Removal of copper, nickel and lead from wastewater using a modified cellulose material: a comparison

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Abstract

Heavy metal waste streams from a variety of industrial sources pose a significant environmental threat to receiving waters. Significant research work has focused on the use of adsorbents and adsorption in the treatment and recovery of these metals from waste streams. This paper focuses specifically on the design of a novel adsorbent based on the naturally occurring material, cellulose and application of this novel material to the removal of selected heavy metals from waste streams. Cellulose material has limited heavy metal adsorbing capability. To enhance its sorption capacity, a sorbent material was prepared by firstly grafting glycidyl methacrylate monomer to cellulose. The grafted product was then functionalised by the addition of imidazole. The novel material was then assessed for its ability to adsorb the heavy metals Cu(II), Ni(II) and Pb(II). Uptake levels on the cellulose-g-GMA-imidazole material were 68 mg g^{-1} Cu(II), 45 mg g^{-1} Ni(II), 71 mg g^{-1} Pb(II). These uptake levels compared favourably with those achieved using other naturally occurring materials. The level of uptake of each metal on the modified cellulose material was found, in all cases, to be significantly influenced by aqueous pH. The optimum pH range in all cases ranged from approximately pH 4 to pH 5.5. The speed of uptake of each metal on the sorbent material ranged from approximately 40 minutes in the case of Cu(II) and Pb(II) to almost 400 minutes for Ni(II) depending on initial metal concentration in solution. The overall kinetics in each case is best described by the pseudo-second order approach. Almost complete recovery of each metal from the modified cellulose material was possible using a 0.1M acid solution; however, re-use of the sorbent materials in further adsorption cycles yielded variable outcomes.

Keywords: wastewater, heavy metals, adsorption, modified cellulose.

1   Introduction

Heavy metals such as copper, nickel and lead are discharged in wastewaters from a variety of industrial sources including acid mine drainage [1], metallurgical industries [2], electronic industries [3] and electroplating [4]. Many of the heavy metals are needed by plants in trace concentrations but higher concentrations can produce significant toxic effects [5–7].

A variety of technologies are currently employed in the removal of heavy metals from waste streams including chemical precipitation [8], membrane technology [9], ion-exchange [8] and adsorption [10]. Adsorption is one of the more popular treatment processes offering flexibility in design and operation and in many cases produces treated effluents suitable for re-use. Adsorption also is potentially reversible so offers the possibility of regeneration of the adsorbent and its re-use.

Currently there is an increasing research emphasis on the use of naturally occurring materials as adsorbents or supports for adsorbents in the removal of heavy metal from wastewaters. Examples of these polysaccharide-based materials include chitosan [11] and cross-linked chitosan [12] in the removal of Cu(II) and cross-linked starch gel [13] for the removal of Pb(II) from wastewaters. Crini [14], in an extensive review of the use of polysaccharide-based materials as adsorbents in wastewaters, has outlined high removal capabilities for certain metal ions as compared to other low cost sorbents and commercial activated carbons. Aswell as excellent sorption capacities, the specificity is mainly influenced by factors such as chemical structure and composition of the polysaccharide based material and by the accessibility of chelating or complexing groups.

Our research work to date [15,16] has focused on the modification of cellulose in a two step reaction. Initially the cellulose is grafted with the monomer glycidyl methacrylate and subsequently it is functionalised with the addition of imidazole. Figure 1 outlines the overall structure of the sorbent
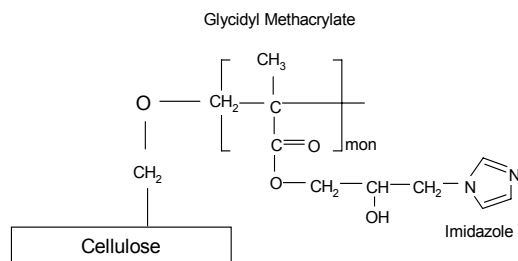

Figure 1:   Cellulose-g-GMA-imidazole structure.

material. The presence of the imidazole provides binding sites for the adsorbing heavy metal. Studies have been carried out in which the binding of copper, nickel and lead to this modified cellulose material and this paper seeks to provide

a comparison of uptake of each metal by the modified cellulose material in comparison to alternative adsorbents.

