

Water treatment sludge can be used as an adsorbent for heavy metals in wastewater streams

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Abstract

Throughout the world, alum is the most widely used coagulant in drinking water treatment. The waste stream from water treatment is alum-derived water treatment sludge and in most localities large quantities of this material are deposited in waste disposal areas. Reuse of this waste stream in an environmentally sustainable manner is therefore a priority. Research has shown that the material is an effective adsorbent of phosphate from aqueous solutions, but its use as an adsorbent for heavy metals has not been investigated. Our research showed that water treatment sludge was an effective adsorbent for Pb(II), Cr(III) and Cr(VI). Adsorption isotherm data fitted equally well to Freundlich and Langmuir equations and kinetic data correlated well to a pseudo-second-order kinetic model, suggesting that the mechanism involved was chemisorption. Adsorption was pH-dependant with percentage sorption of Pb(II) and Cr(III) increasing greatly with increasing pH and that of Cr(VI) decreasing. Cr(VI) could be removed from sludge surfaces with 0.1 M NaOH. At a concentration of 0.1M, HNO₃ was effective at removing adsorbed Cr(III) and Pb(II) from the sludge surfaces and regeneration was successful for eight sorption/removal cycles. Other work showed that water treatment sludge had adsorbent properties for Cu, Zn, Cd, As and Se. It was concluded that water treatment sludge is a suitable material from which to develop a low-cost adsorbent for removal of both heavy metal cations and anions from wastewater streams.

Keywords: water treatment sludge, adsorption isotherms, Cr(III), Cr(VI), Pb(II).



1 Introduction

Unlike organic contaminants, most heavy metals in the environment do not undergo microbial or chemical degradation and therefore total amounts accumulated and their ecotoxicological effects persist for long periods after their introduction. Treatment processes for metal-contaminated wastewater include chemical precipitation, membrane filtration, ion exchange, coagulation/precipitation and adsorption. Adsorption is a process by which the heavy metal contaminants are removed from aqueous solution through sorption onto the surface of a material. Activated carbon has been the conventionally adopted adsorbent, but its use is limited by its high cost and difficulties with regeneration [1]. As a result, there is growing research interest in the use of waste products from industry as inexpensive adsorbents [2].

Alum-derived water treatment sludge is a material deposited in waste disposal areas in many parts of the world [3]. Indeed, alum is the most widely used coagulant in drinking water treatment [4]. Once the alum dissolves, Al^{3+} exists in solution as aluminiumhexahydronium ion $(\text{Al} \cdot 6\text{H}_2\text{O})^{3+}$. These ions can sequentially dissociate as pH increases, leaving OH in place of OH_2 to form species such as $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ and $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$. These positively charged species polymerize to form positively charged polynuclear complexes, which form a gel-like substance that adsorbs and coagulates colloidal materials such as soluble organic matter and fine soil particles. During flocculation, sedimentation and filtration, colloids in the raw water remain entrapped in, or adsorbed to, the Al gel and after dewatering the water treatment sludge is transferred to disposal sites. Beneficial use of this material would reduce both the cost and need for disposal. Research has shown that water treatment sludge can be used as an effective adsorbent for phosphate [3], but little research has centred on its use as a heavy metal adsorbent.

The purpose of this study was to investigate the possibility of removing Cr(II), Cr(VI) and Pb(II) from aqueous solutions using alum-derived water treatment sludge.

2 Materials and methods

Water treatment sludge was collected from Seqwater Mount Crosby water treatment plant (Brisbane). Specific surface area of samples was determined by the BET/ N_2 -adsorption method and zero point of charge was determined using a Laser Zeta meter. Elemental composition of materials was measured by ICP-AES after digestion in a microwave system with HNO_3 , HCl and HF. The sludges were subjected to X-ray diffraction (XRD) analysis to determine their mineralogy. Cation exchange capacity of materials was determined at pH 7.0 using 1M ammonium acetate and pH and electrical conductivity (EC) were measured in a 1:5 material:water ratio [5] using a pH/conductivity meter (Horiba F-54 BW).

