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Removal of Lead by Reverse Fluidization Using Granular Activated Carbon

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Abstract: The adsorption of lead ions on granular activated carbon (GAC) and removal of lead as heavy metal using GAC studied in a reverse fluidized bed. GAC is suitable adsorbent particularly to remove heavy metals from water. A fluidized bed was more suitable technology for GAC, due to its certain advantages over packed bed. The only problem arises in fluidized bed is the low density (0.44 g/cm^3) of GAC, which makes it to float on the liquid surface. A simple concept of reverse fluidized bed can be a better replacement. Experimental investigations were carried out in a reverse fluidized bed. Result for removal efficiency of GAC with change in concentration of solution, change in pH of solution, change in bed height of GAC, change in residence time was investigated. It was observed that % removal of lead increases with an increase in bed height and time, where as it gets decreased with an increase in initial lead concentration and pH of the solution.

INTRODUCTION

Heavy metal pollution is a major environmental issue concerning the industries handling metal process across the world. Since the past fifteen years, there has been increasing activity by many environmentalists in recovery of heavy metals from industrial effluent because of their toxic nature, which is hazardous to living being. The main sources of toxic metals are industrial wastes from processes such as electroplating, metal finishing, mining operations, chemical manufacturing, nuclear fuel processing tanneries, chlor-alkali, radiator manufacturing, smelting, alloy industries and storage batteries manufacture [1]. Since most of heavy metals are non- degradable into nontoxic metals end products, these concentration must be reduced to acceptable levels before discharged them into environment. In addition to this, their increasing price as a precious material has turned the attention of many researchers and industrialists towards its recovery. One of such heavy metal is lead (Pb) found in effluents arising from many industries such as mining, steel, automobile, batteries and paints. Further strict

environmental regulations from federal as well as international level have forced many researchers to investigate and control this pollutant. Metals and their compounds are vital to the industrial, agricultural and technological progress of any nation. Applications of metals for commercial uses in modern science and technology are more. Many industries produces huge amount of heavy metals and release in to the water bodies. It has been estimated that the toxicity due to metallic discharge annually into the environment far exceeds the combined total toxicity of all radioactive and organic wastes as measured by the quantity of waste required to dilute such wastes to the drinking water standard [2-4]. Pollution owing to lead in the environment is mainly due to anthropogenic activities. [5]. As per Abdus-Salam and Adekola, [4], research on Pb has become a dominant topic for environmental and medical scientists because it has no known biological use and it is toxic to most living things. Lead is a metal ion toxic to the human biosystem and is among the common global pollutants arising from increasing industrialization. The assimilation of relatively small amounts of lead over

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a long period of time in the human body can lead to the malfunctioning of the organs and chronic toxicity. The toxic effects of lead ions on humans, when present above the threshold level in the hydrosphere, are well documented [6].

Adsorption is found to be the most effective method for removing dissolved metal ions from wastes. Adsorption is the most commonly used process because it is fairly simple and convenient unit operation and that the cost for its application is relatively low compared to other treatment processes. Adsorption by activated carbon has been widely studied as an effective technique for removing heavy metal from aqueous solution and wastewater. Several researchers have studied the adsorption of heavy metal ions from solution using naturally occurring minerals. Pyrolusite has been used for adsorption of lead and magnesium ions from their aqueous solution [7]. Zeolites have been used for the removal of heavy metals from wastewater [8]. Sigworth and Smith [9] and Muscas [10] have also used adsorption techniques for the removal of heavy metals from polluted water. Other adsorbents that have been used for the removal of heavy metals solution include soils [11] and carbonaceous material developed from fertilizer waste slurry [12]. Adsorption of heavy metal ions from polluted water by activated carbons from date pits [13] and by ferrite and chelating resin method [14] has also been studied.

