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A comparative study of Fly ash and Na-fly ash as adsorbents for removal of Cr (VI), Cu (II) and Fe (II) from aqueous solutions

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***Abstract:** Removal of Cr (VI), Cu (II) and Fe (II) from aqueous solutions has been studied using fly ash (FA) and Na-fly ash (Na-FA) as adsorbents. The process of adsorption has been established to be dependent on the concentration of the metal ions, time of contact, the dosage of adsorbent and on temperature. The adsorptive behaviour has been found to fit in Freundlich adsorption isotherm. Ion exchange and complexation at the surface are the major mechanisms involved in the removal of metal ions from aqueous solution. Na-fly ash is found to have better adsorption capacity than FA which is attributed to the increased content of Na ions on the surface which is readily available for exchange with metal ions. The observed results indicate that Na-FA has excellent adsorption capacity compared to FA and can be used as a potential cost-effective adsorbent for removal of heavy metal ions from industrial effluents.*

***Keywords:** Fly Ash, Heavy Metal Ions, Waste Water, Adsorption, Batch Adsorption Experiments, Na-Fly Ash.*

I. INTRODUCTION

Adsorption from liquid phase has been established to be an efficient technique for the removal of heavy metal ions and organic compounds owing to its simplicity, the cost of adsorption and due to the availability of wide range of adsorbents. High-cost adsorbents do not offer the advantage of reusability which leads attention towards reversible adsorption. Cost effective adsorbents like fly ash [1], saw dust [2], carbonized bark [3], bottom ash [4], rice husk [5], clay [6] and graphite [7] have been established for their effectiveness to remove organic compounds from waste water. Fly ash, a waste generated from coal- based thermal power plants has been proved as a natural adsorbent for removal of heavy metal ions and organic entities from aqueous solutions. Adsorbents are activated by powdering and removing the gases that occupy the pores of the adsorbent by heat treatment. Fly ash is activated by calcination or by alkali treatment to improve its capacity to adsorb metal ions [8].

Fly ash, a residue generated during the combustion of coal comprises of fine particles that rise up along with flue gases. It is collected from the electrostatic precipitators before the flue gases reach the chimneys of coal-fired power plants. The composition of fly ash varies depending on the source and makeup of the coal being burned. In general, fly ash contains SiO_2, Al_2O_3, Na_2O, TiO_2, and CaO [9]. Fly ash is related to several health hazards and it has become mandatory to look into the safe disposal of fly ash. Owing to the environmental hazards related to the disposal of fly ash in landfills, utilization of fly ash has gained attention. Fly ash is used in the production of hydraulic cement, hydraulic plaster, fertilizers, detergents, filling material and so on [10].

The presence of Cr (VI) in aqueous solutions is carcinogenic and may lead to several health hazards including liver problems and hemolysis [11]. Copper poisoning leads to cancer, heart disease, anorexia, anemia and anxiety [12]. Iron poisoning may cause fatigue and dizziness [13]. Removal of heavy metal ions from industrial waste water is of environmental significance. The heavy metal ions in aqueous solutions are non-degradable and can accumulate in tissues which are associated with serious health issues. Through ion exchange resins play a significant role in the removal of heavy metal ions from solution, adsorption using cost-effective adsorbents like Alma dust [14], rice husk [15], mango seeds [16], etc. facilitates the removal of heavy metal ions from industrial waste waters. Aiming at this cost-effective adsorption technique, this work focusses on the use of fly ash and Na-fly ash as adsorbents for the removal of heavy metal ions from aqueous solutions. Batch adsorption experiments were carried out to optimize the effect of contact time, adsorbent dosage, temperature, and concentration on the extent of adsorption.

II. EXPERIMENTAL

A. Materials and methods

Fly ash used for the study was collected from the electrostatic precipitators of Tuticorin Thermal Power Station. $K_2Cr_2O_7$ (Assay 99.5%), FAS (Assay 99.0%) and $CuSO_4.5H_2O$ (Assay 98.5%) of AR grade manufactured by NICE chemicals were used for preparing the required stock solutions in double distilled water. Batch adsorption experiments were carried out in a mechanical shaker manufactured by Supreme Scientific Company, Madurai for the stipulated time and to enable attainment of equilibrium. LR grade NaOH manufactured by NICE Chemicals was used for preparing Na-fly ash. NH_4OH, KI, con HCl, did. H_2SO_4, $KMnO_4$, sodium thio sulphate solution and Starch of AR grade (Assay 99.5%) manufactured by NICE Chemicals were used for estimating the metal ions quantitatively by iodometric experiments.

