Removal of Chromium from Synthetic Wastewater using Adsorption Technique

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Abstract - *In the present scenario pollution of the environment by heavy metals, which are known to be toxic and non-biodegradable has become a serious issue. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. Adsorption processes are being widely used by various researchers for the removal of heavy metals from waste streams. In the present study, removal characteristics of Cr (VI) ion from wastewater using fly ash blended with cement- a low cost adsorbent has been studied. Experiments were carried out by batch mode. The effect of contact time, initial metal ion concentration and fly ash blended with cement at different concentration as an adsorbent on adsorption have been investigated. The optimum contact time of the experiment was found to be 120 minutes for all the adsorbents with batch experiments being performed. The result of the present study showed that, maximum of 30.20% removal efficiency in synthetic wastewater sample was achieved by using fly ash, 97.27% removal efficiency using 25% Fly ash blended Cement, 97.90% removal efficiency using 50% Fly ash blended Cement, 99.01% removal efficiency using 75% Fly ash blended Cement, 99.09% removal efficiency using Cement. The isotherms were in conformity with both Langmuir and Freundlich isotherms and the constants are also evaluated, but the best fit was with Freundlich isotherm.*

Key Words: *Fly ash, cement, adsorption, chromium synthetic wastewater etc…*

1. INTRODUCTION

Heavy metal ions are member of toxic pollutants, these are loosely defined subset of elements that exhibit metallic properties. Some of these are poisonous capable of being assimilated, stored and concentrated in the organisms that are exposed to these substances at low concentrations for long periods or short periods repeatedly. Continuous exposure of these heavy metals is enough to increase the metal concentration in tissues which is sufficient to cause physiological effects. Heavy metals occur in ecosystem naturally with varying concentration. The anthropogenic sources of heavy metals pollution occurs through effluent discharges from a variety of industries such as ore processing, mining, metal processing operations, tanning, electroplating, textile dyeing and the industries which uses metallic compounds like pigments, bio-acidic agents. The presence of heavy metals in wastewater is dangerous due to their solubility in water thus can be absorbed by living organisms and like in turn they enter in the food chain and start to accumulate in the human body. Ingestion of heavy metals beyond the permissible concentration can cause serious health disorders. Because of the problems caused by heavy metals their removal become important and for this several methods like: adsorption, coagulation, flocculation, precipitation, reverse osmosis, biological process, ionization, adsorption, gamma radiations, photo catalysis are being used. But amongst all the adsorption technique is preferred because of its advantages like: low cost, ease of operation, efficiency, simplicity of the equipment and mostly because the adsorbent can be chosen from a wide variety of materials (natural, synthetic and industrial wastes), for example Fly ash, Blast-furnace slag, Rice husk etc. [1, 2,16].

1.1 Chromium

Chromium is a chemical element which is derived from the Greek word "chroma" meaning colour, because many of its compounds are coloured. It is the first element in group 6 having atomic number 24, and symbol Cr. Chromium is a hard metal that has high melting point and it is also colorless tasteless and malleable. Chromium in particular has received attention due to its hazardous nature. The most predominant forms of chromium are trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)]. But Cr (VI) is most hazardous and prominent example of toxic chromium. Although Cr (III) in trace amounts is required for sugar lipid metabolism whereas its absence will lead to chromium deficiency [3, 16].

1.2 Adsorption

Adsorption is the surface phenomenon in which accumulation of atoms or molecules take place on the surface of a material (liquid or solid phase). Adsorption has two components adsorbate and adsorbent. Adsorbate is the substance which gets adsorbed on surface (the molecules or atoms being accumulated). Adsorbent is a substance on which adsorption takes place (it is the solid, liquid, or gas phase onto which the adsorbate accumulates). In general adsorption is a removal process where certain particles are bound to an adsorbent particle surface by either physical or chemical attraction. The process of adsorption arises due to presence of unbalanced or residual forces that arise on the surface of material and these residual forces have tendency to attract and retain the atoms or species with which it comes in contact with a surface. The reverse of this process is called desorption.

The aim of study was to determine chromium removal efficiency from synthetic wastewater using adsorption technique and by using fly ash, cement and fly ash blended cement at different percentages (25, 50 and 75) as an adsorbent to determine chromium removal efficiency. Further analysis was conducted make an adsorption study using Langmuir and Freundlich isotherms.

