Design of a novel cellulose-based adsorbent for use in heavy metal recovery from aqueous waste streams

D. W. O'Connell[1,3], C. Birkinshaw[2,3] & T. F. O'Dwyer[1,3]
[1]*Chemical and Environmental Sciences Department, University of Limerick, Ireland*
[2]*Materials Science and Technology Department, University of Limerick, Ireland*
[3]*Materials and Surface Science Institute, University of Limerick, Ireland*

Abstract

Currently, significant metal-laden waste streams are produced from a number of industries with obvious consequences for the environment. A variety of techniques are being used to treat these wastewaters. One such technique is adsorption and recent focus in this area has been around the preparation of selective adsorbents based on naturally occurring support materials. In our work, a regenerated cellulose wood pulp was grafted with the vinyl monomer glycidyl methacrylate (GMA) and was further functionalised with imidazole to produce a novel adsorbent material, cellulose-g-GMA-imidazole. A series of adsorption studies were carried out on the cellulose-g-GMA-imidazole to assess its capacity in the separate removal of lead and nickel ions (Pb(II), Ni(II)) from aqueous solution. Cellulose-g-GMA-imidazole sorbent showed an uptake of approximately 72 mg g^{-1} of Pb(II) and 45 mg g^{-1} of Ni(II) from aqueous solution. The adsorption process in both cases followed the Langmuir model of adsorption and Pb(II) uptake occurred within 30 minutes while Ni(II) uptake was considerably slower at 400 minutes for maximum uptake. In both cases pseudo second order kinetics best describes the overall process for each metal uptake. The cellulose-g-GMA-imidazole material shows significant promise as a sorbent for the removal of both Ni(II) and Pb(II) and other heavy metal ions from aqueous and waste streams.
Keywords: aqueous waste streams, heavy metals, cellulose, adsorption.

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1 Introduction

Advances in waste stream treatment options are currently being driven by specific requirements such as legislative pressures, more restrictive controls on effluent discharge levels, costs associated with water treatment and purification and economic and environmental benefits associated with recovery of specific contaminants. At a European Union level, the advent of the European Pollutant Emissions Register clearly sets out the current state in respect of priority pollutants, the discharge sources and more importantly the quantities of specific chemicals discharged to various compartments of the environment [1]. Heavy metals such as lead and nickel are but two of the species of particular concern environmentally and are discharged to the environment in the wastewaters associated with industries such as mineral processing, non-ferrous metal porcelain enamelling, electroplating, copper sulphate manufacture, ammunitions and battery manufacture [2]. Discharge concentrations for both Pb(II) and Ni(II) can range from 3.4 to 900 mg dm^{-3} [3]. Pb(II) accumulates in vital organs and bones and causes a number of diseases ranging from anaemia to nervous system degeneration [4]. Ni(II) salts are known to be carcinogenic at high concentrations [5].

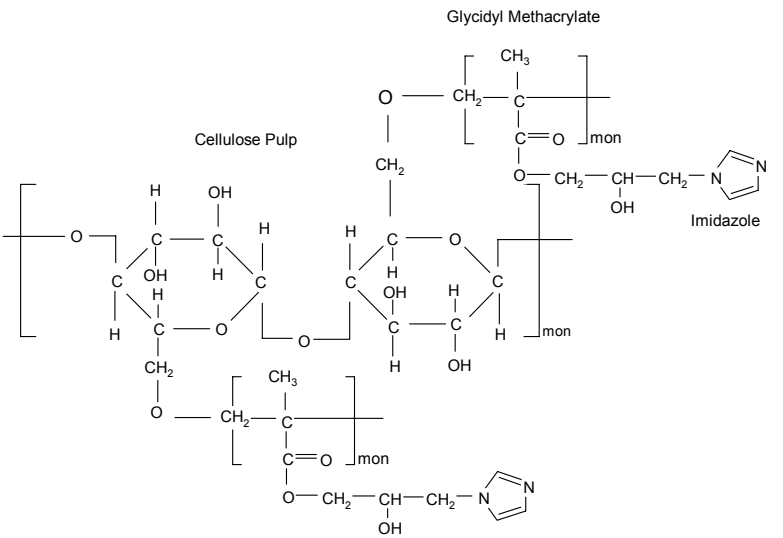

Figure 1: Cellulose-g-GMA-imidazole structure.