B. Preparation of adsorbents

The soluble compounds including K_2O, Na_2O, MgO and CaO in fly ash were removed by stirring it with double distilled water for 48 h at room temperature. It has a high heterogeneity in surface charge which limits its absorption ability. To obtain an optimum surface charge, fly ash was treated with a calculated quantity of 3.5 N NaOH maintained at 110°C in an air oven for 24 hours. The resultant Na-fly ash was washed repeatedly with distilled water, filtered and dried at 110°C for 1 hour in an air oven till constancy in weight is achieved.

C. Batch adsorption experiments

0.1M stock solution of Cr(VI), Cu(II) and Fe(II) were prepared in double distilled water and treated with 1g of coal fly ash in corning bottles and shaken mechanically for a calculated time (30 to 180 minutes) to study the time taken for the attainment of equilibrium. After the stipulated time, it was filtered through a Whatmann No: 40 filter paper and the concentration of unadsorbed Cr(VI) and Cu(II) ions in the filtrate was estimated iodometric ally using standard sodium thio sulphate solution. The concentration of Fe(II) was estimated per manganometric ally. The extent of adsorption of heavy metal ions is calculated using

$$\% \text{ adsorption} = \frac{c_i - c_{eq}}{c_i} \times 100$$

Where c_i and c_{eq} represent the initial concentration and concentration after attainment of equilibrium respectively. The same experiment was carried out using 1g of Na-fly ash as an adsorbent to study the effect of contact time on the extent of adsorption. The extent of removal of heavy metal ions by fly ash and Na-fly ash was studied by varying adsorption parameters such as dosage of adsorbent (1-5 g), the dosage of adsorbate (0.005 – 0.30 M) and temperature (30 – 70^{0}C).

III.RESULTS AND DISCUSSION

A. Effect of contact time:

The time taken for the attainment of equilibrium is an important parameter to be studied as it optimises the time of contact with the adsorbent in waste water treatment. A comparative study of fly ash (FA) and Na-fly ash (Na-FA) for the removal of Cr(VI) shows that equilibrium is attained at 120 minutes. An increase in the % of adsorption increases with contact time as it facilitates more metal ions to occupy the sites of the adsorbent. After the attainment of equilibrium, a further increase in contact time does not show any effect on the extent of adsorption as all the available sites are saturated with heavy metal ions [17]. The extent of removal of metal ions has increased drastically in the case of Na-FA. Adsorption equilibrium for removal of Cu(II) was attained at 150 min for FA and 120 min for Na-FA. Fig. 1 shows the variation in the extent of removal of metal ions with contact time for FA and Na-FA.

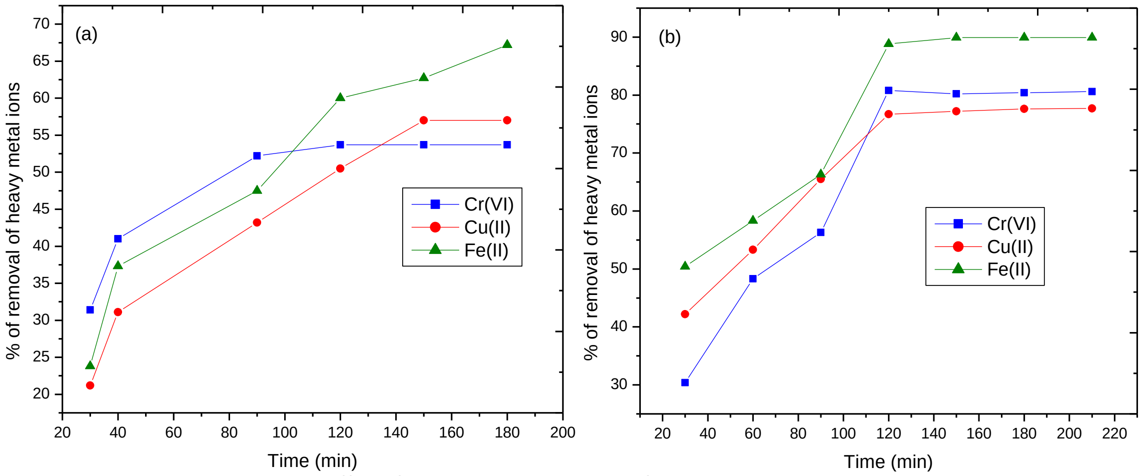

Fig. 1 Effect of contact time on removal of heavy metal ions by (a) FA and (b) Na-FA