2   Methodology

2.1 Preparation of Cellulose-g-GMA-imidazole

Cellulose (0.5 g) was placed in a glass grafting apparatus along with 30 mL of deionized water at 30^oC under a nitrogen atmosphere. Cerium Ammonium Nitrate ($0.05M$) and 10 mL of $0.1M$ nitric acid were added and allowed to react with the cellulose for 15 min. Glycidyl methacrylate monomer ($0.35M$) was then added and left to react for a further 2 hours. On completion of the reaction, the Cell-*g*-GMA product was removed and soxhlet extracted with acetone for 12 h to remove any GMA homopolymer. The Cell-*g*-GMA was then dried at 60°C and imidazole (3.0 g) was reacted with the cellulose-*g*-GMA fibres (3.0 g) in 120 mL dimethyl formamide solution at 70°C. The cellulose-*g*- GMA-imidazole material was then filtered, rinsed with water, soxhlet extracted with methanol for 6 hours and dried in a vacuum oven at 70°C under vacuum.

2.2 Adsorption isotherms

A range of Cu(II), Pb(II) and Ni(II) (20–2000 mg dm^{-3}) adsorption solutions were prepared separately by dissolving appropriate amounts of copper(II)sulphate, $Cu(SO_4).5H_2O$, lead(II)nitrate, $Pb(NO_3)_2$ or nickel(II)sulphate, $NiSO_4.6H_2O$ (Merck, Germany) in deionised water. From each flask, a 25ml aliquot was removed and placed in a separate 50ml plastic vial and 0.2g of the adsorbent cellulose-g-GMA-imidazole was added to each vial. All vials were then sealed and placed in a temperature controlled water bath at 23^oC for either 120mins for Cu(II) and Pb(II) or 400mins for Ni(II). The vials were subsequently centrifuged at 4,000 rpm for 15 minutes. 10 cm^3 of each supernatant was then removed and suitably diluted with de-ionised water and analysed by atomic absorption spectrophotometry (AAS) (Varian SpectraAA 220). Blank solutions containing equivalent initial concentrations of either Cu(II), Pb(II) or Ni(II) but without addition of the adsorbent (cellulose-g-GMA-imidazole) were prepared and put through the identical procedures. Standard AAS solutions were prepared in the range 1–20 mg dm^{-3} for Cu(II), Pb(II) and Ni(II) using 1000 mg dm^{-3} AAS stock solutions (Reagecon Diagnostics, Ireland). Samples and blanks were run in triplicate to ensure reproducibility and accuracy.

2.3 pH studies

The effect of initial solution pH on Cu(II), Pb(II) and Ni(II) adsorption onto cellulose-g-GMA-imidazole was studied at 23 $^{\circ}$C. A 1000 mg dm^{-3} stock solution was prepared by dissolving appropriate amounts of the sulphate salt of each metal in deionised water. A 25 cm^3 aliquot of this stock solution was removed and placed in each of six 50 cm^3 plastic vials and 0.2 g of the adsorbent (cellulose-g-GMA-imidazole) was added. The pH of the solution in each vial

was adjusted to yield pH values ranging from pH 2 to 7. Adsorption was then allowed to proceed for 60 min in the case of Cu(II) and Pb(II) and 400 min for Ni(II) and the metal adsorption level was measured for each of the six vials in an analogous way to that outlined in the adsorption isotherms methodology.