A significant amount of research activity has been done to remove this hazardous metal (lead) from the effluent by various techniques as found in the literature. For example, Ahmad *et al*. [15] used GAC to remove cadmium and lead from the prepared solution in a fixed bed column. They carried out the simulation studies to compare it with experimental data to examine the potential and effectiveness of GAC to remove heavy metals. Another study of lead removal from aqueous systems through GAC and treated GAC in a static and continuous column has been conducted in order to understand the adsorption behaviour [16]. In their studies, the process variables taken for continuous column were bed height, hydraulic load rate and initial feed concentration on breakthrough time and adsorption capacity. Investigation to evaluate the adsorption effectiveness of pecan shell-based GAC in removing metal ions such as Cu^{2+}, Pb^{2+} and Zn^{2+} was done by Bansode *et al*. [17]. Experiments on adsorption of Cu, Zn and Pb in a pretreated fixed-bed columns using GAC were carried out [18]. They have verified the effect of pH, flow rate and increasing concentration. Studies conducted by

Singh *et al*. [19] used agriculture waste (maize bran) absorbent and the effect of various parameters such as contact time, concentration, pH and temperature of the same was determined for the removal of lead II from aqueous solution. Recently, removal efficiency of Cu, Zn, Pb and Cd in industrial wastewater was studied with influence of several parameters on adsorption capacity using activated carbon [20]. Fixed bed column with natural zeolite (clinoptilolite) at different flow rates was used to study the removal efficiency of lead, copper and zinc [21]. However, there was lack of work on lead removal via fluidized bed column and particularly on reverse fluidization. Hence, this was the groundwork for the lead removal using reverse fluidization technique on GAC bed. For industrial applications in the waste water treatment, the most efficient arrangement for conducting adsorption operation is inverse fluidized bed. With almost no exception the fluidized bed process, which are largely applied in various industries, deals with solid which are lighter than fluid. If this is the matter than the normal method of directing the fluid upward will not serve any purpose. Hence for such cases (the most practical one is the liquid-liquid, solid fluidized bed) where the direction of fluid is reversed and hence such phenomenon is called "Reverse fluidization". Banerjee *et al*. [22] studied that point of intersection of rising and constant pressure drop line on log-log graph of pressure drop against velocity gives minimum fluidization velocity. Ganguly *et al*. [23] studied that break point of minimum fluidization velocity are sharp in nature for uni-component or homogeneous system while it gets flattened for multi component system. Couderc [24] found that the point of departure of p-line from linearity gives beginning of reverse fluidization while the point at which it merge the constant fluidization line gives total reverse fluidization velocity.

The basic objectives of the present research work were to investigate the effect of initial concentration, pH, bed height and time on the efficacy of lead removal using GAC in a reverse fluidization mode. Overall, the influence of velocity on removal efficiency of lead for the above parameters was also taken into account.

MATERIALS AND METHODS

Materials: The granular activated carbon (LR grade) was supplied by S. D. Fine-Chem in the size range 2–5 mm. It was manufactured from coconut shells and was treated with acid wash before delivery. These were subsequently pulverized and sieved through 18 to 44 BS mesh to get the activated carbon particles of the desired size range.

Table 1: Characteristics of granular activated carbon

Physical Characteristics	
BET surface area m^2/g	579.23
Specific gravity	0.92
Bulk density g/ml	0.977
Hardness	<1 (in Mohr's hardness scale)
Porosity	24.43 %
Chemical Compositions (wt %)	
Carbon	95.50
SiO$_2$	0.47
Al$_2$O$_3$	0.06
K$_2$O	0.51
Na$_2$O	0.06
CaO	1.54
MgO	0.08
Fe$_2$O$_3$	0.07
H$_2$O	1.20

The uniform sized particles as retained on different sieves were mixed and the average diameter was estimated to be 0.536 mm. In order to remove any fines attached to these particles and any leachable matter, this was further washed a number of times with distilled water. The activated carbon was considered fit for use when the distilled water obtained after washing was visibly clear. After washing the activated carbon, it was dried in an oven at 105°C for 72 h. This time was sufficient to drive off the moisture. After drying, this was stored in a glass bottle until use. Table 1 shows the physical and chemical characteristics of GAC. The lead concentrated water was made in the laboratory. To make lead solution, 0.1599 g of lead nitrate was dissolved in 10 ml of diluted nitric acid and water was added to make exactly 1000 ml of the solution. One ml of this solution contains 0.1 ml of lead. The concentration of lead was measured via spectrophotometer supplied by Chemito UV-2100. Solution pH was measured by cyber scan pH meter having accuracy of ± 0.01. The flow rate of solution was measured through Eureka Make rotameter with an accuracy of ± 2 % of full flow.