B. Effect of adsorbent dosage

Fig. 2 shows the effect of adsorbent dosage on the removal of Cr(VI), Cu(II) and Fe(II). On increasing the dosage of adsorbent, a linear increase in the extent of removal of heavy metal ions has been observed. Increasing the mass of the adsorbent increases its surface area, which in turn increases the number of available sites for adsorption [18]. The same trend has been observed for the removal of Cr(VI), Cu(II) and Fe(II) by FA and Na-FA. However, Na-FA shows a higher adsorption capacity than FA.

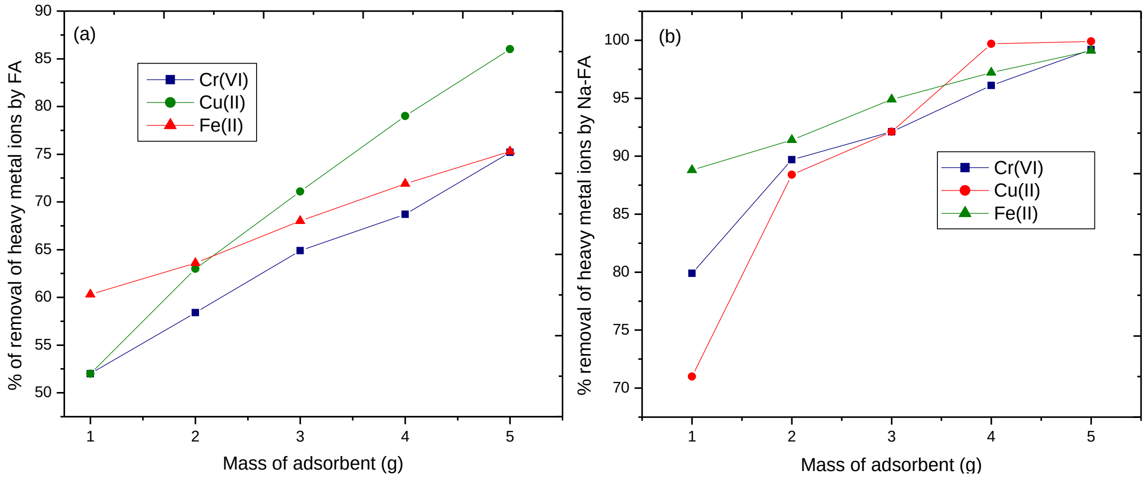

Fig. 2 Effect of adsorbent dosage on removal of heavy metal ions by (a) FA and (b) Na-FA

C. Effect of temperature

A linear increase in the extent of adsorption is observed in fig. 3 with an increase in temperature. This shows a strong interaction between the adsorbent and Cr(VI) ions. If the adsorbate is held to the adsorbent by weak Vander Waals force, an increase in temperature would destroy the force of attraction and a decrease in the extent of adsorption should be observed [19]. Hence, an increase in the extent of adsorption indicates strong affinity between the adsorbent and adsorbate.

D. Effect of concentration of metal ion

The variation in the extent of adsorption with an increase in the concentration of the adsorbate metal ions has been studied with FA and Na-FA and the results are presented in fig. 4. An increase in the metal ion concentration increases the extent of absorption in the case of FA and Na- FA. On increasing the concentration of the metal ion, more adsorbate molecules are available for adsorption to the sites of the adsorbent and thus an increase is observed [20].

