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pH Effects on Hg^{2+} Level by Composite Pellet of Coal-Chitosan Fly Ash

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Abstract: Mercury is one of the carcinogenic heavy metals and harmful for human health at very low concentrations. Modified fly ash, pellet fly ash-chitosan composite absorbs ionic form of Mercury (Hg^{2+}). It is prepared by dissolving 2 g of chitosan in oxalic acid 5%, then 20 mL of the solution was added with 4 g of fly ash and cross fastened using 2% glutaraldehyde. The experiments was conducted at pH 2, 3, 4, 5, 6 and stirred in 60, 120, 180 rpm for each pH. The result shows optimum absorption Hg^{2+} found in pH 6 by adsorption capacity 89.9%. Stirring speed 60 and 180 rpm yielded greater adsorption capacities to 88.51% and 91.89% respectively.
Key words: adsorption capacity, chitosan, fly ash, mercury.

Introduction

Mercury (Hg^{2+}) is carcinogenic heavy metals found in waste water and potentially threaten human health at very low concentrations [1]. The maximum limit level of mercury ions in drinking water is 2.0 gL^{-1} and the total allowed waste mercury ions of 10.0 gL^{-1} [2]. A new, efficient, affordable and easy adsorption method is needed to detect wide range of Mercury before entering watershed [3].

Adsorption is a process of accumulating gases or liquids dissolved in a solid or liquid surface (adsorbent) to form an atomic layer (adsorbate) [4]. The adsorption process is determined by physic and chemical characteristic of adsorbent. An adsorbent, Fly Ash have been studied for metal ions adsorption such as Ni (II), Cu (II) [5], Zn (II) [6], Mn^{2+} [7], Cd^{2+} [8], CR^{2+} [9], and Hg^{2+} [10].

Lightweight fly ash particles produced as a side product of coal combustion[11] which is carried out through the gas flow in the furnace by 85-90% of the total ash produced[12]. Since fly ash has a major component such as silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3), as well as a number of unburnt carbon[13] that play an important role in the adsorption process made this particle as promising method. Modification of fly ash into pellets for absorbing Cu (II) and Cd (II)[14] has also been studied before. However this method is less effective because most of the fly ash mass is lost during the process of adsorption. We need a material that can trap fly ash to increase the adsorption capacity, such as chitosan.

Chitosan is one of D-glucosamine biopolymer produced from chitin through deacetylation using strong

alkali. Chitosan widely used as a co-polymer in the adsorption process. Cross linked of Amine and hydroxyl binding is often applied to modify the chemical structure and texture on its purpose. As a membrane, chitosan is crossed linked to glutaraldehyde at its amine group (-NH_2). Cross link forms pores could enhanced adsorption as a immobilized sites of fly ash[15].

Adsorption process of fly ash is influenced by pH solution, mass, pellet mass and stirring speed. Shetty[16] showed pH 4.0 is the optimum for chitosan to adsorb heavy metal. Meanwhile Ramya *et al.* [17] said it was at pH 5.0. Pellet mass influenced the number of immobilized fly ash on pellet whereas stirring speed posses homogeneity and celerity analyte absorbed in adsorbent.

Research Method

Fly Ash Preparation & Activation for Demineralisation, Dealumination and Calsination

Preparation of fly ash is done in following steps. Fly ash crushed using a mortar then dried for 1 hour at 100°C using an oven. Dry fly ash sieved using 120 mesh sieves and which passes the sieve is used as adsorbent. Total of 1M HCl added to fly ash for 24 hours at room temperature. Then filtered and washed with distilled water. Fly ash dried for 2 hours at a temperature of 100°C. Furthermore, fly ash soaked in 1 M H_2SO_4 for 5 hours followed by dried step once more, and then calcined for 2 hours at 500°C.

Table 1. Fly ash composition elements

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	others
% composition	56.76	18.14	15.35	2.80	2.62	0.17	4.16

Fly Ash and Chitosan Pellet Formation

Adsorbent was prepared by dissolve 2 gram of chitosan in 100 mL oxalate acid 5% on stirring while heated to dissolve. The solutions then brought into room temperature. 20 mL chitosan added with 4 gram of deactivated fly ash, stirred into homogeny. By pippeting, each droplet of chitosan and fly ash compound mixed with 2M NaOH followed by NAOH separation. Mixed solution of fly ash and chitosan was added with 2% glutaraldehyde for 24 h to form fly ash composite pellet. Pellet than washed from solution and let dried. Adjusted of 1 mL of 2.96 rpm $HgSO_4$ to pH 2, 3, 4, 5, 6, and diluted to 100 mL final volume. Solution bring into 100 mL contained composite pellet of fly ash-chitosan then stirred by 60, 120, 180 rpm for 1 hour. Filtrate from prior filtrating process is used to measure Hg^{2+} level by AAS protocol.

Result and Discussion

pH effects on Mercury ion adsorption

This study used 2-6 pH in range because pH level has significant effect on mercury adsorption from fly ash-chitosan composite pellet. Transition metal will react with hydroxide ion formed hydroxide salt precipitate above pH 7[18] and mercury ions as well[19] then forms black hydroxide salt precipitate. Optimum pH in this study was 6 (Figure 1). Chitosan will be dissolved under pH 6 when Hg^{2+} ions adsorptions of fly ash composite-chitosan were low.

