Assessment of Cadmium (II) Removal from Water by Innovative Polyelectrolyte-Coated Fly Ash

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Abstract

Fly ash (FA) is a major industrial waste that adds extra cost for proper disposal. Several studies have recently focused on developing methods to utilize the FA in useful applications. One of the alternative uses of fly ash takes advantage of its adsorptive capacity for the removal of contaminants from water. However, earlier studies showed limited success in this regard indicating the need to improve FA adsorption capacity. This study evaluates the potential capacity of raw fly ash (RFA) and polyelectrolyte-coated fly ash (PE-FA) to remove cadmium (Cd) using layer-by-layer technique. An acid treated FA was coated with 20 layers of cationic polydiallyldimethylammonium chloride (PDADMAC) and anionic polystyrene sulfonate (PSS) solutions. Characterization of the modified FA (PE-FA) was carried out using FE-SEM, and EDX techniques. Adsorbent dosage, pH, and contact time on the adsorption of Cd was studied in batch-mode experiments. Results indicated that in a 50 mL solution, 0.2 g of PE-FA adsorbent has attained a 99% removal of Cd in 15 minutes at agitation rate of 150 rpm and pH 9. While a removal of only 27% Cd was achieved by RFA under the same treatment conditions.

Keywords: Polyelectrolytes; Fly Ash; Adsorption; Cadmium

1.0 Introduction

Cadmium, a deadly trace metal of work-related and environmental concern, has been recognized as a substance that is teratogenic and carcinogenic to human. Cadmium has a maximum permissible concentration of 5–10 ppb in industrial waters (U.S. EPA 2011). If ingested beyond the limit, it would have detrimental effects on internal organs like the kidney. Work related activities like smelting, pesticides, alloy manufacturing, etc. are the anthropogenic ways via which cadmium gets leached to the environment (Rao et al. 2010).

Remediation techniques for water contaminated with Cd that have been employed over time include: membrane separation, ion-exchange, coagulation, softening, solvent extraction and adsorption. The use of the aforementioned methods rely on costs and levels of contamination (Han et al., 2006). Numerous studies have used the adsorption mechanism for heavy metals removal using activated carbon owing to its superior adsorption features, but with comparatively high operating cost (Imamoglu and Tekir, 2008).

Fly ash (FA) is one of the major industrial wastes generated from power stations that cannot be cheaply disposed of. Recent research efforts have consequently focused on developing ways to make use of FA in applications that are environmentally benign. Apart from its limited applications in cement and concrete industries, fly ash alternative use/reuse in environmental study takes advantage of its adsorptive property for water treatment. Limited studies have highlighted the need to improve FA adsorption capacity (Gupta and Torres, 1998b).

Polyelectrolytes are charged organic polymers, soluble in water, and formed from monomers of different kinds. Polyelectrolytes have improved the efficiency of a wide-range of vital processes (Bolto and Gregory 2007). These polymers could be cationic or anionic depending on the functional ionic group. Examples of polyelectrolytes include polyethyleneimine (PEI), polydiallyldimethylammonium (PDADMAC), polystyrene sulfonate (PSS) etc. Several studies had also been made to modify adsorbents with polyelectrolytes. Stanton et al. 2003 showed that alternating polyelectrolyte deposition on porous supports can yield nanofiltration membranes allowing high water flux along with selective ion transport by using pairs of poly (styrene sulfonate)/poly (allylamine hydrochloride) on porous alumina.

The primary focus for this study was to improve the fly ash (FA) surface charges through layer-by-layer deposition (LBL) of two electrolytes, namely PDADMAC and PSS solutions, and its potential efficiency to remove cadmium ions from contaminated water was investigated. Batch adsorption experiments were carried out to evaluate the efficiency of the modified sorbent.
2.0 Materials and Methods

2.1 Reagents
All chemicals and solvents used were of analytical grade. PDADMAC (Mw: 20,000-35,000 g/mol) and PSS (Mw: 7,000 g/mol) were commercially acquired and used. Deionized water was generated in real-time from Milli-Q Ultra-pure water system (Millipore) to prepare aqueous solutions with Cadmium ICP Standard Solution supplied by Ultra Scientific (USA). The pH of the solutions was adjusted using either of 0.1 M HNO₃ and/or 0.1 M NaOH solution.