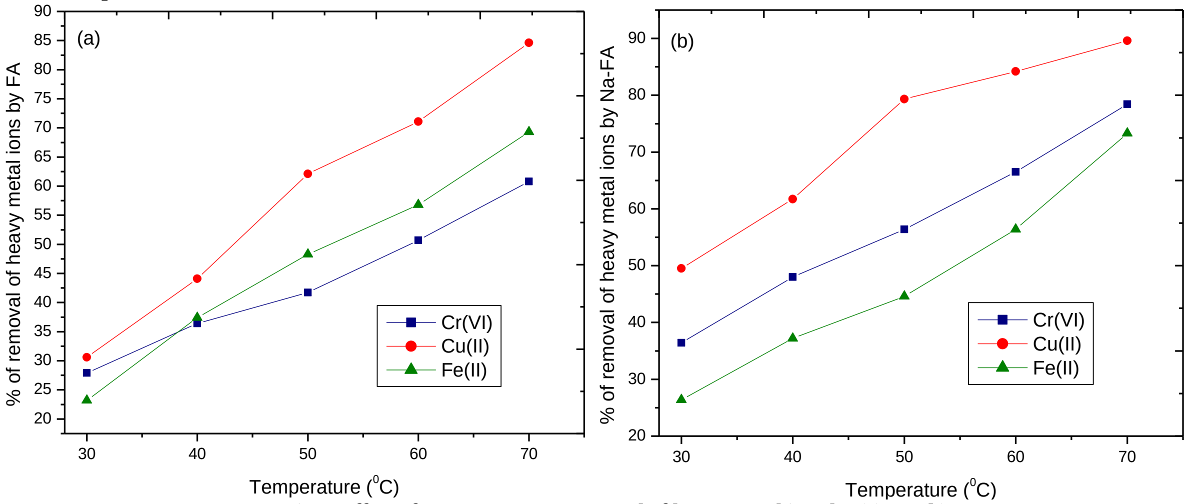

Fig. 3 Effect of temperature on removal of heavy metal ions by (a) FA (b) Na-FA

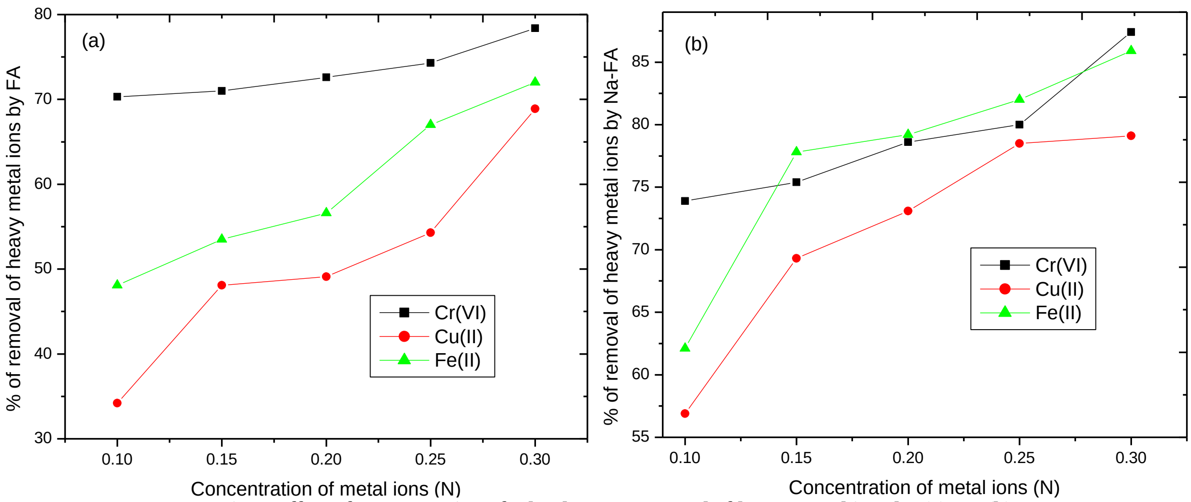

Fig. 4 Effect of concentration of adsorbate on removal of heavy metal ions by (a) FA (b) Na-FA

E. Freundlich adsorption isotherm

The concentration of the metal ion has been varied and the extent of removal of metal ion from its aqueous solution has been studied and the data have been found to fit with Freundlich adsorption isotherm.

$$\frac{x}{m} = kc^{1/n}{}_{eq}$$

Where x and m represent the masses of the adsorbate and adsorbent respectively. C_{eq} represents the equilibrium concentration. k and n are constants for a given adsorbate and adsorbent at a particular temperature. Fig. 5 and fig. 6 show the Freundlich adsorption isotherms for adsorption of Cr(VI) on FA and Na-FA, and Cu(II) and Fe(II) on FA. The results show that the data fit into the Freundlich isotherm.