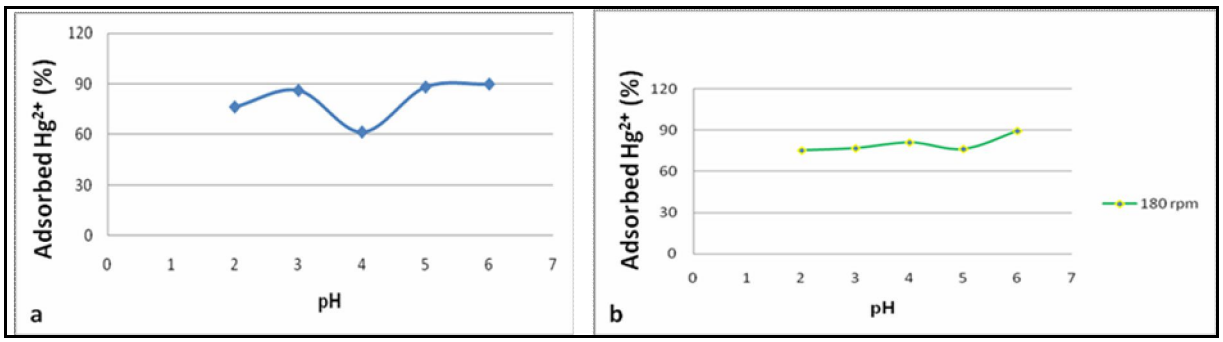

Figure 1. pH effects to Hg^{2+} adsorption in 60 rpm (a) and 180 rpm stirring (b)

Figure 1 present optimum adsorption at pH 3, 5 and 6 in similarity exploration was done by Papandreou *et al.*[14]. However, maximum adsorption only reached at pH 6 because chitosan begin to dissolve and crosslink developed at pH 3 and 5. It causes fly ash adsorbent mass loss while adsorption occurring. At pH 6 showed adsorption stability because chitosan is insoluble at this level of pH with bulging or swelling feature. Those features could facilitate diffusion process that adsorbed Hg^{2+} ions on fly ash pellet-chitosan composite in considerable amount.

Effects of Stirring

Stirring is important step because has affects for rapid adsorption. This research was conducted at stirring speed of 60, 120, and 180 rpm, and the results are presented in Table 2 and Figure 2. It can be concluded the optimum mixing speed for Hg^{2+} adsorption process is 180 rpm with the adsorption capacity of 91.89%. At stirring speed of 60 rpm adsorption capacity is about 88.51%. These results mean that the stirring speed does not significantly affect the adsorption process of Hg^{2+}. Stirring speed has effects on rapid mobility and pressure of Hg^{2+} in water that allowed rapid Hg^{2+} diffusion of chitosan and fly ash adsorption.

Table 2. Adsorbed Hg^{2+} in various speed stirring (%)

Pellet and fly ash mass in 20mL chitosan solution	Adsorbed Hg^{2+} (%)		
	60 rpm	120 rpm	180 rpm
1 : 4	79.39	72.97	86.53
2 : 4	89.87	72.30	89.53
3 : 4	88.51	71.96	91.89

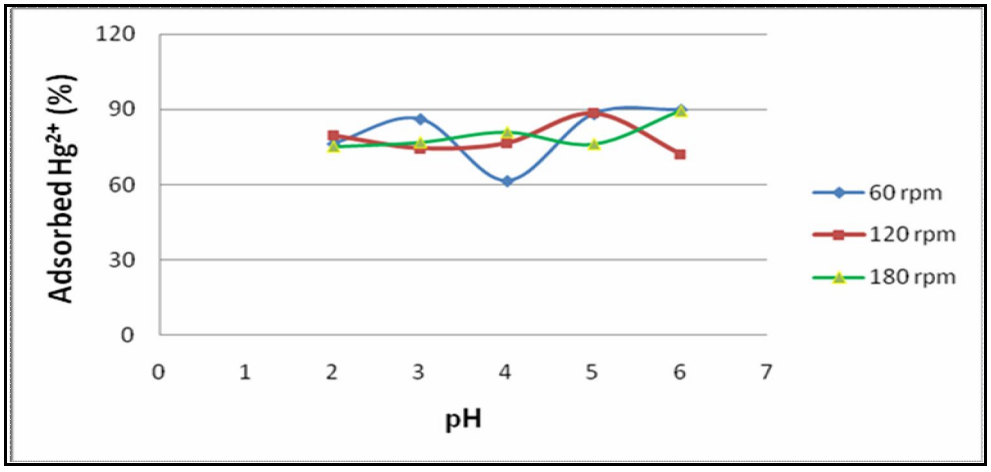

Figure 2. Stirring Effect to Hg^{2+} adsorption

Fly ash can be modified into pellet from Fly ash-chitosan composite crosslinked with Glutaraldehyde. This pellet is useful for Hg^{2+} adsorption. At pH 6 was optimum pH that reached 89.9% adsorption capacity. Meanwhile, 88.51% and 91.89% adsorption capacity were reached in 60 and 180 rpm stirring.

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