Traditionally, the heavy metals, Pb(II) and Ni(II), have been removed from waste streams by a variety of techniques including precipitation, oxidation, reduction, ion exchange, filtration, electrochemical treatment, membrane technologies and reverse osmosis. Most of these methods involve high capital costs and are not suitable for small scale industries [6]. As an alternative, there

has been an increasing emphasis on designing adsorbents based on naturally occurring support materials. Natural support materials are usually available in large quantities, low cost and can be chemically modified to enhance metal binding ability. Extensive research has been carried out on chitosan [7] and clays [8]. For example, chitosan's adsorptive capacity for some heavy metal ions has been greatly increased by chemical modification [9]. To date, a number of methods have been used to modify cellulose [10]. In particular, the graft polymerisation method has gained importance in modifying the chemical and physical properties of pure cellulose for different uses [11]. Adsorption of heavy metal ions is one application which has been studied [12].

In our current research work we have studied the grafting of glycidyl methacrylate monomer onto cellulose fibres. This grafted product contained a number of highly reactive epoxy groups which permitted the introduction of imidazole, a metal binding group, into the grafted polymeric material. The resultant compound produced was referred to as cellulose-g-GMA-imidazole and its structure is presented in figure 1. This research paper assesses the adsorption capacity of cellulose-g-GMA-imidazole in the removal of the heavy metal ions, Pb(II) and Ni(II), from aqueous streams.

2 Methodology

In a typical synthesis of cellulose-g-GMA-imidazole, the same technique was used as described in our previous publication [13]. The regenerated cellulose (Chemcell™) originated from Borregaard Industries, Sarpsborg, Norway. This regenerated cellulose was in a dissolving cellulose wood pulp form and was broken up into its fibrous form using a blender. Ceric ammmonium nitrate (CAN), glycidyl methacrylate (GMA), imidazole, methanol and acetone (technical grade) were provided by Sigma Aldrich, UK. The GMA was distilled to remove stabilisers before use. All aqueous solutions and standards were prepared using deionised water.

2.1 Adsorption experiments

2.1.1 Adsorption isotherms

A range of both Pb(II) (20 – 2000 mg dm^{-3}) and Ni(II) (20 – 2000 mg dm^{-3}) adsorption solutions were prepared separately by dissolving appropriate amounts of lead(II)nitrate, $Pb(NO_3)_2$ or nickel(II)sulphate-6-hydrate, $NiSO_4.6H_2O$ (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°C for either 120 mins or 400mins for Pb(II) and Ni(II) respectively. 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 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} Pb(II) or Ni(II) using 1000 mg dm^{-3} AAS stock solution (Reagecon Diagnostics, Ireland). Samples and blanks were run in triplicate to ensure reproducibility and accuracy.

2.1.2 Kinetics studies

Adsorption kinetics for both 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 Ni(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 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. All samples and blanks were run in triplicate to ensure reproducibility and accuracy.

3 Results and discussion

3.1 Adsorption isotherms

The adsorption isotherms for uptake of Pb(II) and Ni(II) on the cellulose-g-GMA-imidazole material, at 23°C, are shown in figure 2. Pb(II) adsorption reached a level of 71.9 mg g^{-1} while a reduced uptake of Ni(II) of 45.2 mg g^{-1} was observed. Using equation (1) the Langmuir [14] adsorption approach was applied to the isotherm data.

$$q_e = \frac{K_L.C_e}{1 + A_{L.}C_e} \tag{1}$$

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 both metal ions. 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 of both Pb(II) and Ni(II) on the adsorbent. It was calculated as 71.9 mg g^{-1} for Pb(II) uptake and 45.2 mg g^{-1} for Ni(II) adsorption.

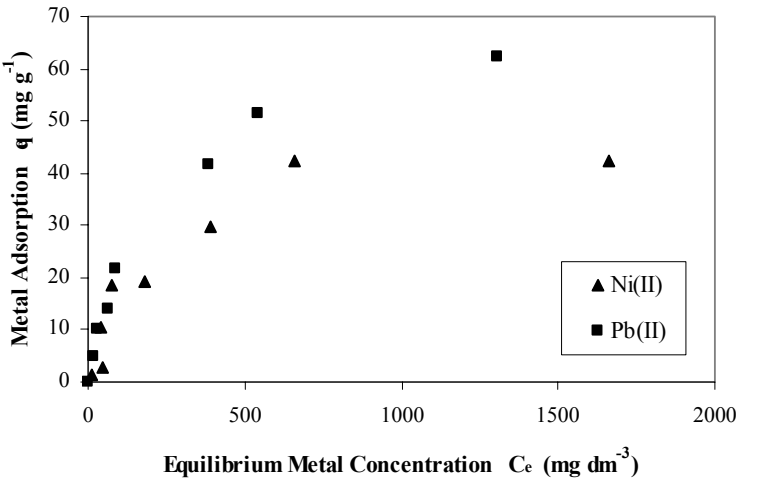

Figure 2: Adsorption isotherms for Pb(II) and Ni(II) on cellulose-g-GMA-imidazole at 23°C.

