

Application of a Pulp Mill Waste for Wastewater Treatment

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Wastes containing ellagic acid, such as those from the neutral sulfite pulping of Eucalypts, have been identified as a potentially valuable resource material. After simple chemical treatment such wastes have been demonstrated to be efficient adsorbents of heavy metals from dilute aqueous solution. A pulp mill waste rich in ellagic acid was treated with methanol and hydrochloric acid to remove bound metal ions and tested as a metal adsorbent. The adsorption of copper(II), zinc and chromium (III) were found to fit the Langmuir isotherm model, with maximum adsorption capacities competitive with other biosorbents and commercial ion exchange resins. Selective adsorption from binary metal ion solutions can be achieved by adjusting the solution pH in the range 3.0 - 6.0. Separation coefficients of up to 19 have been determined for the preferential removal of copper (II) ions over chromium (III) ions from a binary solution. The new adsorbent was regenerated using hydrochloric acid and reused over seven adsorption cycles with minimal loss in capacity. The application of a waste material from the pulping industry to treat heavy metal bearing wastewaters is representative of the potential economic and environmental benefits to be gained by utilising wastes as resources.

INTRODUCTION

The increased use of heavy metals in process industries such as the electroplating, tanning and textile industries often results in the generation of large quantities of dilute effluents containing mixtures of heavy metals, posing environmental disposal problems. In addition, mining, mineral processing and extractive metallurgical operations produce large amounts of metal bearing liquid wastes requiring treatment [1, 2]. Unlike most other toxic pollutants, metals can accumulate throughout the food chain due to their non-biodegradability and thus have potentially detrimental effects on all living species. Thus there is a continuing interest in the development of more cost-effective and environmentally-benign processes of selective removal of heavy metals from dilute wastewater streams.

Biosorption is a form of adsorption process involving the removal of metal ions from a liquid phase onto a solid biomass material. Some biosorbents are expected to be competitive with existing non-biomass based treatments [3]. This will be true particularly if the biomass is produced as a waste product from another industrial process and requires minimal pretreatment. Wastes from the pulp and paper industry containing ellagic acid have been identified as promising candidates for application as biosorbents [4-6]. Ellagic acid (Figure 1) is one of the polyphenolic compounds found in many plants (dicotyledonous, *Eucalyptus*, etc.) and fruits (walnut, strawberry, grape, etc.); it occurs widely in nature either in its free form or in the form of ellagitannins or glycosides [7]. The heartwood of *Eucalyptus* species, commonly used in the pulp and paper industry in Australia, is known to contain large amounts of ellagitannins which can be converted to ellagic acid [8]. Ellagic acid forms complexes with many metal ions including magnesium and calcium, that have very low solubility in water [9, 10]. It has therefore been a nuisance to the pulp and paper industry using *Eucalyptus* species in the neutral sulphite process due to the formation of metal deposits inside the processing equipment. However this property also makes it potentially valuable as a metal scavenger for wastewater treatment.

A waste pipe deposit from a neutral sulphite pulp mill processing *Eucalyptus* has been demonstrated to adsorb copper (II), chromium (III) and zinc (II) ions from dilute single metal solutions after pretreatment of the waste with methanol and hydrochloric acid to remove complexed metal ions [4]. The adsorption kinetics were found to be comparable to those of other biosorbents, with 95% of the equilibrium adsorption of chromium (III) achieved within two hours' contact. The adsorbent capacity for copper (II) ions (up to 6.2 meq.g⁻¹) was higher than many other biosorbents and commercial ion exchange resins described in the literature [11-17]. The primary mechanism of metal uptake was found to be ion exchange of protons from

the adsorbent with metal ions from solution. Thus, the extent of adsorption onto the treated waste was pH dependent with different optimum pH conditions found for each metal tested. This result indicated the promise of this material for selective metal ion separations from multicomponent solutions.

