



Development of adsorbent from fly ash and study their behaviour with $K_2Cr_2O_7$ and methyl red solution

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ABSTRACT

The present environmental concerns over fly ash disposal have sparked interest in its conversion to value added product such as adsorbent. Fly ash derived from coal residues has a potential for conversion to adsorbent. Still more remarkable is the subsequent utilization of these adsorbent synthesized from fly ash as adsorbent for removal of dye and heavy metals in the industry. In the present study the coal based fly ash was used to synthesis adsorbent by alkali fusion, followed by hydrothermal treatment. The synthesis is carried out by thermal method with a temperature of $550^{\circ}C$. Based on adsorption batch studies it can be concluded that the adsorbent developed in the present study is fairly effective in the removal of Methyl Red and $K_2Cr_2O_7$ solution.

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Introduction

Fly Ash

The process of coal combustion results in fly ash. Fly ash is one of the numerous substances that cause air, water and soil pollution, disrupt ecological cycles and set off environmental hazards. The high temperature of burning coal turns the clay minerals present in the coal powder into fused fine particles mainly comprising aluminum silicate. The problem with fly ash lies in the fact that not only does its disposal require large quantities of land, water, and energy, its fine particles, if not managed well, by virtue of their weightlessness, can become airborne. Nearly 73% of India's total installed power generation capacity is thermal, 90% of it coal-based. Such a high amount of fly ash is produced in the country which is hazardous for the environment. Cement and concrete manufacturing consumes most of the coal fly ash (CFA) produced. Adsorbent synthesized from CFA is a minor but interesting product, with high environmental applications. Adsorbent may be easily obtained from CFA by relatively cheap and fast conversion processes. This paper provides an overview on the method for adsorbent synthesis from CFA, and a detailed description of conventional alkaline conversion processes.

In addition to the uses of CFA are as follows :

- 1) Additives for immobilization of industrial and water treatment wastes,
- 2) Extraction of valuable metals, such as Al, Si, Fe, Ge, Ga, V, Ni .
- 3) Land stabilization in mining areas.
- 4) Sorbents for flue gas desulfurization.
- 5) Fire-proof materials. "slash" (fly ash/sludge blend) production for soil amendment.
- 6) Filter material for the production of different products.
- 7) Ceramic applications.
- 8) Synthesis of high cation exchange capacity (CEC) zeolites.

Disadvantages of Cr and dye in water

At many sites around the nation, heavy metals have been mined, smelted, or used in other industrial processes. The waste (tailings, smelter slag, etc.) has sometimes been left behind to pollute surface and ground water. The heavy metals most frequently encountered in this waste include Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, and Zinc, all of which pose risks for human health and the environment. Chromium is a heavy metal which is used mainly in metal industry, tanning industry, refineries. Hexavalent chromium in industrial wastewaters mainly originates from tanning and painting. Chromium compounds are applied as pigments, and 90% of the leather is tanned by means of chromium compounds. Wastewater usually contains about 5 ppm of chromium. Chromium may be applied as a catalyser, in wood impregnation, in audio and video production and in lasers. Chromite is the starting product for inflammable material and chemical production.

Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient. In nuclear fission the ^{51}Cr isotope is released, and this can be applied for medical purposes.

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) and Cr(VI) (hexavalent chromium) are of main biological relevance

Hexavalent chromium is known for its negative health and environmental impact, and its extreme toxicity. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as trivalent chromium. Health effects related to hexavalent chromium exposure include diarrhoea, stomach and intestinal bleedings, cramps, and liver and kidney damage. Hexavalent chromium is mutagenic. Toxic effects may be passed on to children through the placenta.

Chromium (VI) oxide is a strong oxidant

In various industries, the activities involving dyeing generate problems due to the discharge of toxic effluents,

originating from the by products generated. If not treated properly before being discharged into natural water bodies, the effluent from this industry may reach potable, water resources, causing serious ecological concern. Therefore, the development of new technologies for the removal of color from industrial effluents has received a lot attention over the past few years, partly driven by an increasing environmental awareness.

Adsorption has been used successfully in the removal of color from effluents. Due to its high cost and considering the enormous quantity of effluent produced by textile industries, researches are turning toward the use of alternative adsorbents, also called non-conventional low-cost adsorbents. Industries like plastic, paper, textile and cosmetics use dyes to colour their products. These dyes are common water pollutants and they may be frequently found in trace quantities in industrial waste water. Their presence in water, even at very low concentrations, is highly visible and undesirable. When these colored effluents enter rivers or any surface water system they upset biological activity. Ground-water systems are also affected by these pollutants because of leaching from the soil. In addition, many dyes are difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems such as allergic dermatitis, skin irritation, cancer and mutation. In the past a number of conventional biological treatment processes have been used which were not effective, some of which include coagulation and chemical oxidation, membrane separation process, electrochemical, reverse osmosis and aerobic and anaerobic microbial degradation but all these methods suffer from one or more limitations and none of them were successful for the complete removal of dye.