2.2 Preparation of polyelectrolyte enhanced FA
Raw FA collected from a local power plant in the Easter Province of Saudi Arabia was treated with nitric acid in the volume ratio of 1:3 (ash: nitric acid). The mixture was stirred for 24 hrs at 120°C, with an attached condenser. Separation of phases was ensured by allowing the mixture to stand for 2 hrs, after which the acid was decanted and the slurry phase was washed with deionized water. Subsequently, the slurry phase was oven dried at 100°C for 24 hrs and stored until used for the batch experiments.

Forty (40) ml of a PDADMAC solution was poured into a beaker containing 20 g of acid washed FA, stirred 10-15 minutes, phase separation was ensured by allowing the mixture to stand for 1-2 hrs, after which the filtrate was decanted and the residue rinsed with deionized water. Under similar conditions, 40 ml PSS solution was added to PDADMAC layered FA to obtain a one layer PDAD/PSS-FA (Li et al. 2011). The procedure was repeated until desired number of layers was attained, i.e., (PDAD/PSS-FA)_n where n could be 1, 2, 3, 4, 5…20.

2.3 Characterization of adsorbent surface morphology
Characterization of adsorbents (RFA, AFA & PE-FA) surface morphology was conducted to understand elemental compositions. Scanning electron microscopy (SEM) micrographs were documented by FESEM (JSM-5900LV) fitted with an energy disperse x-ray spectroscopy (EDX) detector model X-max.

2.4 Batch adsorption runs
Batch adsorption experiment was conducted at room temperature (25°C) in a 100 mL Erlenmeyer flask with aluminum foil sealing cover. 50 mL Cd solution of 2 mg/L initial concentration was used. Blank experiments were conducted to assess precipitation effect during the sorption process. Three (3) different forms of adsorbent materials (namely; raw FA, acid treated FA and polyelectrolyte coated FA) were used in the study. Dosages of the adsorbent materials, ranging from 1 g/L to 5 g/L were used for the sorption tests and contact time from 5 min to 120 min. Analysis of initial and final concentration of Cd (II) ions was conducted using Optima 8000® ICP-OES Spectrometer (Perkin Elmer, USA). The percent removal as well as adsorption capacity of metal ions was calculated with the equations shown below:

\[
\% \text{ Cd ion removed} = \frac{C_i - C_e}{C_i} \times 100
\]

\[
\text{Adsorption capacity, } q_e (mg/g) = \frac{C_i - C_e}{M_s} \times V
\]

Where \(C_i\) is the metal ion initial concentration in solution (mg/L), \(C_e\) is the final concentration of adsorbate ion in solution (mg/L), \(V\) is the total volume of solution (L), \(M_s\) is adsorbent dosage.

3.0 Results and discussions

3.1 Material Characterization
Surface morphology of as received fly ash (RFA), acid treated FA (AFA) and polyelectrolyte coated FA (PE-FA) were examined with using Field Emission Scanning Electron Microscopy (FESEM) and Energy Disperse X-ray Spectrometry (EDX). The surface morphology of the RFA, AFA and PE-FA are presented in the Figure (1), while the EDX elemental composition of the various materials are shown in Figure 2 below.

Figure 1: SEM micrograph of (a) RFA (b) AFA (c) PE-FA
The SEM micrograph in Fig. 1 (a) shows that the carbon-based RFA material are mostly spherical shape with particle diameters ranges from 50 – 500 microns. Elemental composition revealed by EDX spectra in Fig. 2 (a) shows that RFA particles have 72 % carbon, 16.6 % oxygen and the remaining were silicon, copper, vanadium, aluminium and sulphur with 0.2, 6.0, 0.7, 2.0 and 2.8% composition respectively.