Table 1: Langmuir constants for Pb(II) and Ni(II) adsorption on cellulose-g-GMA-imidazole.

Langmuir Isotherm Data					
Metal Ion	Temperature (^oC)	K_L ($dm^3\ g^{-1}$)	A_L ($dm^3\ mg^{-1}$)	K_L/A_L ($mg\ g^{-1}$)	R^2
Pb(II)	23	0.3341	0.005	71.9	0.991
Ni(II)	23	0.1747	0.003	45.2	0.980

Table 2: Comparison of adsorption levels for Pb(II) and Ni(II) on cellulose based materials.

Sorbent Material	Pb(II) Uptake ($mg\ g^{-1}$)	Ref.
Polymer grafted banana stalk	185.3	[15]
Cellulose-g-GMA-Imidazole	75.8	This study
Modified Cellulose beads	61.74	[16]
Cellulose-g-Polyacrylic acid	23.9	[17]

Sorbent Material	Ni(II) Uptake ($mg\ g^{-1}$)	Ref.
Mod. Lignocellulosic Material	187.8	[18]
Cellulose Modified with PABA	110.4	[19]
(Cellulose-g-GMA-Imidazole)	48.5	This study
Cellulose Containing-nut shells	3.83	[20]

These uptake levels can be compared with the results of other studies as outlined in table 2, where the sorbent materials are presented in descending order of Pb(II) and Ni(II) adsorption capacity. The sorbent material (cellulose-g-GMA-imidazole) used in our own research shows a relatively strong Pb(II) and Ni(II) adsorption capacities of 71.9 mg g^{-1} and 45.2 mg g^{-1} respectively.

3.2 Adsorption kinetics

Two primary issues were addressed namely the contact time for equilibrium adsorption and the influence of initial adsorbate concentration on uptake. The influence of initial concentration on the rate of Pb(II) and Ni(II) uptake can be seen in figures 3 and 4. These tests reveal that equilibrium uptake of Pb(II) is reached within 30 to 40 minutes of contact time whereas Ni(II) uptake is considerably slower and requires a contact time of approximately 400 minutes.

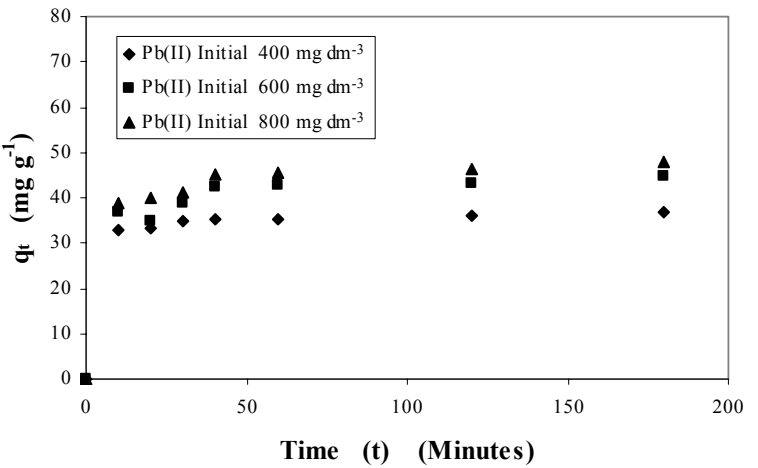

Figure 3: Kinetics of Pb(II) uptake by cellulose-g-GMA-imidazole at different initial concentrations.

