Removal of Heavy Contaminants (Arsenic, Cadmium and Lead) from Synthetic Waste Water using Iron Impregnated Activated Carbon

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Abstract—Arsenic, cadmium and lead are found to be the most toxic elements that pollute the water in high concentrations. These elements are toxic, non-biodegradable and tend to accumulate in the tissues of living organisms that causes various disorders. Various industrial activities such as metal plating, oil refining, petrochemical and dye and paints, mining operations etc. releases large amount of such toxic metalloid elements. Among most of the impurities removal process, adsorption process is found to be more effective and economic. Activated carbon was impregnated with iron through a multi-step procedure using ferrous chloride solution for the impregnation process for removing arsenic, cadmium and lead from the synthetic waste water. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis demonstrated that the impregnated iron was distributed on the internal surface of the activated carbon. Iron impregnated activated carbon was treated with sodium hydroxide to stabilize iron in activated carbon. The impact of the amount of impregnated iron in activated carbon on arsenic, cadmium and lead adsorption capacities and kinetics were investigated in this study.

1. INTRODUCTION

Today, as the industrialization is increasing day by day; pollution in the environment is also increasing with the same speed. Wastes coming out from the industries deteriorating the environment and thus the living organisms; resulting in severe effects [1]. Waste water that are discharged from the chemical industries such as paint industry, glass industries, metal refining, petrochemical, etc. releases large amount of toxic elements; which when consumed by living organisms produces harmful effects [2]. Arsenic, Cadmium and Lead are found to be the most toxic elements that needed to be removed. Arsenic pollution has been reported recently in the USA, China, Chile, Mexico, Argentina, Canada, Hungary, New Zealand, Japan and India [3]. The largest population at risk with arsenic contamination is in Bangladesh, followed by West Bengal in India [4].

Cadmium is produced mainly as by-product from mining, smelting and refining of sulphide ores of zinc [5]. Cadmium released from these industries get introduced into the water bodies and when consumed produces harmful effects including a number of acute and chronic disorders [6].

Lead is also one of the most toxic metals arising from the increasing industrialization. Relatively small amount of lead presence over a long period of time creates malfunctioning of the organs and chronic toxicity. Lead is released into natural waters from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations [7].

These metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time [8].

Heavy metals can cause great harm to humans, animals and the aquatic eco-system. The huge source of water pollution is industry, it produces pollutants that are extremely harmful to people and the environment. Toxic heavy metals that were discharged in streams and industrial waste waters particularly arsenic, lead and cadmium need to be removed to protect humans, animals, and the aquatic ecosystem. Throughout the world, arsenic is creating potentially serious environmental problems for humans and other living organisms. Arsenic occurrence in the environment, its toxicity, health hazards, and the techniques used for speciation analysis are well known. Long term drinking water exposure causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea. Arsenic in natural waters is a worldwide problem. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India. The largest population at risk among the 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India.

Cadmium (Cd) is produced mainly as a by-product from mining, smelting, and refining of sulphide ores of zinc. Cadmium is introduced in to bodies of water from smelting, metal plating, Cadmium-Nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of Cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy.

Lead is a metal ion toxic to the human bio system, and is among the common global pollutants arising from increasing industrialisation. The assimilation of relatively small amounts of lead over 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.

2. MATERIALS AND METHODS

2.1. Materials used

Activated carbon, ferrous chloride, sodium hydroxide, sodium arsenate salt ($Na_2HAsO_4.7H_2O$), cadmium nitrate tetra hydrate salt [Cd (NO_3)₂.4H₂O], and lead nitrate salt [Pb (NO_3)₂], distilled water. All chemicals used in this study were of reagent grade and used as received.