Batch adsorption studies were performed to determine the extent of adsorption of each individual heavy metal ion at room temperature (25°C). All



experiments were carried out in triplicate at a constant ionic strength provided by 0.01 M NaNO₃. Metal solutions, with the desired metal concentration, were prepared in 0.01 M NaNO₃ using Pb(NO₃)₂, Cr(NO₃)₃ and Na₂CrO₄. A measured amount of sludge was weighed into 50 mL centrifuge tubes and 10 mL of 0.01 M NaNO₃ was added. The mixture was shaken for 1 h and then adjusted to desired pH using HNO₃ or NaOH. Once the pH had stabilized, 10 mL of an individual heavy metal solution (at twice the desired final metal concentration) was added and the pH was adjusted again. The mixture was shaken on an end-over-end shaker for 2 h. During adsorption, the pH was checked and readjusted, if necessary, every half-hour. The resulting solution was centrifuged (4,000 rpm for 10 min.), filtered and the supernatant was analysed for the appropriate aqueous heavy metal by ICP-AES. The percentage of metal adsorbed was calculated from the difference between that added and that remaining in solution.

The effect of pH on adsorption was investigated over the pH range of 2 to 9 with an initial metal concentration of 1 mM and adsorbent dosage of 10 g L⁻¹. Sorption was found to be highly pH-dependant and at pH 5.0, adsorption amounted to approximately 60% of that added for all three ions. As a result, pH 5 was chosen to study the effects of initial metal concentration, contact time, temperature and adsorbent dose on metal removal.

Eight different initial concentrations of Cr (III), Cr (VI) and Pb (II) ranging from 0.4 mM to 8 mM were used (at an adsorbent dosage level of 10 g L⁻¹) to measure the effect of initial metal concentration on adsorption. Adsorption data (equilibrium metal concentration versus quantity adsorbed) were fitted to the Langmuir and Freundlich equations. The effect of contact time, varying from 15 min to 360 min., was studied at a dosage level of 10 g L⁻¹ and an initial concentration of 1 mM. The data was fitted to pseudo-first-order and pseudo-second-order kinetic models. The effect of adsorbent dose (2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20 g L⁻¹) was studied at an initial concentration of 1 mM (contact time = 120 min.) and the effect of temperature was determined at 20, 30, 40, 50 and 60°C (adsorbent dose = 10 g L⁻¹).

3 Results and discussion

3.1 Properties of the material

As expected, the main metallic element present in water treatment sludge was Al (122 g kg⁻¹) and some Fe (24 g kg⁻¹) was also present. The material had an organic C content of 103 g kg⁻¹. X-ray diffraction analysis revealed the sludge consisted of poorly crystalline amorphous material and small amounts of gehlenite (Ca₂Al₂SiO₇) were also present. Adsorption of inorganic and organic anionic species to the hydroxyl-Al polymers during coagulation probably inhibits crystallization to Al(OH)₃ [6] and as shown here, the water treatment sludge exists as a relatively stable amorphous material with a high surface area.

The surface area of the material (97.3 m² g⁻¹) is similar to that recorded by Lee et al. [7] of 61-67 m² g⁻¹ for water treatment sludge but much greater than that reported for other waste adsorbents such as coal fly ash (2-8 m² g⁻¹) [8] or



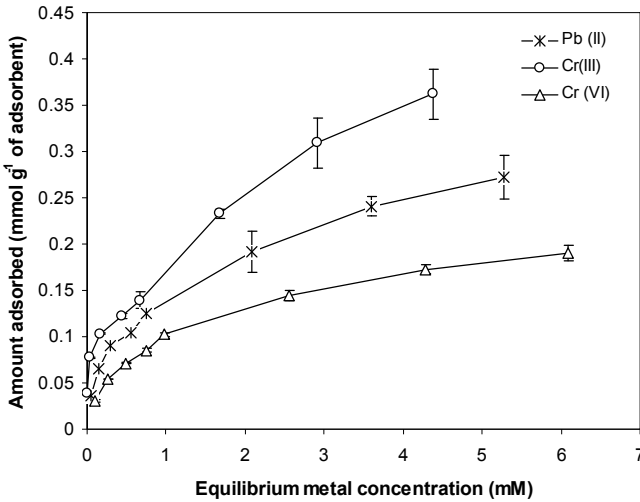


Figure 1: Effect of initial metal concentration on the quantity of Pb(II), Cr(III) and Cr(VI) adsorbed by water treatment sludge.

Table 1: Isotherm constants and correlation coefficients (R^2) for the adsorption of Pb(II), Cr(III) and Cr(VI) onto water treatment sludge.