2.4 Kinetics studies

Adsorption kinetics for Cu(II), Pb(II) and Ni(II) uptake on the cellulose-g-GMA-imidazole adsorbent were studied separately using a batch technique at 23°C. At each of three initial metal ion concentrations of 400, 600 and 800 mg dm^{-3} for Pb(II) and 100, 300 and 600 mg dm^{-3} for both Ni(II) and Cu(II), a kinetic experiment was carried out. Known weights of the adsorbent (0.2g) were added to each of 10 vials containing 25ml of the initial concentration metal ion solution. Each vial was shaken in a temperature controlled water bath for a specific time period ranging from 10 minutes to 120 minutes contact time for Cu(II) and Pb(II) and up to 400 minutes in the case of the Ni(II) experiments and subsequently centrifuged. The concentration of each metal ion before and after adsorption was determined by AAS. The amount of each metal adsorbed was calculated from its initial and final concentrations in the aqueous phase.
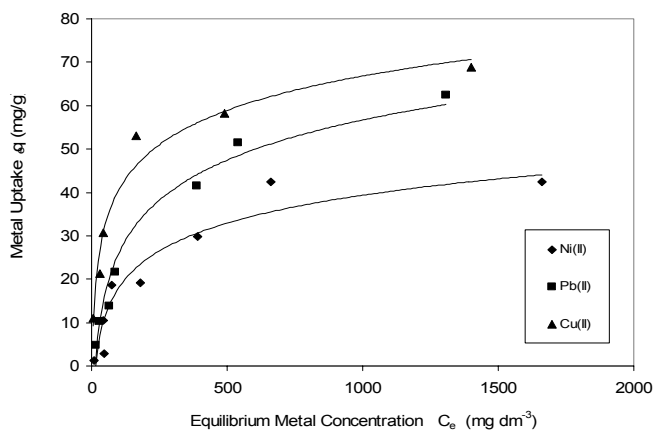

Figure 2:   Adsorption isotherm plots for metal uptakes on Cellulose-g-GMA-imidazole.

3   Results and discussion

3.1 Adsorption

The adsorption isotherms for uptake of Cu(II), Pb(II) and Ni(II) on the cellulose-g-GMA-imidazole material, at 23°C, are shown in figure 2. The uptake of Cu(II), Pb(II) and Ni(II) reached levels of 68.5, 71.9 and 45.2 mg g^{-1} respectively. Using equation (1) the Langmuir [17] adsorption approach was applied to the isotherm data:

$$q_e = \frac{K_L . C_e}{1 + A_L . C_e} \qquad (1)$$

Where q_e is the amount of metal ion adsorbed in mg g^{-1}, C_e is equilibrium concentration of metal ion in solution in mg dm^{-3}, K_L and A_L are Langmuir constants. A plot of C_e/q_e versus C_e from the linear form of eqn (1) was used to determine the values of K_L (intercept) and A_L/K_L (slope). Saturation coverage on the adsorbent was obtained as K_L/A_L. Application of the Langmuir model to the adsorption isotherm data resulted in a strong correlation between the Langmuir approach and the uptake of each metal ion. The calculated parameters for the Langmuir constants for each adsorption process are presented in table 1. K_L/A_L was used to estimate the saturation coverage for Cu(II), Pb(II) and Ni(II) on the adsorbent.

Table 1:   Langmuir Constants for Cu(II), Pb(II) and Ni(II) adsorption on Cellulose-g-GMA-imidazole.

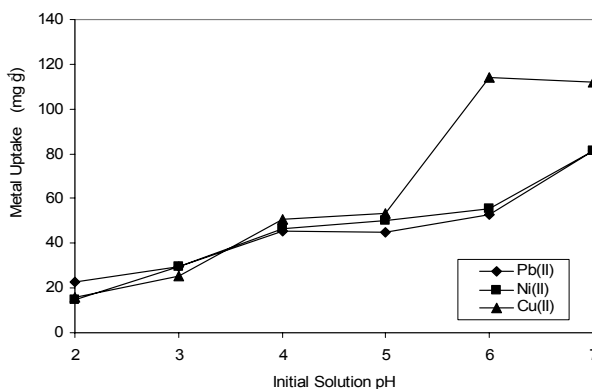| Langmuir Isotherm Data					
Metal Ion	Temperature (^{o}C)	K_L (dm^3 g^{-1})	A_L (dm^3 mg^{-1})	K_L/A_L (mg g^{-1})	R^2
Cu(II)	23	1.55	0.023	68.5	0.995
Pb(II)	23	0.33	0.005	71.9	0.991
Ni(II)	23	0.17	0.003	45.2	0.980

Figure 3:   Influence of solution pH on metal uptake.

