Preliminary Adsorption study for Heavy Metal Removal with Ion-Exchange Resins in the Teaching Laboratory

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ABSTRACT

This paper reports on the adsorption of Cr(VI), Cu(II) and Pb(II) from laboratory solution by the use of Chelex 100 (C100) and Amberlite IRA400 ion exchange resins. Metal loading at initial pHs of 3 to 8 at 1-100 mg/L were studied based on Q_{max} and K_f values of the Langmuir and Freundlich isotherm models, respectively. Lead was sorbed the most (Q_{max} = 75.19 mg/g, at pH 6), followed by Cu (Q_{max} = 58.07 mg/g, at pH 5) with C100 and Cr (Q_{max} = 49.02 mg/g at pH 4) with IRA400. Overall adsorption capacity were as follows: Pb(II) > Cu(II) > Cr(VI) and dependent on the initial pHs.

Key words: ion exchange, resins, heavy metal, metal loading, adsorption, metal removal.

INTRODUCTION

Heavy metals are of primary concern due to its non-degradable nature in the environment unlike organic pollutants. The presence of heavy metal ions will only elevate over time because of its persistence, which necessitates that its disposal be carefully regulated and monitored. More so, heavy metals tend to accumulate in living organisms and pose serious hazardous effect towards man and the environment[1]. Listed as a scheduled waste, heavy metal sludge is one of the main waste produce in the country recording 71,793 metric tonnes in 2007[2]. Due to this, heavy metals ought to be removed from any wastewater before it can be safely discharged into the waterways. Although excessive release of the polluting metals originate from the industry, it is necessary as well to check on less reported but known discharge sites such as from the teaching, learning, and research laboratories. Most laboratory preparation and experimental procedures requires the use of heavy metals obtained from its salt form (i.e. $PbCl_2$, $PbSO_4$, $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $CuCl_2$, $CuSO_4$, $PbCrO_4$, CrO_3, K_2CrO_4, $K_2Cr_2O_7$, Na_2CrO_4, and $(NH_4)_2CrO_4$ among others). Generally, heavy metal

containing waste can be found in solid or aqueous form from these sites. Importantly, the waste needs to be sorted and collected as much as possible after each experimental or research activity.

Current conventional physico-chemical treatment techniques for metal related remedial caters for large or bulk metal residue. Treatment options include amongst others, chemical precipitation, reverse osmosis, ion exchangers, cementation, freeze purification, floatation, membrane filtration, and electro-dialysis. Selected methods usually depend on the type of metal/s to be treated[3]. These methods generally require high reagent use, are cost intensive, waste specific, inefficient for low concentrations of metals ($\leq$ 100 mg/L) and produce toxic chemical sludge or other waste by-products [4, 5]. It has been reviewed that ion exchange and membrane filtration are the two most effective and widely applied techniques in the treatment of metal laden waste[6].

In our context, ion exchange is the most suitable as readily available, safer, cleaner, and flexible, and can fit well in any laboratory setting. An ion exchanger can be classified to either cationic exchange or anionic exchange based on the ion selective resins used. The technique involves reversible chemical reaction by exchange of ions on the resins with the ones in the aqueous solution[7]. For example, cationic resins have sodium ions which can exchange with ions such as Ag, Ca, Cr(III), Cu, Mg, and Ni. Whereas anionic resins contains chloride ions that readily exchange with acid radicals such as sulphates, nitrates, carbonates, and chromates. In terms of application, the solution's pH is the most critical factor governing metal uptake and removal. A good exchanger should be able to support high binding capacity in a wide range of pH[3, 6].

This preliminary work explores the use of ion exchange resins that is/are already available in a teaching laboratory with the view of employing them to remove heavy metal ions from laboratory waste and spent solution. The resins opted for the study, are the two common forms of resins available in a biology or chemistry laboratory. We studied the extent of metal binding capacity (q, mg/g) through thermodynamic adsorption isotherms for Chelex 100 (C100) a cationic ion exchange system often used for DNA extraction and purification[8]; and Amberlite IRA400 (IRA400) an anionic ion exchange system at varying initial pH's. As such, it will provide a feasible two-pronged use for experiments as well as to adsorb metal from laboratory waste solution. The metal ions of choice were Pb(II), Cu(II) and Cr(VI), as being among the most ubiquitous pollutant in the environment as well as being extensively used in the laboratory.