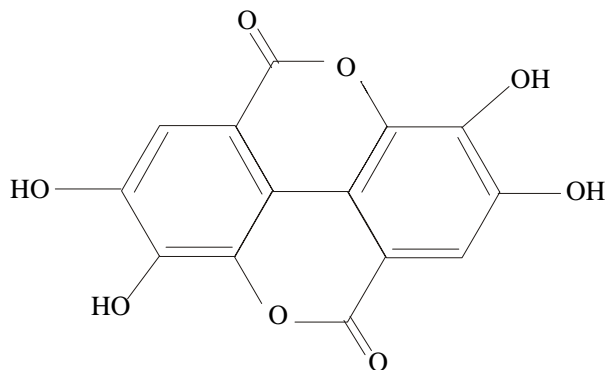


Figure 1. Ellagic acid

In order to be successfully applied for metal removal from wastewater, adsorbents must also perform well in multicomponent solutions which are typical of industrial wastes. Therefore, this paper compares the performance of an ellagic acid adsorbent obtained from a pulp mill waste in removing metal ions from single and binary metal solutions. The regeneration and reuse of the adsorbent have also been studied, as this will be a further prerequisite for its effective application to industrial wastewater treatment.

MATERIALS AND METHODS

An ellagic acid waste pipe deposit generated from the neutral sulfite processing of *Eucalyptus* (kindly supplied by Amcor, Australia) containing 64.4% ellagic acid was used for this study [4]. The waste was pretreated to partially purify it, with the main objective of removing metal ions complexed with ellagic acid in the waste as received from the plant. The waste was initially washed with methanol (10ml.g⁻¹ of solid) for 4 hours at room temperature, filtered and dried at 105°C overnight. It was then digested in boiling hydrochloric acid (2 M) for 10 minutes before being filtered again, rinsed with distilled water until a stable wash pH of 5.5 was reached and dried at 105°C overnight. Finally, samples were ground with a mortar and pestle and passed through a series of sieves to obtain a consistent range of particle size (0-200µm) for metal sorption experiments. The ellagic acid content of the treated adsorbent was determined by UV-visible spectroscopy (Varian Cary 1E spectrophotometer) to be 81 %. Details of the purification method of physicochemical characterisation of the adsorbent have been reported elsewhere [4].

Analytical grade salts dissolved in distilled water were used to make up the metal bearing solutions (Cu(NO₃)₂·3H₂O, ZnSO₄·7H₂O and Cr(NO₃)₃·9H₂O). All other chemicals were analytical grade. Batch adsorption trials were performed in sealed glass vessels agitated for 24 hours (unless otherwise stated) at 20 ± 1 °C. Previous studies indicated that equilibrium was reached in much less time than this (e.g., 4 hours for copper (II) at pH 4) [5]. HNO₃ or NaOH (0.1-1.0M) was used to adjust the initial pH of the metal solutions to the desired values before adding the adsorbent. After contact, the suspensions were filtered through 0.22 µm syringe filters (Millipore Co.) and metal concentrations in the filtrates were determined using a Perkin-Elmer Optima 3000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with a Perkin-Elmer AS 90 automatic sampler. Solution depletion analysis was used to determine the amounts of each metal adsorbed by comparing the initial and final solution concentrations.

Single and binary metal solutions were tested using identical experimental conditions. In the binary systems, copper (II) was used as the main metal, the initial concentration of which was varied to determine the maximum amount adsorbed (Q_{max}), in the presence of a fixed initial concentration of a co-ion – either zinc (II) (10 ppm) or chromium (III) (50 ppm). The initial solution pH was varied from 3.0 to 5.0. For comparison of the effect of co-ions on adsorption, the data obtained for the main metal in the binary systems were fitted to the simple Langmuir isotherm equation:

$$Q_e = Q_{\max} \frac{C_e}{b + C_e} \quad (1)$$

where Q_{\max} is the maximum adsorption capacity and b is a constant related to affinity. The adsorption uptake at equilibrium, Q_e , is expressed in millimoles of metal adsorbed per gram of the dry adsorbent. C_e is the equilibrium concentration of metal in solution [18].

The regeneration performance of the ellagic acid adsorbent was tested by first loading the adsorbent with copper (II) ions via a batch adsorption run with an initial pH of 4.0 and a metal concentration of 50 ppm. The adsorbent and solutions were mixed on magnetic stirrer for 10 hours at $20 \pm 1^\circ\text{C}$. The metal-laden adsorbent was then separated from the solution by centrifuging and the supernatant liquid filtered and analysed for residual metal concentration. Then the adsorbent was added to 50ml of hydrochloric acid of various concentrations and agitated for 24 hours to remove the adsorbed copper ions. Following desorption, the suspension was centrifuged and the adsorbent washed with distilled water repeatedly to remove any residual free protons. It was then dried in the oven at 100°C overnight and weighed before being used in the next cycle of adsorption and desorption. This process was repeated for seven cycles.