2. MATERIALS AND METHODOLOGY

A.R. grade of chromium metal was used to prepare a stock solution of concentration of 1000μg/mL by dissolving 1.0000g of chromium metal in 50ml of concentrated hydrochloric acid and diluting it to 1 liter.

The adsorbents used in the present study is class F fly ash of 75 μm sieve size from BTPS (Bellary Thermal Power Station), 43 grade Ordinary Portland cement (Keshav cements) of 75 μm sieve size and different blends of fly ash with cement at different percentages (25, 50 and 75).

2.1 Batch mode adsorption experiment

The absorbance was determined by AAS (Atomic Absorption spectroscopy).15 ppm of chromium standard solution was taken in series of 30 ml glass vial then 1gm of the adsorbent was added to each of the vials and agitated at different time intervals of 20, 40, 60, 80, 100 and 120 min, respectively by keeping it in a rotor (30rpm).Once the agitation was completed for 20 min the solution was filtered using filter paper (Whatman filter paper 42).From the filtered solution 20ml was taken and used for analysis. Then the absorbance of chromium was measured at wavelength of 425.4 nm using AAS. The same procedure was carried out with different time intervals of 40 min, 60 min, 80 min, 100 min, 120 min, and different adsorbent type like fly ash, cement ,and 25% fly ash blended cement, 50% fly ash blended cement , 75% fly ash blended cement. To determine the amount of Cr (VI) ions adsorbed (q_e) in mgg-1 and for percentage removal following mass balance equations were used:

$$q_e = \frac{V(c_i - c_e)}{m}$$

$$Removal\ \% = \frac{100(c_i - c_e)}{c_i}$$

Where C_i and C_e are Cr (VI) ion concentration in mg/L before and after adsorption respectively, V is the volume of adsorbate solution in liter, m is the weight of the adsorbent in grams.

3. RESULTS AND DISCUSSIONS

The percentage removal of chromium at different time intervals (20 min, 40min, 80min, 100min, and 120min) using different adsorbents [Cement, Fly ash and Fly ash blended with cement at different percentages (25, 50 and 75)] having different initial concentrations in synthetic wastewater (15 ppm, 20 ppm, 25 ppm, 30 ppm and 35 ppm) with adsorbent dosage of 1gm was studied.

3.1 Effect of adsorbent materials and contact time

Fig.1 illustrate the experimental results on removal of chromium using different adsorbent (1 gm of dosage).The maximum removal efficiency for different adsorbent (fly ash, 25% fly ash blended cement, 50% fly ash blended cement, 75% fly ash blended cement and cement) at 120 minutes with 1gm dosage was 30.20%, 97.27%, 98.17%, 99.01%, 99.09%. The crystalline structure of cement helps in adsorption of chromium from wastewater and uptake of chromium ions by cement particles is due chemisorption and precipitation with alteration of crystal structure of cement. It can be observed that the removal efficiency of chromium increases with an increase in time this is because more the contact time better the efficiency.

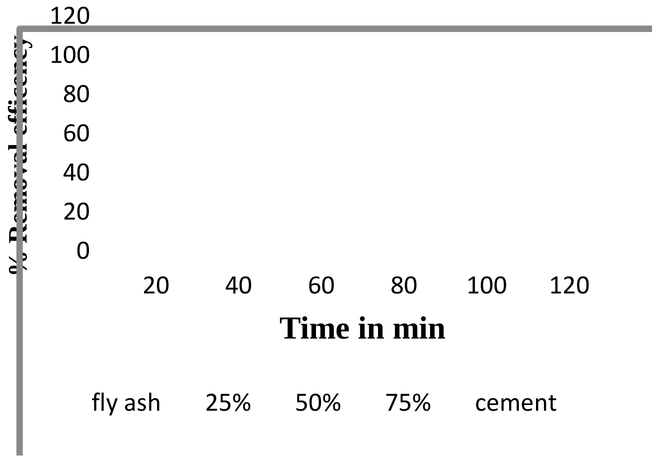

Fig -1: Percentage removal of chromium using different adsorbent

3.2 Effect of initial metal ion concentration

Fig 2 illustrates about percentage removal of chromium at different initial metal ion concentration. The reason that percentage removal decreases with increase in metal ion concentration might be due to the fact that adsorbents possess a limited number of active sites which becomes saturated at certain concentration. The reason might be that higher concentration provides necessary driving force to overcome the mass transfer resistance of Cr (VI) ion between the aqueous phase and solid phase.