MATERIAL AND METHODS

Ion exchange resin systems

Two resin systems were used, i.e., Chelex 100, (Sigma, USA), a cation exchange resin in sodium form with iminodiacetic acid groups (50-100 mesh) on 1% cross-linked polystyrene matrix; and Amberlite IRA400 (Sigma, USA), an anion exchange resin in chloride form with quaternary ammonium groups (16-50 mesh) on 8% cross-linked styrene-divinylbenzene matrix. The amount of resin used was in the range of 5-10 mg.

Stock solutions of metals

Stock solutions (1000 mg/L) were prepared from the following salts; Cr(VI) from K_2CrO_4, Cu(II) from $Cu(NO_3)_2$ $2.5H_2O$ and Pb(II) from $Pb(NO_3)_2$ in NANOpure ddH_2O. Working solutions were prepared by diluting the stock solutions to the desired concentrations in ddH_2O.

Effect of initial pH and metal uptake

The effect of initial pH (3, 4, 5, 6, 7, 8) towards the binding of Pb(II), Cu(II) and Cr(VI) at various concentrations (1, 10, 20, 40, 60, 80 and 100 mg/L) was studied as batch sets. Experiments were conducted up to pH 8 as to evade precipitation of metal ions at higher pH's. Buffer use was avoided to eliminate unknown effects of their components in the presence of metallic ions[9] as well as to minimize needs for any pre-treatment. The initial pH was adjusted with 1N NaOH and 1N HNO_3 as necessary. Reaction tubes were incubated for 24 h at room temperature under static conditions. The final volume was made up to 10 mL with ddH_2O. All tests were done in triplicates and the appropriate controls were included. At the end of the incubation period, resins were separated by centrifugation (4000 rpm, 10 min), and the supernatant analyzed for residual metal content.

Adsorption isotherms

Metal uptake (q) capacity of the resins was expressed using the general definition[10, 11]:

$$q = \frac{(C_i - C_e) \ \text{x} \ V}{W}$$

q is the metal uptake (mg metal/g dry weight of resin) from the solution, V the volume of solution (L), C_i the initial concentration of metal in the solution (mg/L), C_e is the residual metal concentration (mg/L) in the solution at equilibrium, and W (g) is the dry weight of resins used. Concentrations of Cr(VI) in the solution were determined spectrophotometrically using the 1,5-diphenylcarbazide method[12], and total metal concentrations in the solution were measured by atomic absorption spectrophotometer (AAS; Perkin Elmer PE 1100B).

To characterize and compare the metal loading capacities of the resins at varying pHs; obtained data were plotted as metal uptake (q, mg/g) against residual metal concentration at equilibrium (C_e, mg/L). The ensuing curve was fitted to the Freundlich and Langmuir isotherm models[10, 11, 13]. The linearised Freundlich[14] isotherm model is given as:

$$\log \ q = \log \ K_f \ + \ n \ \log \ C_e$$

q is the metal loading capacity (mg/g), K_f, a constant relating to metal loading at a lower equilibrium concentration of log $C_e = 0$ ($C_e = 1$ mg/L) and n, a constant describing the intensity of the process.

The Langmuir[15] model was chosen for estimation of the maximal metal loading capacity of the resins by evaluating its maximum loading (Q_{max}, mg/g resin) and binding site affinity (b, L/mg) expressed as:

$$q = \frac{Q_{max} b C_e}{1 + b C_e}$$

Q_{max} is the maximum amount of metal bound per unit of weight resin to form a complete monolayer on cell surface at high equilibrium

concentration, C_e. The Langmuir parameter b, is the ratio of the adsorption rate constant to desorption rate constant, which indicate the affinity of the resins toward metal ions. A higher value of b indicates higher affinity of resins towards metals.

Statistical analysis

Experimental data and isotherms were subjected to statistical analysis for mean tests, t-tests, least squares regression and the analysis of variance (one-way ANOVA) by SPSS (SPSS Inc., Chicago, IL). Significant levels were set at $\alpha = 0.05$.