RESULTS AND DISCUSSION

The adsorption of copper (II) ions onto the ellagic acid adsorbent from single metal solutions was negligible at pH 3 or below. For initial solution pH values of 4 and 5 substantial amounts of copper were adsorbed and the data fitted the Langmuir isotherm model well (Figure 2). The amounts adsorbed under these conditions did not differ significantly, with maximum adsorbed amounts according to the Langmuir isotherm model fits of $2.7 \text{ mmol}\cdot\text{g}^{-1}$ at pH 4 and $2.4 \text{ mmol}\cdot\text{g}^{-1}$ at pH 5.

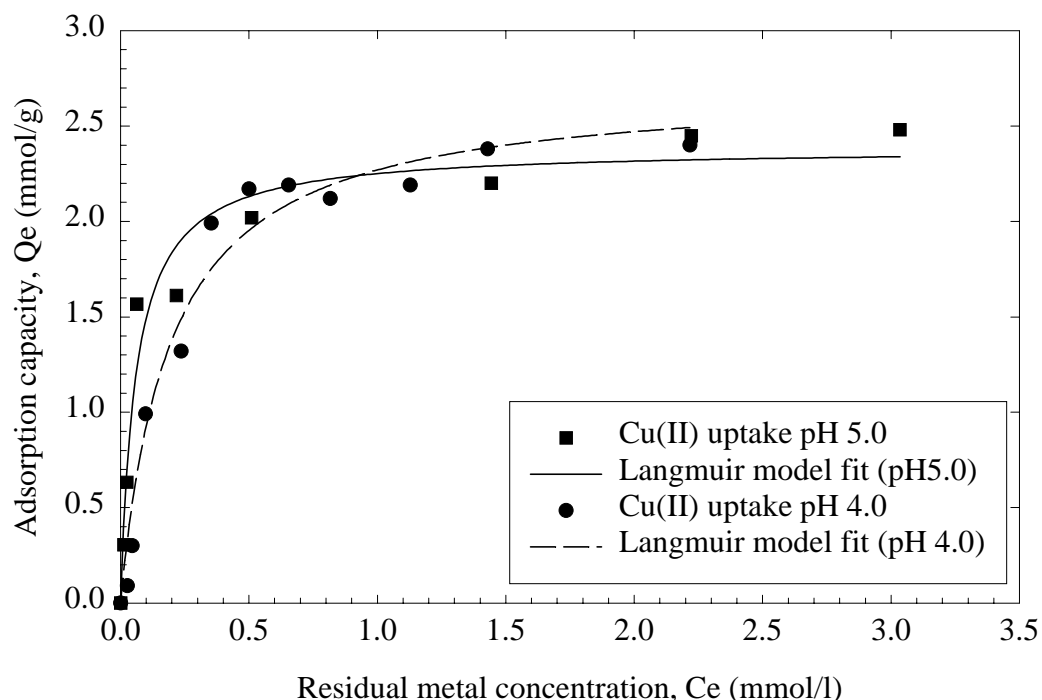


Figure 2. Adsorption isotherms for copper (II) ions at two initial solution pH values

The effects of chromium (III) and zinc (II) ions on the uptake of copper (II) ions by the ellagic acid adsorbent at an initial pH of 4.0 are shown in Figure 3. Copper adsorption was inhibited by the presence of the co-ions compared to its adsorption from the single metal solutions and the total molar amount of metal ions adsorbed from the binary solutions was less than that adsorbed from the copper solution at the same pH. Chromium (III) ions were adsorbed from the binary solution in which it was the co-ion and the presence of chromium (III) reduced the copper uptake more than did zinc (II). In contrast, zinc (II) was not discernibly adsorbed at this pH from either a single metal solution or the binary copper-zinc solution. Thus the

selectivity of the ellagic acid adsorbent for copper (II) over zinc (II) at pH 4.0 was very high, demonstrating its potential as a selective adsorbent.