Experimental Methodology: The study of lead removal was carried out in a lab-scale fluidized bed having dimension of 55 mm (inner diameter) and 1000 mm (height). The experimental set up (Figure 1) essentially consisting of a fluidizing column, water reservoir, centrifugal pump, bottom water reservoir to collect water stream after separating the solid if any through the screen and rotameter. A 200-mesh screen was fitted at the top of the fluidized bed in order to capture the solid coming out of the column. A conical distributor was placed at the top to ensure proper distribution of fluid. A short cylindrical
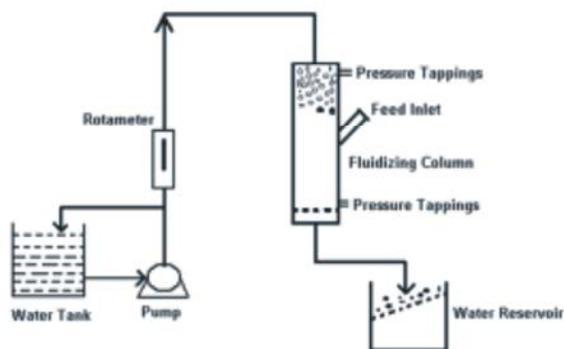

Fig. 1: Schematic diagram of experimental set-up

feed inlet was fitted at the middle section of the column to allow a predetermined quantity of solid or mixture of solid to be introduced at start of the experiment. Water was introduced into the column when the solid started to float and got collected under the top screen to form what is termed as static bed height. The pump was started to admit the working fluid into the column at an increasing rate at interval of time. The observed pressure drop across bed (P_o) for a particular flow rate, when subtracted from blank pressure drop, gives the actual pressure drop, at that flow rate. From the graph of actual pressure drop against velocity, a minimum reverse fluidization velocity was obtained. At particular velocity, the efficiency of reverse fluidized bed at different condition was observed.

RESULTS AND DISCUSSIONS

Effect of Initial Concentration of Lead: The effect of initial concentration of lead on removal efficiency is as shown in Figure 2. It was seen that the removal efficiency of fluidized bed decreases appreciably with increase in concentration at both the velocities. There are several reasons for this effect to take place. Firstly, the loading rate of the lead in water increases due to increase in concentration. In contrast to this, the size and shape of the GAC would remain constant. It means that higher diffusion was occurring at lower initial lead concentration and it decreased as the initial concentration of lead increased. This shows that the diffusion process was concentration dependent as observed by Goel *et al.* [16]. Their results showed that the change in concentration gradient affects the saturation rate. They have remarked that sorption was almost quantitative at low concentrations and it decreases at higher concentrations. Further, for low metal concentrations, the adsorption taken places at high energy surfaces and it saturates as the concentrations increases. At a concentration of
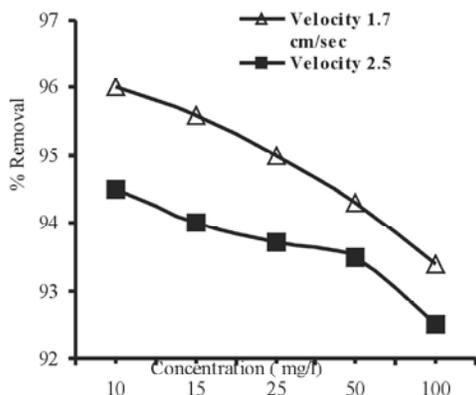
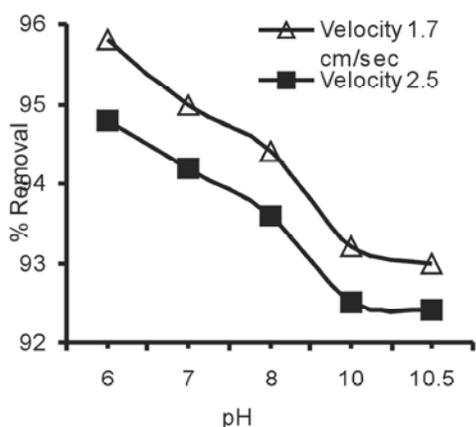Fig. 2: Effect of Initial Concentration of Lead on % removal of lead