RESULTS AND DISCUSSION

The metal uptake capability comparison was made on two basis, first the Langmuir model provided an estimate of maximal metal loading (Q_{max}, mg/g) by assuming complete monolayer is formed on the sorbent's surface at high equilibrium concentration. Secondly, metal loading at lower equilibrium concentration, $C_e = 1$ mg/L (K_f, mg/g) was ascertained from the linearised Freundlich model. These isotherm parameters are widely used to evaluate and compare metal loading capacity of a given sorbent system[11].

Table 1 presents the obtained isotherm parameters for Langmuir (Q_{max} and b) and Freundlich (K_f and n) with Cr, Cu, and Pb at concentrations ranging from 1-100 mg/L with the tested resins when the initial pHs are varied from 3 to 8. Generally, the Freundlich and Langmuir (for monolayer adsorption) model fitted well ($R^2 > 0.5$) to describe metal adsorption. The isotherm constants were significant at $\alpha = 0.05$.

In terms of maximal metal loading, Pb was sorbed the most ($Q_{max} = 75.19$ mg/g, at pH 6), followed by Cu ($Q_{max} = 58.07$ mg/g, at pH 5) with C100 and Cr ($Q_{max} = 49.02$ mg/g at pH 4) with IRA400. The highest loading for Cr with C100 was at pH 3 ($Q_{max} = 28.74$ mg/g). Chromium metal, which predominantly exists as anions at all pHs, was highly favoured by IRA400, an anionic exchanger as IRA400 displayed better sorbing capacity as opposed to C100. The highest Cr loading was observed at pH 4 and pH 3 (49.02 and 45.45 mg/g,

respectively) (p < 0.05) with IRA400. Higher metal loading (Q_{max}) was observed with increasing binding affinity (b) with Pb at all pHs. But no such correlation was seen with Cr and Cu. Generally, binding sites affinity (b) and adsorption intensity constant (n) showed no direct correlations to the degree of metal loading by the respective resins. Metal speciation is known to be largely affected by pH, which was reflected from the metal binding capacity of the resins.

Higher Pb loading capacity was similarly observed at a lower equilibrium concentration (C_e = 1 mg/L) with C100 (K_f in the range of 2.31-3.63 mg/g) as opposed to copper (1.57-2.85 mg/g). Although with C100, Pb had the higher metal loading of K_f = 3.63 mg/g at pH 6 however, for both Cu and Pb ions, the K_f values at lower residual metal concentrations with varying pHs were not significantly different. For Cr, C100 worked better at pH 3 and 4 (K_f = 1.76 and 2.14 mg/g, respectively).

Table 1: Langmuir and Freundlich isotherm parameters for the loading of Cr, Cu and Pb by the selected resins as a function of initial pH

Metals	Resins	Langmuir				Linearised Freundlich		
		pH	Q_{max} (mg/g) *	b **	R^2	K_f (mg/g) ***	n ****	R^2
Cr	C100	3	28.74	1.5430	0.900	1.76	1.5468	0.942
	IRA400	3	45.45 ^ #	1.5029	0.837	5.08	1.4397	0.955
	C100	4	26.95	2.1000	0.928	2.14	1.6507	0.909
	IRA400	4	49.02^ #	1.8744	0.913	2.22	1.4554	0.968
	C100	5	17.21	0.4830	0.809	0.42	1.1932	0.917
	IRA400	5	30.03^	1.5446	0.983	1.84	1.5939	0.958
	C100	6	17.12	0.6813	0.945	0.65	1.3530	0.938
	IRA400	6	27.40^	1.4474	0.980	1.48	1.4883	0.942
	C100	7	15.60	1.5186	0.990	1.53	1.8116	0.906
	IRA400	7	16.89	0.7226	0.936	0.67	1.3417	0.886
	C100	8	6.67	0.2535	0.943	0.48	1.5501	0.711
	IRA400	8	19.49^	0.6187	0.953	0.68	1.3642	0.938
Cu	C100	3	44.05	2.0738	0.906	1.85	1.6391	0.984
	C100	4	52.63	1.6821	0.847	1.94	1.3600	0.974
	C100	5	58.07#	1.2922	0.724	1.62	1.2700	0.985
	C100	6	54.94	1.5380	0.790	1.84	1.3515	0.975
	C100	7	28.25	1.2653	0.945	1.57	1.5509	0.971
	C100	8	34.25	0.9210	0.727	1.85	1.7232	0.971
Pb	C100	3	37.45	2.3480	0.982	2.31	1.4870	0.945
	C100	4	40.65	2.4783	0.970	2.98	1.6441	0.981
	C100	5	40.82	2.6925	0.969	3.05	1.6458	0.982
	C100	6	75.19#	4.2200	0.982	3.63	1.4037	0.933
	C100	7	53.19	3.1230	0.863	3.47	1.4788	0.781
	C100	8	45.87	3.6617	0.984	3.16	1.5033	0.955