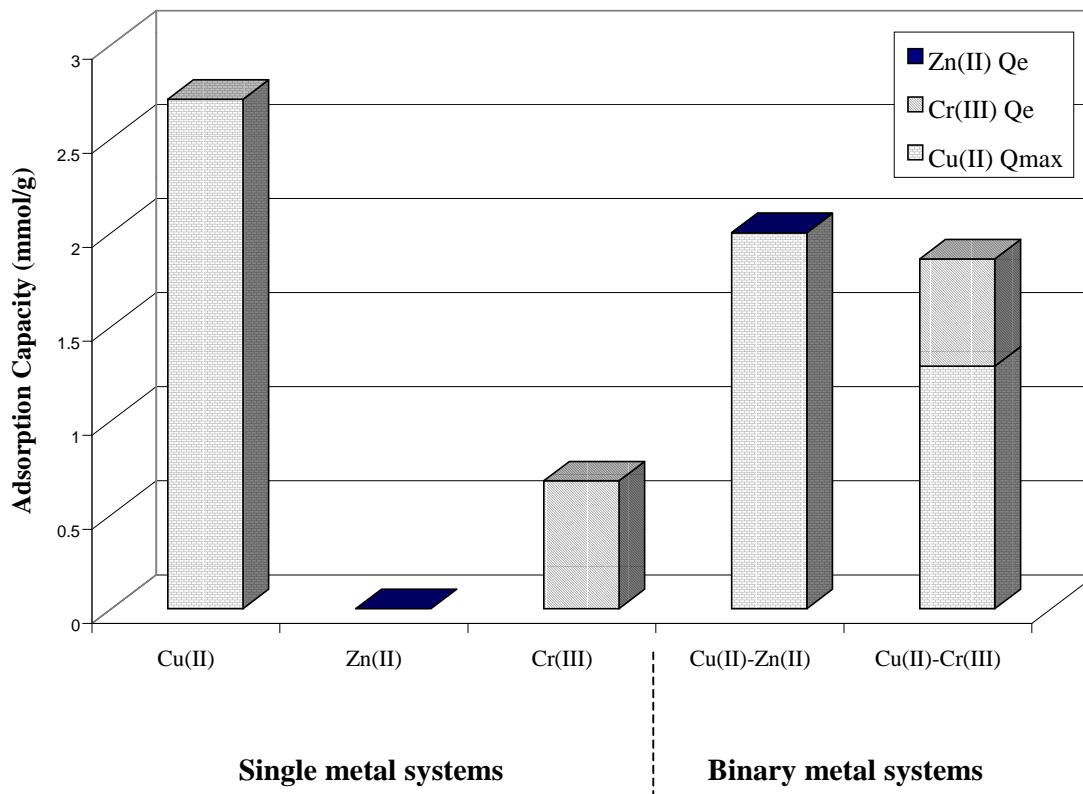


Figure 3. Copper (II) uptake from binary solutions at an initial pH of 4.0 (initial Zn (II) concentration 10 ppm, initial Cr (III) concentration 50 ppm).

Interestingly, the presence of zinc ions in the copper-zinc binary system still reduced the copper uptake significantly. This inhibition despite zero adsorption of zinc (II) may be attributed to the mechanisms of metal uptake by the ellagic acid adsorbent. Similar findings have been reported previously for other biomass adsorbents; for example, the Cd^{2+} binding capacity of an algal biomass was decreased in the presence of Na^+ and Ca^{2+} [19]. This phenomenon can be explained by the fact that the non-binding co-ions lower the intraparticle concentrations of the adsorbing ion by contributing to balancing the negative charges on the biomass surface (i.e., the requirement for electroneutrality) by electrostatic attraction. This can indirectly suppress binding of the main metal even though the co-ion is not itself bound to the biomass to any significant degree.

