky (1998b) reported that qualities of a good biosorbent include a high q_{max} value and a low value for the constant b. Low values of b can be seen in an isotherm with a steep initial slope, indicating a high affinity of the sorbate for the sorbent. This isotherm is reasonably steep at low equilibrium concentrations, indicating that these biosolids would be suitable for the treatment of dilute zinc solutions.

3.2. Biosorption kinetics of zinc uptake onto biosolids

The kinetic profiles of the zinc biosorption at various concentrations are shown in Fig. 2. The system attained equilibrium quickly, although not as fast as reported in other investigations.

Biosolids in the 0.076 mM solution had adsorbed 24% of the total zinc uptake after 15 min, and 62% after 1 h. 34% of the total zinc uptake had been removed by the biosolids in the 0.3 mM solution after 15 min and 54% after 1 h. Both solutions had attained equilibrium after 5 h of reaction. The 1.5 mM solution had a slower rate of adsorption. The biosolids in this solution had only removed 13 and 34% of its equilibrium uptake after 15 min and 1 h, respectively. The 1.5 mM solution reached equilibrium after 24 h of reaction time.

The 1.5 mM solution took longer to reach equilibrium due to the proportionally higher mass of zinc present. The solutions containing a smaller mass of zinc were able to attain equilibrium quickly because the zinc adsorbed on to unhindered sites first. The more concentrated solution filled these sites initially, and then took longer to fill the hindered sites with the remaining zinc atoms. Although the 1.5 mM zinc solution took longer to reach equilibrium, it displayed a higher metal removal capacity. After 24 h, it showed a removal capacity of 0.12 mM Zn/g dry sludge, compared to 0.026 mM Zn/g and 0.006 mM Zn/g for the 0.3 and 0.076 mM solutions, respectively.

Matheickal and Yu (1996) reported 100% lead uptake from 0.5 to 2.5 mM solutions within 15 min of contact with *Ecklonia radiata* seaweed and Zhao et al. (1999) reported that 70% of Zn(II) was adsorbed from a 1.5 mM solution by *Azolla* within the first 3 min of incubation. Xie et al. (1996) used an equilibrium time of between 16 and 24 h whilst investigating the uptake of zinc by *Zoogloea ramigera* bacteria. Mameri et al. (1999) indicated that the limiting zinc concentration was reached after 4 h of contact between a 1.5 mM solution and fungal biomass.

The reaction rates in this study are slower than those reported in other research. This may be explained by the non-homogeneous nature of the biosorbent. Biosolids consist of inert materials that pass through the wastewater treatment process as well as a heterogeneous colony of microorganisms including *Microthrix parvicella, Norcardia amarae and Proteobacteria*. Other researchers (Mameri et al., 1999; Zhao et al., 1999; Xie et al., 1996) used a single strain of microorganisms, making the biosorbent homogeneous. A homogeneous biosorbent would have similar functional groups available for metal sequestration. A heterogeneous biosorbent, such as biosolids, would have a host of different functional groups present due to the different components in the microorganism cell walls. These different groups providing adsorption sites may have differing rates of metal adsorption onto the sites, resulting in different rates of metal uptake by the biosorbent and hence a longer time to reach equilibrium.

Matheickal et al. (1999b) reported on the slow equilibration of metals adsorbing onto biosorbents and reasoned the slow kinetics were due to the non-homogeneity of the biosorbent surface, which could contain a number of functional groups. Mameri et al. (1999) also reported that available adsorption sites on the biosorbent are the limiting factor for metal uptake.

3.3. Effect of pH on zinc uptake

The equilibrium metal uptake of the biosolids from 0.076 to 0.3 mM Zn(II) solutions at various pH values is shown in Fig. 3. The metal uptake at pH 2 is negligible, thus indicating the possibility for using this pH effect for metal elution and biomass regeneration. In fact, at pH 2, Zn(II) has been leached out of the biomass and into solution. It is clearly demonstrated that zinc uptake increases with solution pH. This increase in zinc removal with increasing pH has also been shown by Mameri et al. (1999) using fungal

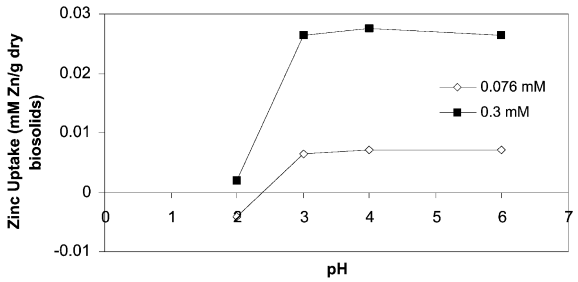

Fig. 3. Zinc uptake as a function of pH.

biomass and by Ouki and Kavannagh (1999) using natural zeolites. The pH dependence of metal uptake could be related to the functional groups of the biomass and also to solution chemistry. At pH values less than four metals are in their free ionic form (Zn^{2+}) and as such the sharp increase in metal uptake between pH 2 and 4 cannot be described by the change in metal speciation (Matheickal et al., 1999b). This leads to the hypothesis that the cell wall functional groups and their associated ionic state are responsible for the extent of adsorption.

Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid–base equilibria that, in the pH range 2.5–5, the binding of heavy metal cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials (Kratochvil and Volesky, 1998b; Puranik and Paknikar, 1997). The ionic states of cell wall functional groups can be used to explain the pH dependence of biosorption. Low pH conditions allow hydrogen and hydronium ions to compete with zinc for metal binding sites on the biomass, causing poor zinc uptake. At higher pH values, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater zinc sorption.

3.4. Infrared spectra analysis

In order to determine the functional groups responsible for metal uptake, infrared spectroscopy was used. A raw, unreacted biosolids sample (Fig. 4) and biosolids pretreated with a 100 mg/l zinc solution (Fig. 5) were analysed. The spectra indicate the presence of carboxyl groups. Carboxylic acids display a broad, intense –OH stretching absorption from 3300 to 2500 cm^{-1}, although the bands are dominated by the –OH stretch due to bonded water. Weaker –CH stretch bands are superimposed onto the side of the broad –OH band at 3000–2800 cm^{-1}. The strong peak at 1647 cm^{-1} is caused

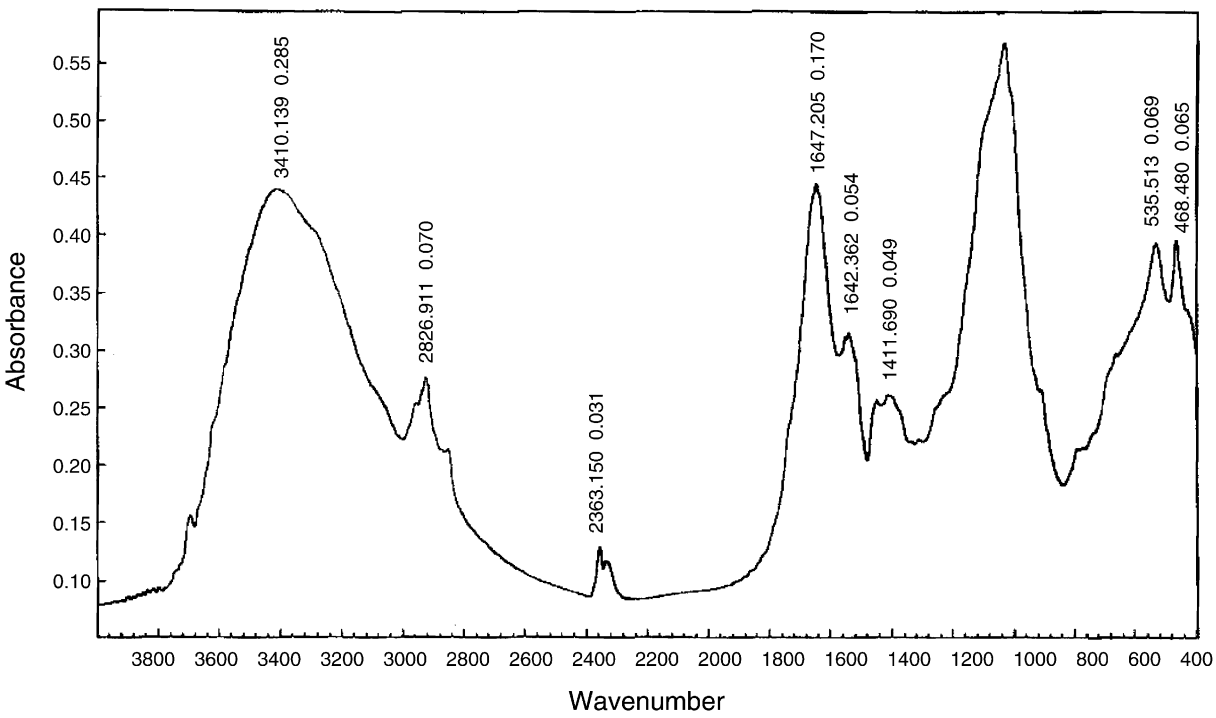

Fig. 4. Infrared spectra of raw biosolids.