Metal	Langmuir isotherm			Freundlich isotherm		
	q_{max} ($mmol\ g^{-1}$)	b ($L\ mmol^{-1}$)	R^2	K_f	$1/n$	R^2
Pb (II)	0.30	1.31	0.98	0.14	0.42	0.99
Cr (III)	0.37	1.67	0.92	0.19	0.32	0.94
Cr (VI)	0.21	1.12	0.99	0.09	0.43	0.99

bauxite processing residue mud (red mud) ($13\text{--}30\ m^2\ g^{-1}$) [9]. The high surface area of water treatment sludge is a positive attribute when it is being used as an adsorbent. The sludge had a pH of 6.8, an EC of $1.21\ mS\ cm^{-1}$ and a PZC of 6.7.

3.2 Effect of initial metal concentration

Adsorption of Pb(II), Cr(III) and Cr(VI) increased with increasing equilibrium concentration of the metal ion and reached a maximum value as the adsorbent became progressively saturated (Fig. 2). Data fitted equally well to either the Freundlich or Langmuir models [10] with correlation coefficients close to unity (Table 1). The Freundlich equation explains adsorption onto a heterogeneous surface with uniform energy. The linear form of the model is expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (1)$$

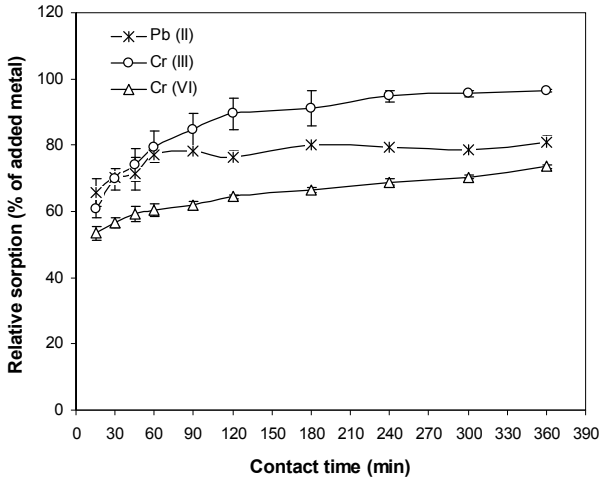


Figure 2: Effect of contact time on the quantity of Pb(II), Cr(III) and Cr(VI) adsorbed by water treatment sludge.

where q_e and C_e are the equilibrium concentrations of metal in the adsorbed (mmol g^{-1}) and liquid phases (mmol L^{-1}) respectively. K_f and n are the Freundlich constants which are related to adsorption capacity and intensity, respectively. On the other hand, the Langmuir equation is based on monolayer adsorption on active sites of the adsorbent. The linear form is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (2)$$

where q_e and C_e are equilibrium concentrations of metal in the adsorbed (mmol g^{-1}) and liquid phases (mmol L^{-1}) respectively. Q_m and b are the Langmuir constants which are related to the adsorption capacity and energy of adsorption, respectively.

For the Freundlich model, the slope $1/n$ is the sorptive intensity and values between 0.1 and 1.0, as recorded here, indicate beneficial sorption [11]. The maximum sorption capacity (q_{max}) obtained by the Langmuir model was highest for Cr(III) and showed the order: Cr(III) > Pb(II) > Cr(VI) (Table 1). A similar trend was apparent for the Langmuir intensity factor b and the Freundlich K_f factor. This supports results of research with other adsorbents which has generally shown that at equimolar concentrations, Cr(III) is preferentially adsorbed compared to Cr(VI) and that sorption of Cr(III) exceeds that of Pb(II) [12, 13].

3.3 Effect contact time

The effects of contact time on the adsorption of Pb(II), Cr(III) and Cr(VI) are shown in Fig. 2. The adsorption process was rapid and at a contact time of 120 min., 90% or greater of maximum sorption had occurred. Thus, for batch studies, a period of 120 min. is adequate for adsorption of these ions onto sludge surfaces. In order to evaluate the kinetic mechanisms that control the adsorption process, pseudo-first-order and pseudo-second-order models were employed to interpret the experimental data. The pseudo-first order equation can be represented by:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, q_t is the amount adsorbed at time t (min) and q_e denotes the amount adsorbed at equilibrium, both in mmol g^{-1} . The pseudo-second-order equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 [g (mmol min)^{-1}] is the adsorption rate constant of pseudo-second-order.