The effect of the initial solution pH on adsorption from the Cu/Cr binary system is depicted in Figure 4. The uptake of chromium (III) ions increased with increasing pH while the uptake of copper (II) ions was highest at pH 4.0. This correlates well with the single system data for these metals – copper (II) adsorption is close to its maximum at pH 4.0 with only a slight increase in capacity at pH 5.0, whereas chromium (III) adsorption increases significantly between pH 4.0 and 6.0 [4]. The highest degree of separation between copper (II) ions and chromium (III) ions occurred at pH 3.0, with a separation coefficient ($\eta = Q_{\text{max}}(\text{Cu}) / Q_{\text{e}}(\text{Cr})$) of 19, but the total metal uptake at this pH was relatively low ($1.1 \text{ mmol}\cdot\text{g}^{-1}$). As the pH increased the separation coefficient decreased but the total metal uptake increased to be close to the single system capacity for copper (II) at pH 5.0 ($2.4 \text{ mmol}\cdot\text{g}^{-1}$). Hence the optimum conditions for metal adsorption using the ellagic acid adsorbent for metal adsorption from a copper-chromium binary system would depend on whether selectivity or total metal uptake was most important.

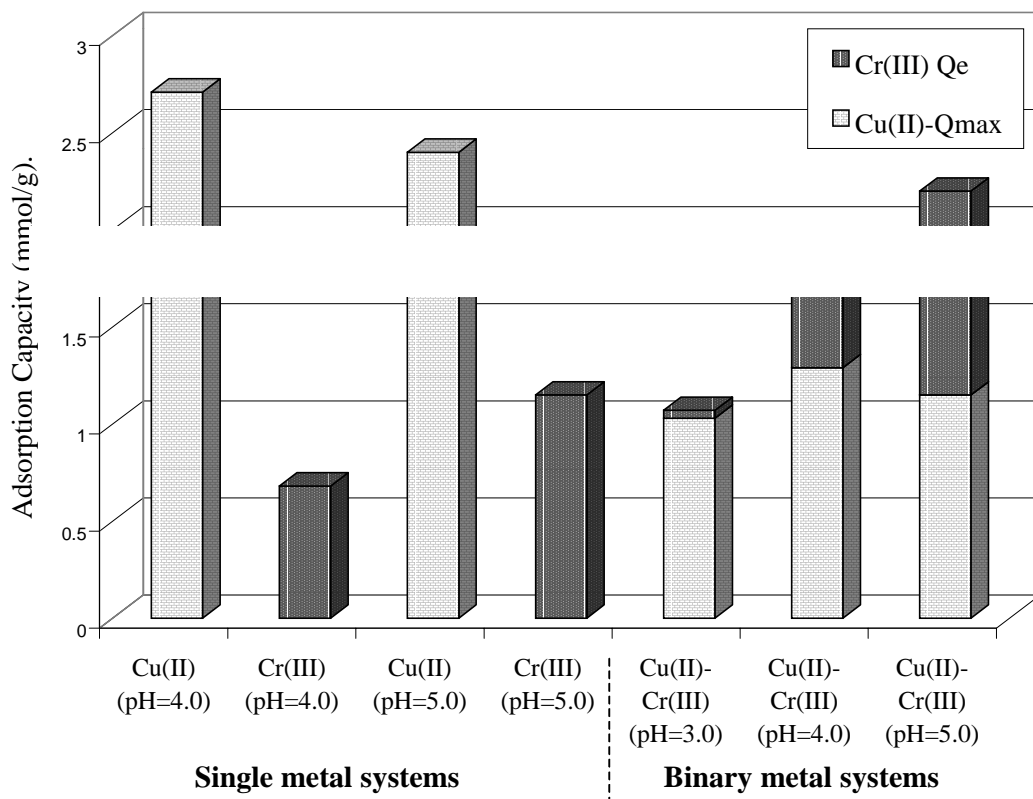


Figure 4. Effect of initial solution pH on metal uptake from binary Cu(II)/Cr(III) solutions (initial Cr concentration 50 ppm).

The above results demonstrate that mutual inhibition in the uptake of both primary and co-cations by the ellagic acid adsorbent occurred in all the single and binary systems studied. This was due to direct competition between different metal ions and protons for the same binding sites by the primary adsorption mechanism of ion exchange, as well as secondary mechanisms such as electrostatic attraction. Thus the uptake of individual metals by the ellagic acid adsorbent were generally found to be lower than those from the single metal solutions at the same solution conditions.