*Maximum metal loading (mg/g) forming a complete monolayer on surface of resins at higher equilibrium concentration

**Affinity of binding sites constant (mg/L)

***Metal loading (mg/g) at lower metal equilibrium concentration of 1 mg/L

**** Intensity of adsorption constant

^Maximum metal loading significantly different between C100 and IRA400 resins (p < 0.05)

#Metal loading significantly different at varying initial pHs

However, the IRA400 anionic exchanger showed the highest metal loading capacity of 5.08 mg/g at pH 3 ($p < 0.05$). Overall, the loading capacity of IRA400 in terms of maximal metal loading and at lower metal equilibrium concentration was up by 2 folds higher than C100 ($p < 0.05$). Overall, metal loading was in the following order: Pb > Cu > Cr.

Experimental observation suggests that solution pH was the critical factor in determining resin surface chemistry. It has been reported also that initial solution pH's affects more on process behaviour as opposed to solution's final pH[16]. In general, the uptake of cations (i.e. Pb and Cu) increases with elevated pH. As noted from Table 1, metal loading capacity for cations generally decreased with decreasing pH that can be explained as due to the competition with H^+ ions for the available ion-exchange sites (sodium ions) present on the resin. Conversely, the resin systems seem to work better in acidic conditions with Cr (known to exist as oxyanions) as the resin's capacity dropped significantly as pH increased. A comparative study[5] using Purolite CT-275, Purolite MN-500, and Amberlite XAD-7 ion exchangers, suggested otherwise, that the uptake of Cr(VI) was insensitive to pH changes of the adsorption media. Similarly optimum adsorption for Cr(VI) was noted at pH 3. Removal of chromium by the use of chitosan powder was observed at pH 5-8 and they concluded that pH is the most significant factor that determines the percentage removal[17]. Similarly in this study it was found that metal removal capacity was dependent upon initial pH of solution. At lower pH, protons (H^+) compete with the cations for the non-specific sodium ion-exchange sites resulting in higher repulsion from the positive ions hence lowering Pb and Cu loading capacity. On the other hand, Cr(VI) in the oxy-anionic complex form (CrO_4^{2-}, $Cr_2O_7^{2-}$ or $HCrO_4^-$) undergoes non-competitive ionic exchange with chloride (with IRA400) as observed from higher Cr loading at acidic pHs. Even though C100 resin is usually limited to the cations (Cu and Pb), it was used for Cr as well in addition to IRA400 as sometimes cationic trivalent chromium is present at acidic conditions. And interestingly a study on ion exchange behaviour in weakly acidic medium reported that under varying acidic conditions and interactions with matrix support, C100 can act as an anionic exchanger[18]. This may explain the slightly higher Cr loading observed with C100 at pH 3 (Q_{max} = 28.74 mg/g; K_f = 1.76 mg/g) and pH 4 (Q_{max} = 26.95 mg/g; K_f = 2.14 mg/g) in contrast to the reduced loading at higher pHs (Q_{max} = 6-17 mg/g; K_f = 0.4-1.5 mg/g). The use of Amberlite resins for cations however is not much preferred as it has been reported to be unsuitable for recovery and reuse[7]. Other researchers have also worked on related resin systems as for the removal of Cu(II) from aqueous phase by Purolite C100-MB cationic exchange resin[19]. Similarly, C100 resin can be used to remove di- and trivalent cations, including transition metals[20]. However, not many findings are available that discusses on an on-site laboratory bench scale heavy metals removal.