Based on the obtained correlation coefficients, the pseudo-second order equation gave a better fit to the experimental kinetic data than the pseudo-first order model and calculated pseudo-second order q_e values were in good agreement with the experimental values (data not presented). This suggests that chemisorption rather than diffusion/ion exchange was the rate-limiting step to sorption [14]. Such a finding is not surprising since chemisorption of metal cations, as well as anions such as phosphate, onto the surface of amorphous hydroxyl-Al is a well-recognised phenomenon [6, 15]. Chemisorption includes both specific adsorption and surface precipitation with precipitates forming beyond a certain level of metal sorption [16].

In addition, there will be some metal adsorption onto surfaces of organic matter which was coagulated with the hydroxyl-Al. Adsorption to organic matter occurs through formation of coordination complexes and chelates with surface functional groups (e.g. carboxylic, phenol, enolic, alcoholic OH and C=O) [17].

3.4 Effect of pH

Adsorption edges for Cr^{3+} and Pb^{2+} showed increasing sorption from near zero to near complete over a relatively small pH range (Fig. 3). This is because the variable charge on hydroxyl-Al surfaces arises from protonation and deprotonation of the potential determining $\text{M-OH}_2^{0.5+}$ and $\text{M-OH}^{0.5-}$ groups. The surface becomes increasingly negatively charged as hydroxyl ion activity (and pH) increase, thus favouring specific adsorption of cations. In addition, as pH is

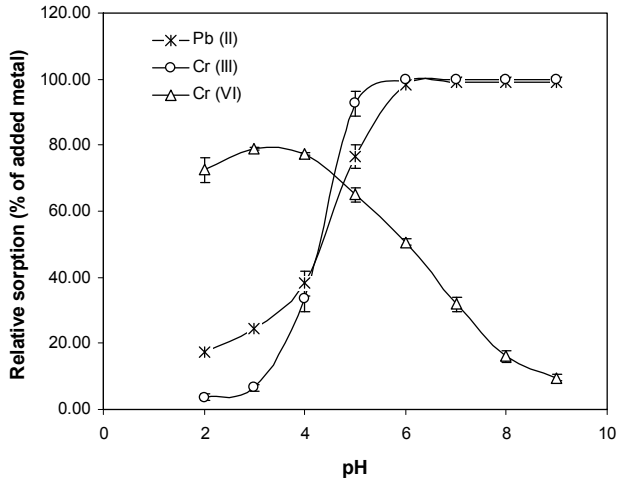


Figure 3: Effect of pH on the quantity of Pb(II), Cr(III) and Cr(VI) adsorbed by water treatment sludge.

raised, hydrolysis of hydrated cations proceeds and their adsorption generally occurs preferentially as hydrolysed ions (i.e. PbOH^+ rather than Pb^{2+}). As adsorption sites become saturated, ultimately precipitation of metal hydroxides/oxides at the surfaces occurs. As a result, adsorption edges reach 100% sorption.

By contrast, the increasingly negative surface charge conferred by increasing pH, hinders anion adsorption and, as a result, Cr(VI) sorption showed a maximum between pH 3 and 4 and declined thereafter with increasing pH (Fig. 1). Hexavalent Cr may exist in the aqueous phase in a number of anionic forms with hydrogen chromate (HCrO_4^-) predominating in dilute solutions between pH 1-6, chromate (CrO_4^{2-}) above pH 6.4 and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) below pH 3 in concentrated solutions ($> 1.0 \text{ mM}$) [18]. The predominant form of Cr(VI) adsorbed to sludge surfaces under our experimental conditions is likely to have been HCrO_4^- .

At intermediate pH values of between 4.5 and 6.0, the sludge samples were equally effective for Cr(III)/Pb(II) or Cr(VI) sorption (Fig. 1). Thus, this pH range would be desirable where Cr(III) and Cr(VI) or Pb(II) and Cr(VI) were present together in contaminated wastewater and water treatment sludge was being used as an adsorbent.

3.5 Effect of temperature

Results showed that percentage adsorption of Cr(III), Pb(II) and Cr(VI) all tended to increase with increasing temperature between 20 and 50°C suggesting that their sorption onto sludge surfaces is an endothermic process (data not shown). From a practical viewpoint, the small temperature-induced changes

observed suggest that sludge can be used successfully as an adsorbent between 20 and 50°C.