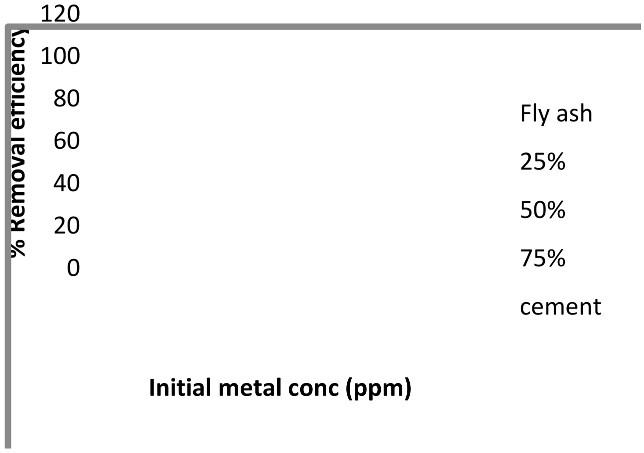

Fig -2: Percentage removal of chromium at different initial metal ion concentration

3.3 Adsorption Isotherms

Freundlich and Langmuir isotherm plot of chromium adsorption on 1 gm of Fly ash as an adsorbent dosage at different initial concentration (15 ppm, 20 ppm, 25 ppm, 30 ppm and 35 ppm) is as shown below.

3.3.1 Freundlich and Langmuir Isotherm Plot of Chromium Adsorption on Fly Ash

The coefficient of regression R^2 is found to be 0.992 and 0.994 for Freundlich and Langmuir isotherms, respectively. From the regression coefficients, it can be said that both Freundlich and Langmuir isotherms fits well.

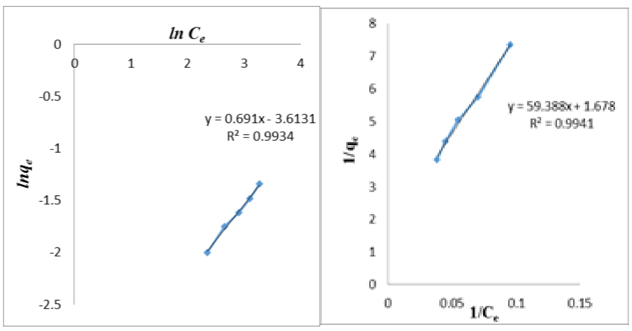

Fig -3: Freundlich and Langmuir isotherm plot of chromium adsorption on Fly ash

3.3.2 Freundlich and Langmuir Isotherm Plot of Chromium Adsorption on 25% Fly ash blended cement

The coefficient of regression R^2 is found to be 0.965 and 0.874 for Freundlich and Langmuir isotherms, respectively. From the regression coefficients, it can be said that Freundlich isotherms is the best fit out of two.

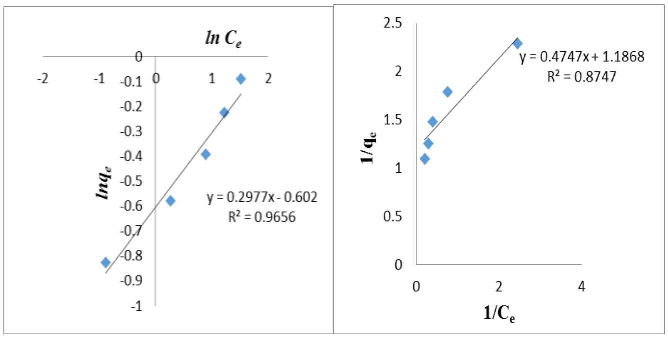

Fig -3: Freundlich and Langmuir isotherm plot of chromium adsorption on 25% fly ash blended cement

3.3.3 Freundlich and Langmuir Isotherm Plot of Chromium Adsorption on 50% Fly ash blended cement

The coefficient of regression R^2 is found to be 0.961 and 0.845 for Freundlich and Langmuir isotherms, respectively. From the regression coefficients, it can be said that Freundlich isotherms is the best fit out of two.