Table 2: Proposed metal uptake (q, mg/g) summary model
by linear regression for the selected resin systems

Resins	Metal	Model *	Correlation
C100	Cr	q = 11.76 + 1.24 (C_i) − 1.24 (C_e) − 1.52 (W) + 0.156 (pH)	R^2 = 0.992
	Cu	q = 19.40 + 1.26 (C_i) − 1.27 (C_e) − 2.47 (W) + 0.062 (pH)	R^2 = 1.000
	Pb	q = 21.51 + 1.26 (C_i) − 1.26 (C_e) − 2.68 (W) − 0.015 (pH)	R^2 = 1.000
IRA400	Cr	q = 17.03 + 1.56 (C_i) − 1.57(C_e) − 2.87 (w) + 0.422 (pH)	R^2 = 0.980

C_i: initial metal concentration (mg/L)

C_e: residual metal concentration at equilibrium after 24 h (mg/L)

W: amount (dry weight) of resins (g)

pH: initial pH of solution

* Coefficients effect significant at a = 0.05

Table 2 presents a simple model to describe the metal uptake process by the respective resins. The regression equation obtained after analysis of variance gave the level of metal uptake onto the resins as a function of initial metal concentration (C_i, mg/L), residual metal concentration at equilibrium (C_e, mg/L), amount of resins used (W, g), and initial pH of solution.

In this study, the linear conformation ($R^2 > 0.5$) attained in both Langmuir and Freundlich models suggest that no interaction is present between the sorbed metal ions during the formation of a complete monolayer. Even though the Langmuir model assumes that all binding sites are uniform in affinity levels and adsorption energy, sites having higher affinity towards a particular metallic ion will be occupied first. As the Freundlich and Langmuir model were not able to describe the type of binding sites present and binding behaviour, the adsorption data were plotted as q/C_e (L/g) against q (mg/g) to conform with another known model, i.e. Scatchard[13,21] (data not shown) and linearity was compared. The linear trends ($R^2 > 0.5$) observed through the Scatchard plot and model conformation indicated that metal adsorption involved single type of binding sites and binding occurred uniformly on the resins surfaces.

Most of the ion-exchange resin systems are reusable but problems such as specificity, system damage, lowered of system efficiency due to the presence of oil, grease, clay, silicates, organic materials, and microbes limit its usage[18]. An apparent advantage is that resin systems are not hindered by extreme or highly toxic conditions as opposed to bacterial or biological system. It can also be effective as a tool for primary or secondary treatment of heavy metal containing solution. This is to polish the waste solution after it has gone through the major treatment. One emphasis in pollution control is the need to reduce or minimize waste produced and secondly, if possible, to treat the waste produced at the source of generation itself. Amongst which redistribution, reuse, and recycling of supplies and reagents is listed as one of strategies to use[22]. The importance of waste minimization in the teaching and research laboratories have to be looked cautiously. This will have to start with proper governance in terms of material balance, and up-to-date inventory keeping to prevent over buying. Any experiment conducted will have to incorporate a waste minimization strategy plus a possible recovery method if deemed viable. For students, this will indirectly create awareness and help them learn ways to treat laboratory waste, and to address the issue of pollution control. The other advantage is that ion exchange resins can be regenerated as most resins have high affinities towards the hydrogen ion resulting in auto-regeneration at low pHs. This is beneficial for metal recovery. The sorbed metals can be eluted with volumes of acids, i.e. HNO_3, which protonates the iminodiacetate groups[23].

This paper explored the option to treat heavy metal ions by the use of two ion exchange resins (C100 and IRA400) that is available in the teaching laboratory. This in turn will lead to an on-site metal removal practice, and possible metal recovery system setup that can be absorbed as a part of any experimental or research procedure in the laboratory. A pilot study is the next planned action to evaluate on practicality. Future studies will move in to set-up a laboratory based ion-exchanger column to remove and recover heavy metals from the waste solution. We hope to reduce the generation of heavy metals on site as one measure to contain and address heavy metal release into the waterways from known sources.

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