Studies were conducted to desorb the metal ions and regenerate the ellagic acid adsorbent for reuse as would be required for its application in wastewater treatment to be economically feasible. Experiments were conducted with copper (II) ions for which the ellagic acid adsorbent had the highest capacity under the conditions tested. Dilute hydrochloric acid (0.1M-1M) has been employed previously [20, 21] to strip adsorbed cadmium and from algal biomass and for desorbing nickel from fungal biosorbents [22]. Since the primary adsorption mechanism for metal ions onto the ellagic acid adsorbent was ion exchange, hydrochloric acid was also selected for regeneration in this work. The effect of the HCl concentration used for regeneration on the adsorption capacity for copper (II) ions after regeneration is shown in Figure 5. The data are presented as the percentage of the initial adsorbent capacity for copper (II) ions that was preserved in the second adsorption cycle, following regeneration. It was evident that the regeneration efficiency increased with increasing HCl concentration. More than 75% of the biosorption capacity was regenerated when 0.5 M HCl was used and only a slight further increase in capacity was observed when the concentration of HCl was higher than 0.5 M, which is the usual concentration used in ion-exchange operations [23].

Based on the above results, regeneration of the ellagic acid adsorbent in multiple adsorption-desorption cycles of copper (II) ions was then carried out with 0.5 M HCl as the regenerant. It was found (Figure 6) that the adsorbent capacity was retained during a further six cycles after the initial loss of 20% of the capacity in the first cycle, exhibiting performance after regeneration superior to that of peat moss [13] and comparable to those of various forms of microbial biomass [24]. The loss of adsorption capacity in the first cycle may be attributable to leaching out of active organic components and limited metal desorption effectiveness of

0.5 M HCl due to the strong affinity of the adsorbent for copper (II) ions. Greater recovery of adsorption capacity might be achieved with other regenerants, such as the chelating agent EDTA (ethylenediaminetetraacetic acid), however an economic assessment would be required to determine whether the improvement gained in the extent of regeneration would justify the additional costs of using such a regenerant.

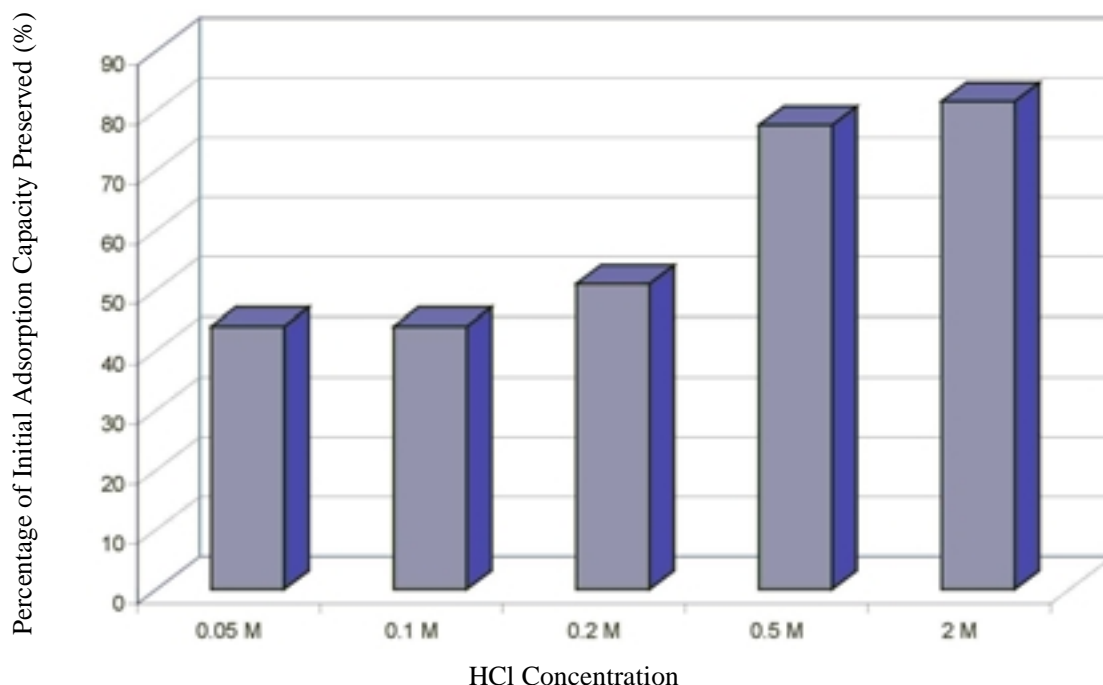


Figure 5. Adsorbent capacity for copper (II) ions at an initial solution pH of 4.0 after regeneration with HCl, as a function of HCl concentration.