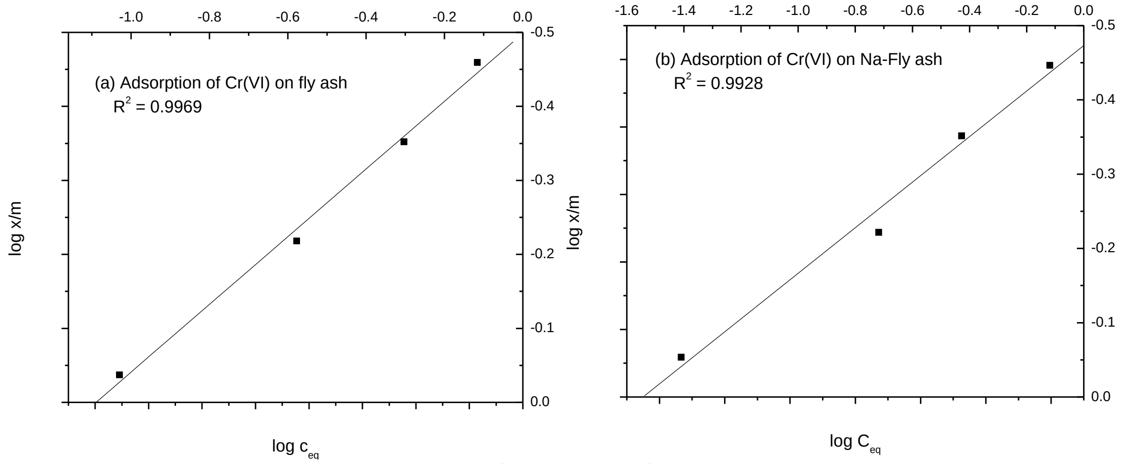

Fig. 5 Freundlich adsorption isotherm for adsorption of Cr(VI) on Na-FA and FA

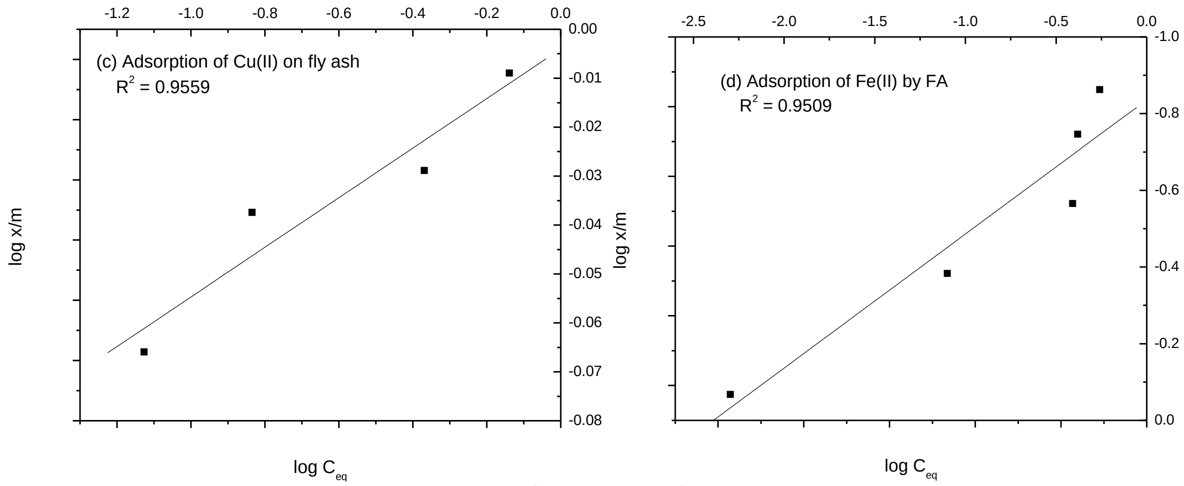

Fig. 6 Freundlich adsorption isotherm for adsorption of Cu (II) and Fe(II) on FA

IV. CONCLUSIONS

Fly ash is a waste that is generated in coal-fired power plants which are a cheap and effective adsorbent for the removal of heavy metal ions from aqueous solutions without any pre-treatment. The different parameters that affect the extent of adsorption have been monitored. Fly ash has been modified by treatment with sodium hydroxide to improve its capacity of adsorption. A comparative study of adsorption of heavy metal ions in aqueous solutions using FA and Na-FA as adsorbents indicates that sodium treatment has drastically improved the adsorption capacity of Na-FA due to the extensive distribution of sodium ions on the surface of the adsorbent which can facilitate removal of heavy metal ions from aqueous solution.

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