For the separate uptake of both metal cations two rate equations, pseudo-first and second order reaction kinetics were used to analyse the adsorption data. Pseudo-first-order kinetics were firstly evaluated and uptake of both Pb(II) and Ni(II) by the cellulose-g-GMA-imidazole yielded extremely poor correlation with this approach. The results for the alternative pseudo-second order approach are presented in table 3. Pseudo-second order kinetics (eqn. 2) can be used to assess the dependency of the process on the sorbed Pb(II) or Ni(II).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

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}). Re-arrangement of equation (2) yields the linearised form as outlined in eqn. (3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{qe} t \tag{3}$$

The initial sorption rate, h , as $t \rightarrow 0$ can be defined as in equation (4)

$$h = k_2 q_e^2 . \tag{4}$$

The initial sorption rate, h, the equilibrium sorption capacity, q_e, and the pseudo-second-order rate constant, k_2, can be determined experimentally from the slope and intercept by plotting t/q_t against t.

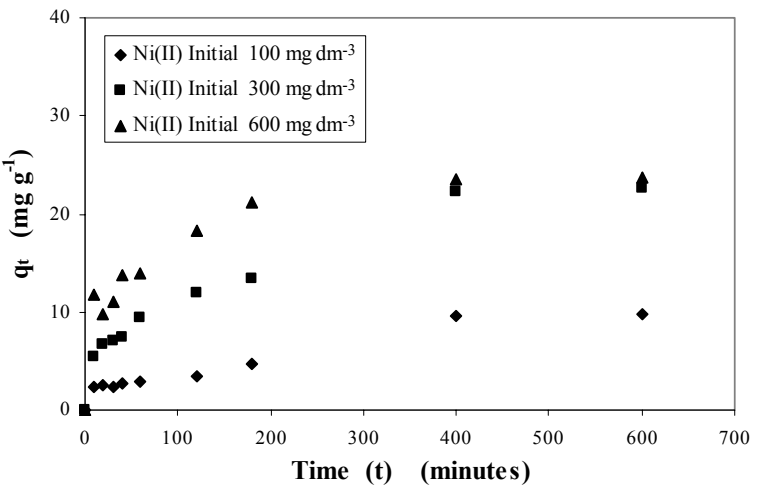

Figure 4: Kinetics of Ni(II) uptake by cellulose-g-GMA-imidazole at different initial concentrations.

The constants obtained for the pseudo-second order approach are listed in table 3 where the linear plots showed high correlation co-efficients (R^2) and good compliance with the proposed pseudo-second order equation. The data also shows that the initial sorption rates (h values) decreased with an increase in initial Pb(II) concentration and increased with a decrease in initial Ni(II) concentrations. The initial metal ion concentrations also influenced the contact time necessary to reach equilibrium and sorption capacity increased for higher initial metal ion concentrations. The values of the overall sorption rate constants,

k_2 were found to decrease with increasing initial Pb(II) and Ni(II) concentrations. Correlation coefficients (R^2) for the pseudo-first-order equations were considerably lower than the comparable pseudo-second-order equation coefficients. This gives a strong indication that the sorption of Pb(II) and Ni(II) by cellulose-g-GMA-imidazole is more accurately represented by the pseudo-second-order kinetics process.

Table 3: Effect of initial Pb(II) and Ni(II) concentrations on sorption data on cellulose-g-GMA-imidazole using the pseudo-second order and pseudo-first order approaches at 23°C.

Pseudo-second order kinetic parameters - Pb(II)				
Initial Pb(II) Concentration (mg dm^{-3})	Correlation Co-efficient R^2	Equilibrium 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 Ni(II) Concentration (mg dm^{-3})	Correlation Co-efficient R^2	Equilibrium 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

4 Conclusions

The graft copolymerisation of the vinyl monomer, GMA, on regenerated cellulose wood pulp and subsequent functionalization of this grafted polymer with imidazole proved to be an efficient adsorbent for the removal of both Pb(II) and Ni(II) from aqueous solution. The adsorption isotherms indicated clearly that the reaction product has an adsorptive capacity of approximately 72 mg g^{-1} Pb(II) and 45 mg g^{-1} Ni(II) at a temperature of 23°C. These adsorption levels compared very favourably with similar studies using other modified cellulose based adsorbent materials. Both adsorption processes followed a Type I uptake and fit the assumptions of the Langmuir model of adsorption. Kinetic data on the adsorption process indicated that Pb(II) uptake reached a maximum at approximately 30-40 minutes contact time. In contrast, Ni(II) uptake was significantly slower and required a contact time of 350 to 400 minutes. Further examination of the kinetics of both adsorption processes revealed a strong correlation with the pseudo-second-order kinetics model. In light of these findings, cellulose-g-GMA-imidazole material exhibits significant potential as an adsorbent in the removal of both Pb(II) and Ni(II) from aqueous solutions.

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