3.6 Effect of adsorbent dose

The effects of adsorbent dose on percentage sorption of Cr(III), Pb(II) and Cr(VI) are shown in Fig. 4. As expected, percentage sorption increased with increasing dose and tended to reach a saturation level at high doses. This is attributable to the surface area and number of adsorption sites being increased with increasing dose. The effect was more pronounced for Pb(II) and Cr(VI) than for the more strongly sorbed Cr(III).

3.7 Desorption/regeneration

The ease and extent of desorption of metals from adsorbent surfaces is important since once the material becomes saturated with contaminant metals, and is no longer effective, it needs to be regenerated and reused. When desorption was carried out in the 0.01M NaOH electrolyte, very small quantities of metal ions were desorbed (data not presented). For this reason acid and sometimes alkaline solutions are commonly used for regeneration [19].

The metal cations Pb(II) and Cr(III) were effectively desorbed with HNO₃ (at 0.1 and 0.5 N concentrations) and the anionic Cr(VI) by NaOH (at 0.01, 0.1 and 0.5 N concentrations) (data not presented). The vast majority of metal was removed in the first desorption cycle. Such results reflect the fact that an acidic environment is least favourable for Pb(II) and Cr(III) adsorption (and favours desorption) whilst an alkali one is least favourable for Cr(VI) adsorption (Fig. 3).

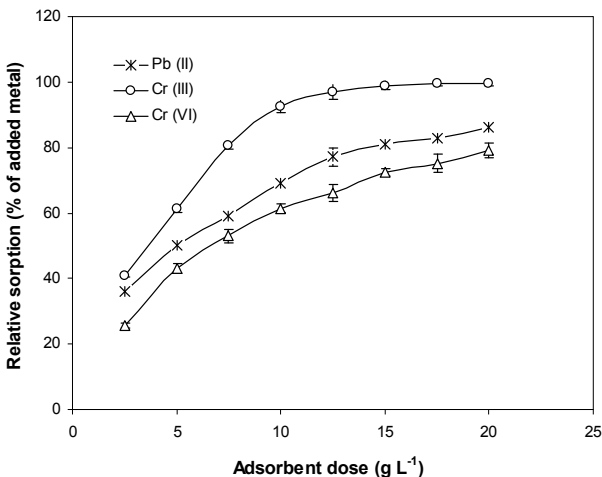


Figure 4: Effect of adsorbent dose on the quantity of Pb(II), Cr(III) and Cr(VI) adsorbed by water treatment sludge.

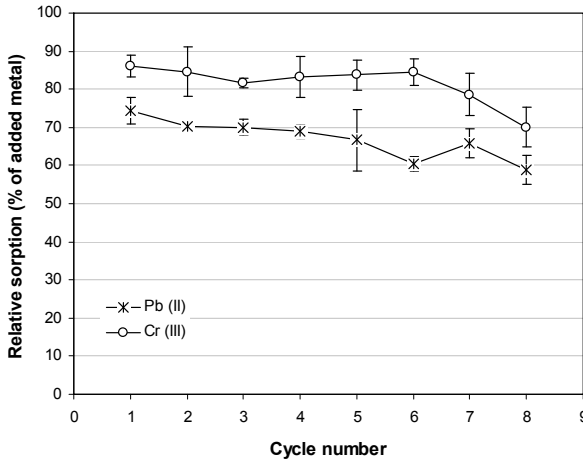


Figure 5: Relative sorption of Pb(II) and Cr(III) over eight successive adsorption/regeneration cycles using 0.1 N HNO_3 as the regenerating agent.

As shown in Fig. 5, subjecting the two samples of water treatment sludge to eight successive cycles of sorption/regeneration using 0.1 N HNO_3 resulted in only a very small loss in adsorption efficiency for Pb(II) and Cr(III). This suggests that a water treatment sludge-based metal cation adsorption system would be able to function over many operational cycles without deleterious effects to its sorption capabilities.

4 Conclusions

The present study reveals that spent alum-derived water treatment sludge, a material which is often disposed of in landfills, can be employed as an effective adsorbent for sorption of Cr(III), Pb(II) and Cr(VI) from aqueous solutions. Adsorption capacity is strongly dependent on initial metal ions concentration, initial pH and dosage, experimental data can be fitted well to Freundlich and Langmuir equations, kinetic data is strongly correlated to a pseudo-second-order kinetic model and for Cr(III) and Pb(II) the adsorbent surfaces can be regenerated using 0.1M HNO_3 . Water treatment sludge is suitable material for development of a low-cost adsorbent for removal of Cr and Pb from wastewater streams.

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