2.2. Preparation of Adsorbent

Iron impregnated activated carbon(AC) is prepared by dissolving the ferrous chloride salt in distilled water. For preparing 0.1M iron solution, dissolve 19.88 gm of ferrous chloride salt in distilled water to complete the solution up to 1 litre. The activated carbon was coated with iron by the impregnation method and thermo-chemical reactions by using the ferrous chloride solution. In this process, pH of the suspension was adjusted and maintained to ~8 by the addition of sodium hydroxide and nitric acid (0.1M) solution; this increases the slurry pH and leads to negative charge abundance on activated carbon and enhance the impregnation process. The activated carbon in the powder form was stirred thoroughly in the iron salt solution using magnetic stirrer to obtain a uniform mixture. The suspension temperature was controlled and maintained at 70°C. After continuous stirring of 24 hours, the suspension was collected and filtered by using filter paper. The required solid phase was collected and dried in an oven at 120°C for 10 hours. After complete drying of the solid phase, the product was cooled to room temperature and washed thoroughly with distilled water until a clear supernatant was obtained.

The Fe-AC was treated with 1N sodium hydroxide solution for 10 hours. This treatment with sodium hydroxide solution provides the stabilization step in the development of the iron impregnated activated carbon. This stabilization step improves the iron impregnation efficiency by reducing the loss of impregnated iron in the impregnation process; thus enhances the stability of impregnated iron, and increases the adsorption capacity by the generation of favoured iron species-hydrous ferrous hydroxide that has poor crystalline structure and large surface areas.

2.3. Characterization of Fe-AC

The solid structures of Fe-AC were analyzed using scanning electronic microscopy (SEM) and energy dispersive X-ray (EDS) technique. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis demonstrated that the impregnated iron was distributed evenly on the internal surface of the activated carbon. Distribution and morphology of impregnated iron were measured by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).





Fig. 2.1: EDS image of the iron impregnated activated carbon

The Fig. above is the EDS image of the iron impregnated activated. The green colour shows the iron content which is adsorbed on the red colour surface activated carbon. The Fig. shows that iron has impregnated everywhere on the surface of activated carbon. The high density of green colour shows that iron has impregnated with high percentage on the surface of carbon.



Fig. 2.2: XRD pattern of iron impregnated activated carbon



Fig. 2.3: SEM image of iron impregnated activated carbon



Fig. 2.4: SEM image of unimpregnated activated carbon

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Result type (spectrum label)	Spectrum (Weight%)
С	84.55
Si	0.34
Cl	7.63
Ca	0.23
Fe	7.24
Total	100.00

Table 1: SEM analysis data

2.4. Preparation of As Synthetic Water

Sodium arsenate $(Na_2HAsO_4.7H_2O)$ salt was used for the preparation of stock solution of arsenate. For preparing 500 ppm solution, 1.04 gm of the sodium arsenate salt was dissolved in small amount of water and raise the extent using distilled water up to 500mL.

2.5. Preparation of Cd Synthetic Water

Cadmium nitrate tetra hydrate salt was used for the preparation of the stock solution of cadmium. For the preparation of 500 ppm of cadmium solution, dissolve 0.6875 grams of cadmium salt in 10 mL of distill water and raise the extent upto 500 mL using distilled water.

2.6. Preparation of Pb synthetic Water

Lead nitrate salt was used for the preparation of master solution of lead. 0.40 grams of lead salt was dissolved in small amount of water and the extent was raised up to 500 mL for the preparation of 500 ppm of the lead stock solution.

3. RESULT AND DISCUSSION

3.1. For Arsenic



Time (min) Fig. 3.1.2: Effect of contact time

100

150

200

50

0

In fig. 3.1.1, the removal of As (V) by using iron impregnated activated carbon and activated carbon without impregnation by varying different amount of adsorbent dose is shown. From this figure, it is evident that the % removal of arsenic species increases with increasing amount of both AC and Fe-AC. It is very clear from the Fig. that at lower adsorbent dose, the % of adsorption is high as compared to the higher adsorbent dose [11]. At higher adsorbent dose, the adsorption becomes negligible for both AC and Fe-AC. Beyond the adsorbent dose of 60 g/l and 35 g/l for AC and Fe-AC resp. the % removal of arsenic becomes very less. Hence, the optimum removal of arsenic species can be obtained by using 60 g/l AC and 35 g/l Fe-AC. For AC, the optimum removal is 52.33% and for Fe-AC, the optimum removal is 67.72%.