Fig. 3: Effect of pH of the Solution on % removal of lead

10 mg/l, about 96.5 and 94.8 % lead was removed at 1.7 and 2.5 cm/s velocity, respectively. This indicates that the removal efficiency of lead decreases at high velocity, whereas the initial concentration of the lead was kept constant. This might be due to less contact time between the solution and the GAC bed which causes to diminish the adsorption capacity of GAC fluidized bed. In other words, the higher was the empty bed contact time.

Effect of pH of the Solution: The pH of solution has important role to play on the extent of removal efficiency of lead in a fluidized bed. The removal efficiency of fluidized bed at different pH is illustrated in Figure 3. It has been found that the removal efficiency of lead decreases appreciably with increase in pH of the solution and maximum removal of lead was found in the acidic range (6 to 7 pH). Further, the removal efficiency of lead decreases drastically from 8 to 10 pH value. This might be due to precipitation of lead oxide or lead ions on the GAC surface. The pH value of lead solution was observed [16]

increasing with respect to time, indicating the release of alkali ions from the activated carbon surface. They also suggested the mechanism of lead removal via activated carbon initially depends on surface precipitation followed by ion exchange at high pH. Another reason for decrease in removal efficiency at higher solution pH might be the change in GAC bed pH itself. However, exchange of metal ions resulting in metal oxide formation and deposition of the same on GAC at high pH was the most convinced observation in view of present authors. Hence, the formation of this metal oxide gets detached at low pH values (acidic region) of solution due to acidic nature of both solution as well as GAC. While, the deposition of the metal oxide formed due to ion exchange adheres to GAC surface due to basic nature at increased value of pH. Moreover, the entering solution with higher initial pH value can even add to deposition of more oxides or cannot take away the deposited metal oxide, eventually diminishing the removal efficiency of GAC fluidized bed. Recently, investigation conducted for lead removal via maize barn adsorbent revealed very analogous results whereby percentage removal increased from 23.6 to 96.8 % with an increase of pH from 3.2 to 6.5 [19]; thereafter the percentage removal decreased from 96.8 to 31.2 % with an increase of pH from 6.5 to 8.0. In their study, the optimum pH for removal of lead was 6.5. The reason explained by thm was the formation of metal oxides which was nearly the same discussed by present authors. The percentage removal efficiency in the present study was high even at high pH values because of fluidization technique compared to fixed bed or batch mode [19] using activated carbon adsorbent. The optimum pH value for the present study was around 6 and the removal efficiency remains unaffected at higher pH values (above 10). This might show the saturation point of GAC bed after which the metal ion exchange balances in both direction. More supporting observations have been given by Stylianou *et al.* [21] on the ion exchange mechanism due to pH variation for metal removal such as Cu, Pb and Zn. Overall, the metal removal efficiency was critically associated with pH.