The results presented demonstrate that adsorbents generated from pulp mill wastes containing ellagic acid show promise for applications requiring adsorption of metal ions from dilute solutions of acidic pH. Other chemically similar industrial wastes, such as tanning wastes containing ellagic acid, are also expected to have potential for generation of useful metal adsorbents. Further work is underway to optimise the selectivity, regeneration and fixed bed performance of ellagic acid adsorbents obtained from industrial wastes.

CONCLUSION

This study has shown that an ellagic acid-based adsorbent obtained by partial purification of a pulp mill waste has promise to compete with other adsorbents for heavy metal removal from wastewater. It adsorbs a range of metal ions including copper (II), chromium (III) and zinc (II) ions from dilute acidic solutions of pH 3 - 7. Its capacity for copper ions has been shown to be comparable or superior to other biosorbents and ion exchange resins. Its selectivity from binary solutions can be altered by appropriate selection of the solution conditions, with copper (II) ions removed in preference to zinc (II) or chromium (III) under the conditions tested. The adsorbent can be regenerated and reused over at least 7 cycles with approximately 20 % of the original adsorption capacity for copper (II) ions lost in the first cycle, but no further loss thereafter.

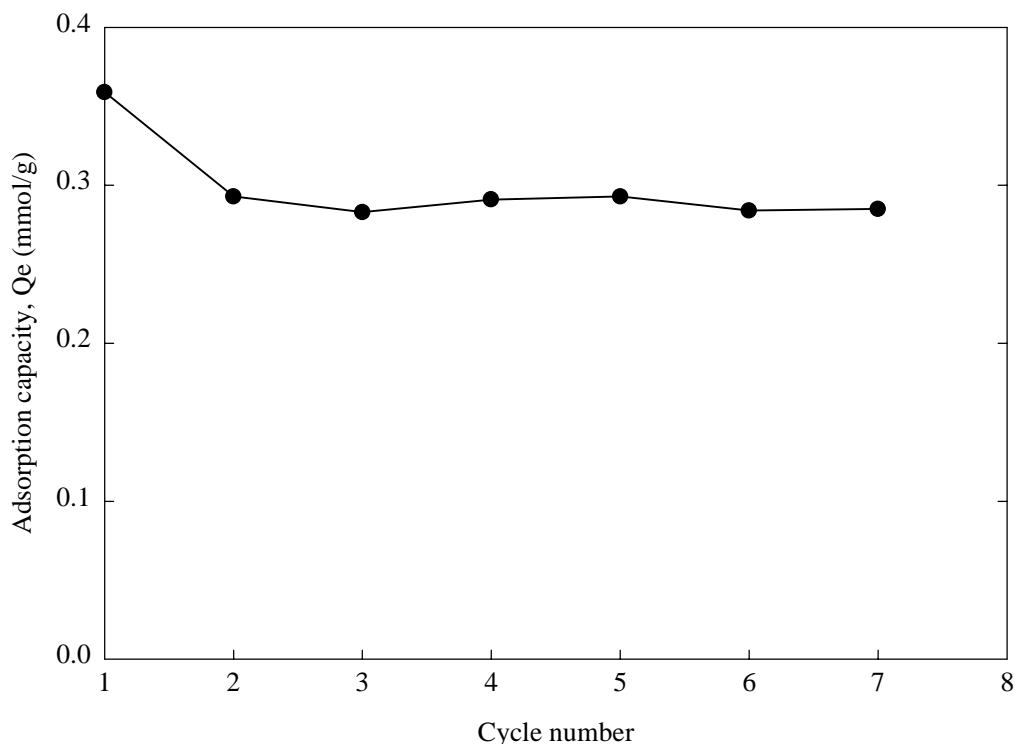


Figure 6. Adsorbent capacity for copper (II) ions at an initial solution pH of 4.0 over repeated adsorption/desorption cycles when regenerated with 0.5 M HCl.

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