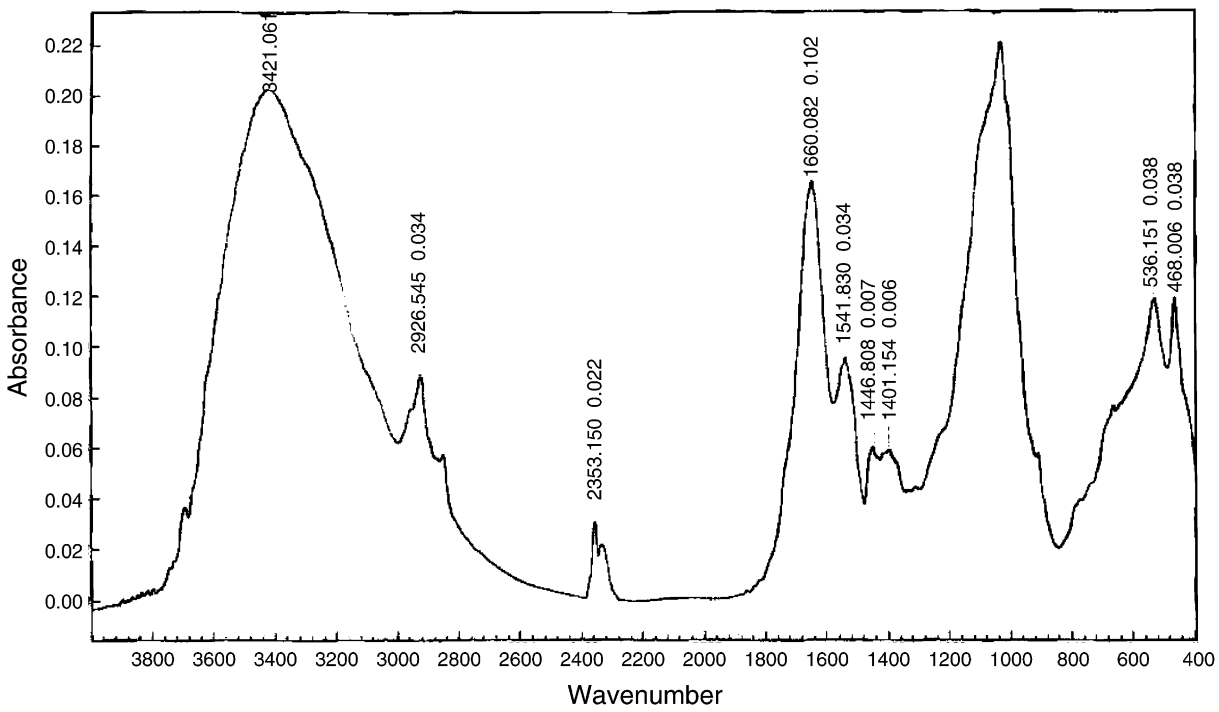

Fig. 5. Infrared spectrum of biosolids reacted with 100 mg/l Zn(II) solution.

by the C=O stretching band of the carboxyl group. The peak at approximately 1100 cm^{-1} is due to either the C–O stretch of the –OH bend. The presence of amine groups is also possible. However, the N–H stretch (3300 cm^{-1}) and the C–N stretch (1000 cm^{-1}) are not seen in this spectra due to the dominance of the –OH stretch. The absorbance of the peaks in the reacted sample is substantially lower than those in the raw sample. This indicates that bond stretching occurs to a lesser degree due to the presence of zinc, and subsequently peak absorbance is attenuated. Experiments conducted by Mameri et al. (1999) when investigating zinc biosorption by non-living *Stretomyces rimosus* biomass support this.

4. Conclusions

From the laboratory-based experiments, the following conclusions can be reached:

- Langmuir adsorption isotherms at pH 4 indicate the adsorption capacity of the dry unground biosolids to be 0.564 mM/(g dry biosolids);
- kinetic experiments show that the metal uptake equilibrium took 5 h for zinc concentrations below 0.3 mM and 24 h for 1.5 mM solutions;
- pH values between 4 and 6 are optimum for zinc biosorption;
- pH 2 would be suitable for metal elution; and
- infrared spectra analyses indicate that carboxyl groups are responsible for zinc removal.

The adsorption capacity of the WAS biosolids at pH 4 was 0.564 mM/(g dry biosolids). This compares favourably with other alternate biosorbents including mycelial waste biomass (0.33 mM/g at pH 5) and the natural zeolite, chabazite (0.08 mM at pH5). This indicates the potential for further study into the use of biosolids for zinc biosorption.

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