Effect of Bed Height: The percent removal of lead is found improved with an increase in the bed height of granular activated carbon in the fluidized bed. It was found (Figure 4) that the removal efficiency increases initially with bed height. Further, it will remain constant with respect to bed height. This may be because of incomplete fluidization after appreciable bed height. This could have lead to reduced contact time between activated carbon
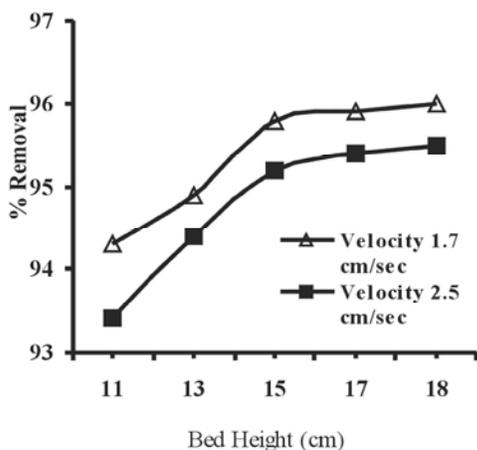
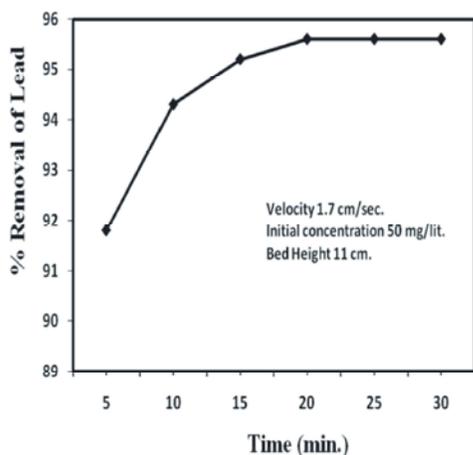Fig. 4: Effect of Bed Height on % removal of lead

Fig. 5: Effect of Time of Fluidization on % Removal of Lead

and solution. However, this decrease of the contact time will result in premature penetration to occur, thus reducing the service time of the bed [15]. The highest removal efficiency of about 96 % could be achieved above bed height of 15 cm at 1.7 cm/s velocity. The removal efficiency of the metal concentration from solution increases as the bed height increases since the length of the bed through which the solution passes increases. Since in fluidization the bed is constantly moving which results in maximum exposure of GAC adsorbent to the solution. Thus, even at less quantity of bed mass maximum amount of removal efficiency can be obtained.

Effect of Time of Fluidization on Percentage of Lead Removal: The removal efficiency of lead is also influenced by the time of fluidization in fluidized bed at constant velocity, bed height and initial concentration. Figure 5 depicts the effect of time of fluidization on the removal

efficiency, which is found to be increased initially with an increase in time and thereafter it was observed to be constant. This is due to the saturation of an activated carbon as the time progresses. About 95.5 % removal efficiency was obtained within 20 minutes of the operation. The results revealed that the equilibrium time was reached at about 17 min and this does not depend on initial adsorbent concentration.

Effect of Velocity on Lead Removal: Lead removal efficiency has been also influenced by the flow velocities of lead solution. It can be seen from Figures 2 to 5 that, the lead removal efficiency has been decreased with an increases in flow velocities of the lead solution. Study of Ahmad *et al*. [15] revealed that removal of lead was more efficient at low flow rate which was consistent with the present studies. This may be due to the increase in contact time between solution and GAC at low velocities. The results depicts that the velocity of 1.7 and 2.5 cm/s gave maximum of 96 and 94.8% removal efficiency, respectively. Chen and Wang [18] reported that the empty bed contact time was directly proportional to flow rate in a fixed bed column which resulted in higher removal of metal ions. This was the most appropriate reason for increase in removal efficiency for lead at low velocities. Lower flow rates results in high residence time for solution in column [21]. However, some side effects of low flow rate were found in fixed bed operation [21] due to maldistribution of solution because of liquid hold-up is lowered in the bed. Also assurance of complete wetting of the material is required in fixed bed and in down flow mode this might not be possible without proper designing of distributor. Hence, liquid maldistribution leads to a phenomenon called channeling in which that the portion of the bed remains dry and remains inactive during process. At this stage, fluidization technique would be of advantage where constant moving bed removes these demerits of fixed bed operations. Thus, the difference in removal efficiency at different velocities was narrow or insignificant.

CONCLUSIONS

Granular activated carbon used in fluidized bed has shown fairly good removal potential at higher lead concentration. The maximum removal efficiency of fluidized bed using granular activated carbon was in the acidic range of around 6 pH. Further, the removal efficiency increased initially with the bed height up to some extent and then remains constant. The optimum bed

height found was about 16 cm. The saturation time for GAC was found about 17 min after which there is no appreciable increase in removal efficiency of the lead. The removal efficiency is also influenced by the flow velocity. High removal efficiency of lead is observed at low velocity.

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