3.2 Influence of pH

The effect of initial solution pH on the sorption of each metal onto cellulose-g-GMA-imidazole was studied at room temperature by varying the pH between 2.0 and 7.0 (Fig. 3). The plot can be divided into three pH regions. In the first region, from pH 2 to 4, competition for adsorption sites on the cellulose-g-GMA-imidazole between protons (H$^+$) and the metal ions exists. Uptake of the metal

ions ranges between 25–40% of the expected maximum adsorption level. In the second region of pH 4.0–6.0, the influence of H^+ is minimised and maximal Pb(II) and Ni(II) uptake occurs. This maximal range is narrower for Cu(II) uptake (pH 4–pH 5). In this central region of each plot the level of uptake corresponds with uptake levels based on each isotherm plot. The final region of the plot extends from pH 5.5 to pH 7 where a sharp apparent increase in uptake is observed. This sharp increase is largely due to precipitation of Cu(II), Pb(II) and Ni(II) as their respective hydroxide species and is not as a result of an adsorption process.

3.3 Kinetics of uptake

The influence of initial metal concentration on the rate of Cu(II), Pb(II) and Ni(II) uptake was assessed. In the case of Cu(II) and Pb(II) equilibrium adsorption was achieved within 40 minutes of contact. Ni(II) uptake proved considerably slower and required a contact time of approximately 400 minutes. Pseudo-second order kinetics (eqn. 2) can be used to assess the dependency of each process on the sorbed Cu(II), Pb(II) or Ni(II) concentrations.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{qe}t \qquad (2)$$

where k_2 is the overall rate constant for the adsorption process [dm^3 (mg min^{-1})], q_e is the amount of metal ion adsorbed at equilibrium (mg g^{-1}) and q_t is the amount of metal ion adsorbed at any time t (mg g^{-1}). The initial sorption rate, h , as t → 0 can be defined as

$$h = k_2 q_e^2. \qquad (3)$$

The overall results and constants for the pseudo-second order approach are presented in table 2.

   High correlation co-efficients (R^2) in all cases were observed indicating overall compliance with the pseudo-second order approach. The data also shows that the initial sorption rates (h values) decreased with an increase in initial Pb(II) concentration and increased with an increase in initial Cu(II), Ni(II) concentrations.

3.4 Regeneration of cellulose-g-GMA-imidazole

Table 3 outlines the extent of recovery of adsorbed metal versus pH of regenerant solution. Varying results were obtained when the metal loaded cellulose-g-GMA-imidazole sorbent was regenerated. Using acid solutions of pH 1, almost complete recovery of each of the metal was achievable. Increasing the pH of the regenerating solution to pH 2 led to a considerable drop in metal recovery levels to approximately 30% of the adsorbed metal. As the pH was raised further towards neutrality the extent of metal recovery continued to decline further. While 100% recovery of the metals was feasible at pH 1, it was also found that the adsorbent material, after metal recovery, showed only limited capacity to re-adsorb the metals in a second cycle of the process.

Table 2:   Effect of initial Cu(II), Pb(II) and Ni(II) concentrations on sorption data on Cellulose-g-GMA-imidazole using the pseudo-second order approach at $23^{\circ}C$.