From fig. 3.1.2; it is clear that an optimum time of 210 minutes is required for AC and 120 minutes is required for Fe-AC to reach equilibrium. Beyond this time of stirring, the % removal of arsenic species becomes very less or negligible.

3.2. For Cadmium



Fig. 3.2.2: Effect of Contact time

In fig. 3.2.1, the % removal of cadmium by using both AC and Fe-AC is shown. An optimum amount of 55 g/l AC and 35 g/l of Fe-AC is required to reach an equilibrium adsorption process. Beyond this adsorbent dose, the % removal of cadmium becomes less and adsorption process becomes insignificant.

From fig. 3.2.2, it is evident that 180 minutes is required for AC and 90 minutes is needed for Fe-AC to reach the equilibrium adsorption. Beyond, this time limit, the adsorption process becomes insignificant. The time required by impregnated activated carbon to reach the equilibrium is just half the time required by unimpregnated AC. The % removal of cadmium by AC and Fe-AC is 49.01 and 60.98 resp.

3.3. For Lead

Lead nitrate salt was used for the preparation of master solution of lead. 0.40 grams of lead salt was dissolved in small amount of water and the extent was raised up to 500 mL for the preparation of 500 ppm of the lead stock solution.



Fig. 3.3.1: Effect of adsorbent dose



Fig. 3.3.2: Effect of contact time

The removal of lead by using both AC and Fe-AC is shown in fig. 3.3.1. Initially, in both the adsorbents, the % removal of lead is increasing on increasing the adsorbent dose. On increasing the adsorbent dose, the adsorption process is not taking place as much high speed as in low adsorbent dose. The % removal of lead reduces on increasing the adsorbent dose. The optimum adsorbent required for the removal of lead is 75 g/l and 40 g/l for AC and Fe-AC resp. Continuous stirring of 180 minutes and 120 minutes is required for AC and Fe-AC resp. to reach an optimum equilibrium adsorption process. The maximum % removal which took place was 51.23 and 71.26 resp. for AC and Fe-AC.

3.4. Mechanism behind the adsorption process

In the above removal processes, initially the % removal was high, when there is low amount of adsorbent dose; and on further increasing the amount of adsorbent dose, the removal process was not significant as before. This means that high amount of adsorbent dose is not satisfactorily required for the higher % of removal.

With the increase in adsorbent dose, the number of active sites in unit volume of solution increases, which leads to the increase in % removal of the impurities. However, after an optimum adsorbent dose at equilibrium contact time, the % removal of impurities with the increase in adsorbent dose is less.

This can be better explained as follows: Initially, there are more vacant active sites available on the amorphous surface of AC which tends to more accumulation of the impurities from water. This tends to the formation of monolayer of adsorbed molecules on the surface of the adsorbent. Thus, on further increasing the amount of adsorbent, as the active vacant sites get already filled up, there is no significance of increasing the adsorbent dose.

On impregnating the AC with iron, the surface of AC gets modified. Electrostatic charges are produced between the adsorbate and the adsorbent, which enhances the adsorption process due to the presence of negatively charged vacant sites [12].

4. CONCLUSIONS

From the above discussions, the following conclusions are made:

- 1) The treatment of arsenic containing waste water with Fe-AC removes 67.72% of the arsenic by using 35 g/l of the adsorbent in the time duration of 120 minutes. This removal is 52.33% by using unimpreganated AC with the adsorbent dose of 60 g/l in the time duration of 210 minutes.
- 2) The removal of cadmium from waste water with Fe-AC as adsorbent is 60.98% with an adsorbent dose of 35 g/l in the time duration of 90 minutes; whereas by using AC, this removal is 49.01% by using an adsorbent dose of 55 g/l in an optimum time duration of 90 minutes.
- 3) The treatment of lead containing waste water with Fe-AC removes 71.26 % of lead from waste water with an adsorbent dose of 40 g/l in the time duration of 120 minutes; while by using AC, this removal is 51.23% with

an adsorbent dose of 75 g/l in the time duration of 180 minutes.

4) The impregnation of AC with iron modifies the surface of the AC and thus enhances the adsorption process by increasing the active sites due to the formation of charges.

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