When RFA was treated with nitric acid (HNO₃), most of the heavy metals impurities were removed as shown in Fig. 1 (b). Moreover, it was observed that more pores were visible as a result of the treatment with nitric acid. On the other hand, the EDX spectrum in Fig. 2 (b) reveals that the carbon content increased from 72 to 92 % and an increase in the silicon content from 0.2 to 0.4%. While impurities such as copper, vanadium, and aluminium have diminished as a result of acid treatment.

The SEM micrograph in Fig. 2 (c), shows a thin pore linen coated with PDADMAC-PSS with an increase sulphur content (2.77-5.03%) of the fly ash upon coating with polyelectrolyte which might be due to the component of our polymer that has a Styrene-sulfonate compound (i.e PSS) in its composition.

**Figure 2:** EDX spectrum of (a) RFA (b) AFA (c) PE-FA

**Figure 3:** The effect of pH on Cd (II) removal using RFA, AFA & PE-FA at 2 mg/L Cd concentration, 4 g/L adsorbent dosage, 50 ml volume of aqueous solution, mixing rate 150 rpm, 15min. contact time

3.2 Effects of Adsorption parameters on Cd Removal

3.2.1 Effect of pH

Different forms of cadmium (Cd) species occurs in deionized water as Cd²⁺, Cd(OH)₂, Cd(OH)+ (Leyva-Ramos et al. 1997). The pH was a leading factor affecting Cd (II) ion removal under the investigated conditions. Nonetheless, Cd²⁺ often exists as a complex [Cd(H₂O)₆]²⁺ at low pH and also as prevailing species (Ihsanullah et al. 2015). With specific focus on PE-FA, the adsorption of Cd (II) ions by RFA, AFA and PE-FA were investigated at pH 4 – 10 to identify the optimum pH removal. As illustrated in Fig. 3, an increase in Cd (II) removal % occurred with an increased in pH of the aqueous solution. Maximum sorption of Cd (II) ions was attained at pH 9 due to the fact that in acidic medium Cd (II) ion sorption is low as a result of available large number of hydrogen ions (H⁺) which out compete Cd ions for active sites. However, as the pH increases, the number of positively charge ions available for active sites reduces with a rise in negatively charged ion for binding (Rathod et al. 2015)

3.2.2 Effect of contact time

Contact time is the time required for equilibrium to be attained in the process of adsorption when no substantial
The mass of adsorbent has effect on the active site available for binding of Cd (II) ions in aqueous solution (K.G. Akpomie and Dawodu 2015; Asmaly et al. 2016). In this study, batch mode experiments were conducted by applying varying quantities of RFA, AFA and PE-FA from 1 to 6 g/L at pH value of 9, 2 mg/L, 150 rpm mixing rate, 50 ml volume aqueous solution and 298 K temperature. As illustrated in Fig. 5, Cd (II) ion sorption rises with increase in dose of adsorbents up till 4 g/L and there was little or no significant adsorption for remaining dosage. Sorption increase with an increase in dose of adsorbent could be attributed to surface area increase, rise in the exchange site ability of the ion, and an increase in active sites (Ali 2014; Gupta and Torres 1998a; Rathod et al. 2015). PE-FA reach optimum at 4g/L unlike RFA and AFA with 5 g/L and 6 g/L as well as removal efficiency of 48 and 84 % respectively. Incomplete adsorbent aggregation which leads to a decline in Cd ion uptake active surface area may be the reason for drop in removal efficiency of at higher concentration for RFA. 4 g/L adsorbent dose was used for other investigation.
4. Conclusion

This study has demonstrated that polyelectrolyte coated fly ash (PE-FA) is an excellent sorbent for Cd (II) ion removal from aqueous solution. Adsorption of cadmium ions on PE-FA surface was observed to be dependent on the dosage of adsorbent, pH of aqueous solution, and contact time. This research highlights that fly ash material, a hazardous industrial waste, that poses serious concern for its disposal, has great potential in water treatment application.

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Reference