Pseudo-second order kinetic parameters – Cu(II)				
Initial Conc. Cu(II) $(mg\ dm^{-3})$	Correlation Co-efficient R^2	Cu(II) uptake $(mg\ g^{-1})$	Rate Constant, k_2 $(g\ mg^{-1}\ min^{-1})$	Initial sorption Rate, h $(mg\ g^{-1}\ min^{-1})$
100	0.999	11.7	3.59×10^{-2}	4.9
300	0.999	33.1	1.36×10^{-2}	15.0
600	0.999	55.6	6.54×10^{-3}	20.2
Pseudo-second order kinetic parameters – Pb(II)				
Initial Conc. Pb(II) $(mg\ dm^{-3})$	Correlation Co-efficient R^2	Pb(II) uptake $(mg\ g^{-1})$	Rate Constant, k_2 $(g\ mg^{-1}\ min^{-1})$	Initial sorption Rate, h $(mg\ g^{-1}\ min^{-1})$
400	0.999	36.1	2.75×10^{-2}	35.9
600	0.998	43.8	9.95×10^{-3}	19.1
800	0.998	46.9	8.82×10^{-3}	19.4
Pseudo-second order kinetic parameters – Ni(II)				
Initial Conc. Ni(II) $(mg\ dm^{-3})$	Correlation Co-efficient R^2	Ni(II) uptake $(mg\ g^{-1})$	Rate Constant, k_2 $(g\ mg^{-1}\ min^{-1})$	Initial sorption Rate, h $(mg\ g^{-1}\ min^{-1})$
100	0.983	4.7	1.38×10^{-2}	0.1754
300	0.982	13.38	2.78×10^{-3}	0.4993
600	0.983	21.17	1.71×10^{-3}	0.7692

Table 3:   Recovery of adsorbed metals from Cellulose-g-GMA-imidazole.

	% Metal Recovery					
pH	1	2	3	4	5	6
Cu(II)	96	28	12	10	9	9
Pb(II)	99	36	19	22	6	6
Ni(II)	100	34	16	14	13	14

3.5 Comparison of Cu(II), Pb(II) and Ni(II) on alternative adsorbents

The Cu(II), Pb(II) and Ni(II) uptake levels on the cellulose-g-GMA-imidazole material were compared with the results of other research studies as outlined in table 4.

   The sorbent material (cellulose-g-GMA-imidazole) used in our own research shows a relatively strong Cu(II), Pb(II) and Ni(II) adsorption capacities of 68.5, 71.9 and 45.2 mg g^{-1} respectively. In the case of Cu(II) uptake, sawdust modified with acrylic acid yielded highest adsorption values with chabazite, a zeolite

Table 4:   Comparison of adsorption levels for Cu(II), Pb(II) and Ni(II) on a range of natural/modified sorbent materials.

Adsorbent	Cu(II)	Pb(II)	Ni(II)	Ref.
Cellulose/cysteine	22	28	8	[18]
Sawdust/Acrylic acid	104		97	[19]
Cellulose-GMA-Imidazole	68.5	71.9	45.2	This research
Clinoptilolite	25.4	124	0.9	[20][21]
Chabazite	5.1	6.0	4.5	[22]
Chitosan	16.8	16.4	2.4	[23]
Crosslinked chitosan	62.5			[11]
Cross-linked starch gel		433		[13]

material, showing limited adsorption capacity. Cross-linked chitosan also shows strong Cu(II) uptake. Cross-linked starch gel showed extremely high uptake of Pb(II) with chabazite showing weak uptake of Pb(II). Our material can best be described as mid-range in terms of Pb(II) uptake relative to the other adsorbents. Many of the adsorbents show limited Ni(II) uptake with the cellulose-g-GMA-imidazole material from this work showing strong Ni(II) uptake.

4   Conclusions

The prepared adsorbent, cellulose-g-GMA-imidazole, proved to be an efficient adsorbent for the removal of Cu(II), Pb(II) and Ni(II) from aqueous solution. The adsorption isotherms indicated clearly that the reaction product has an adsorptive capacity of approximately 69 mg g^{-1}, 72 mg g^{-1} and 45 mg g^{-1} for Cu(II), Pb(II), Ni(II) respectively, at a temperature of 23°C. The Langmuir model best described each of the metal adsorption processes. The speed of adsorption for Cu(II) and Pb(II) was rapid (40min) with uptake of Ni(II) being considerably slower (400min). The overall adsorption levels of Cu(II), Pb(II) and Ni(II) on the cellulose-g-GMA-imidazole compared very favourably with uptake levels outlined in a range of research studies using other unmodified and modified naturally occurring materials.

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