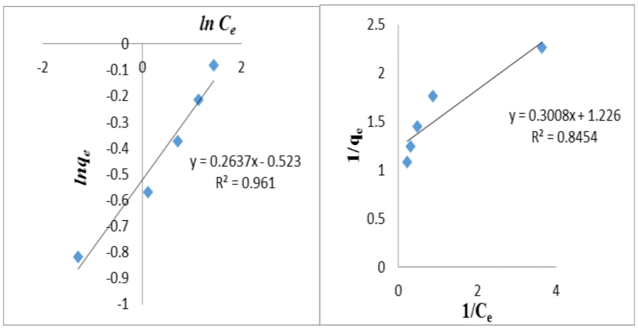

Fig -4: Freundlich and Langmuir isotherm plot of chromium adsorption on 50% Fly ash blended cement

3.3.4 Freundlich and Langmuir Isotherm Plot of Chromium Adsorption on 75% Fly ash blended cement

The coefficient of regression R^2 is found to be 0.942 and 0.803 for Freundlich and Langmuir isotherms, respectively. From the regression coefficients, it can be said that Freundlich isotherms is the best fit out of two.

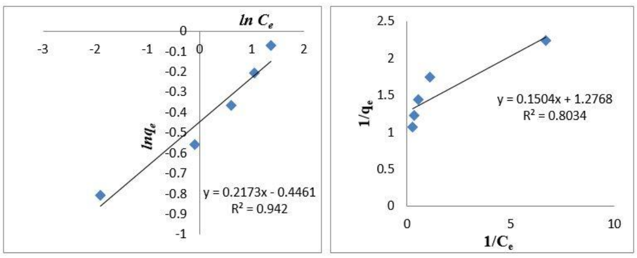

Fig -5: Freundlich and Langmuir isotherm plot of chromium adsorption on 75% Fly ash blended cement

3.3.5 Freundlich and Langmuir Isotherm Plot of Chromium Adsorption Cement

The coefficient of regression R^2 is found to be 0.969 and 0.841 for Freundlich and Langmuir isotherms, respectively. From the regression coefficients, it can be said that Freundlich isotherms is the best fit out of two.

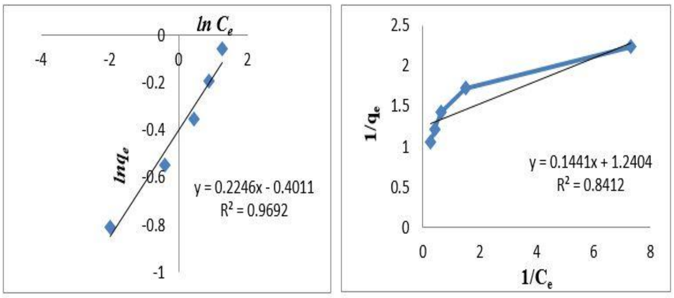

Fig -5: Freundlich and Langmiur isotherm plot of chromium adsorption on cement

3.4 Fitted isotherm parameters for all adsorbents

The comparative results on the fitted isotherms using Freundlich isotherm and Langmuir isotherm are presented in Tables 1 and 2 with different adsorbents and different initial concentration at 120 minutes. The Tables indicate that the Freundlich Isotherm better results as compared with Langmuir Isotherm giving higher correlation coefficient value (R2~ 0.9). In all the previous investigations, Freundlich Isotherm was found to be more promising than Langmuir Isotherm.

Table -1: Fitted Freundlich Isotherm parameters using 1gm of different adsorbents

Adsorbent	n	K	R^2
Fly Ash	0.1449	0.0340	0.992
25% blended	3.367	0.5477	0.965
50% blended	3.802	0.593	0.961
75% blended	4.61	0.640	0.942
Cement	4.464	0.67	0.969

Table -2: Fitted Langmuir Isotherm parameters using 1gm of different adsorbents

Adsorbent	Q_0	b	R^2
Fly Ash	0.595	0.028	0.994
25% blended	0.643	3.28	0.874
50% blended	0.715	4.66	0.845
75% blended	0.784	8.51	0.803
Cement	0.801	8.611	0.841

4. CONCLUSIONS

1. Low cost adsorbents used in the present study shows a great potential for the elimination of heavy metals from wastewater.
2. The use of commercially available activated carbon for the removal of the heavy metals can be replaced by the utilization of inexpensive, effective and readily available byproducts as adsorbents.
3. The removal efficiency is higher when it is blended with cement because the crystalline structure of cement helps in adsorption of chromium from wastewater and uptake of chromium ions by cement particles.
4. The decrease in percentage removal with an increase in metal ion concentration might be due to the fact that adsorbents possess a limited number of active sites which becomes saturated at certain concentration
5. The Freundlich isotherm gave the best fit compared to the Langmuir isotherm.
6. By blending the fly ash with 25% cement by weight gave good removal efficiency of about 97.27%. Hence this fly ash can be used for removal of chromium effectively which in turn solve the disposal problem of fly ash

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