Dyes are chemicals, which on binding with a material will give color to them. Dyes are ionic, aromatic organic compounds with structures including aryl rings, which have delocalized electron systems. The color of dye provided by the presence of a chromophore group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons.

Experimental method

The adsorbent were synthesized from fly ash (collected from Khaperkheda Thermal Power Plant) using hydrothermal treatment. Sodium Hydroxide and Hydrochloric acid and different dyes such as Methyl Red, $K_2Cr_2O_7$, NaOH, were procured from Stores Department of Laxminarayan Institute of Technology. All reagents were analytically pure (99%) and used without purification. The fly ash samples contained both amorphous (mainly SiO_2 , Al_2O_3) and crystalline components (mainly quartz and mullite).

Equipment used

Colorimeter
Hot air oven & crucible
Electronic weighing balance
Muffle furnace

Preparation of adsorbent

Preparation of Adsorbent from Fly ash

Fly ash was procured from thermal power plant of Khaperkheda. It is washed with distilled water to remove water soluble impurities and further it is treated with dilute HCl to remove the acid soluble impurities, Again it is washed with distilled water this is the raw fly ash. It is further mixed with NaOH solid powder in a plastic bottle. The weight ratio of fly ash to NaOH powder was 1:1.2. After making the mixture homogeneous the mixture is poured in crucible and heated at $550^\circ C$ in furnace for 1hr. To avoid contamination of the powders by the chemical reaction of crucible the inert material

crucible is preferred. The fused fly ash is Ground in a mortar and pestle and poured in a plastic bottle followed by the addition of distilled water. The weight ratio of fused fly ash powder to water was 0.2. The mixture was aged 1 day with stirring at room temperature and ambient pressure. Further the fly ash is several times washed with hot distilled water to remove free NaOH. After the treatment, the adsorbent is filtered and dried in a dryer at $80^\circ C$ in air for 12hr.

Preparation of methyl red solution

In a clean beaker 400 ml Distilled water is heated, in this boiling water 0.8 gm Methyl Red powder (i.e. 2gm/lit) added with constant stirring .The solution is allowed to boil for 5 minute and cooled, then filter the cooled solution to remove suspended matter and undissolved matter .The clear solution is collected and store in beaker for further use. The various reducing concentrations of Methyl Red solution are calibrated on colorimeter to study effect of adsorbent on the solution.

Preparation of $K_2Cr_2O_7$ solution

In a clean beaker 1000 ml Distilled water is heated, in this boiling water 4.528 gm $K_2Cr_2O_7$ powder added with constant stirring. The solution is allowed to boil for 5 minute and cooled, then filter the cooled solution to remove suspended matter and undissolved matter. The clear solution is collected and store in beaker for further use. The various reducing concentrations of $K_2Cr_2O_7$ solution are calibrated on colorimeter to study effect of adsorbent on the solution.

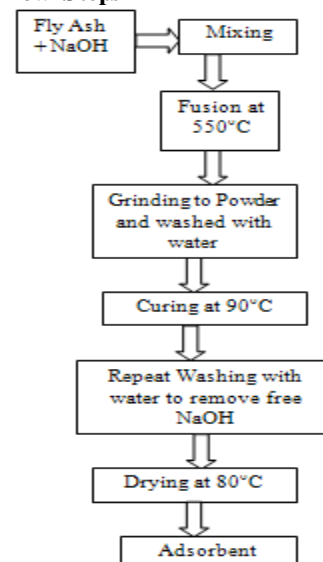
Batch Studies of Fly ash:

The fly ash samples are taken and put in dryer for about 30 minutes. After the sample is dried, the various samples are weighted ranges from 0.2 gms to 4 gms and are placed in the conical flask with the various laboratory prepared solutions. The batch studies are performed as 100 ml of solution is taken in a conical flask and different weight dosages of adsorbents are contracted for about 2 hours with constant stirring. After 2 hrs the resultant sample is filtered and the reacted fly ash is collected and the filtered samples of $K_2Cr_2O_7$ and Methyl Red solution are further investigated in the colorimeter.

Colorimeter reading

The collected solution after the experiment is used for calculating percentage adsorption. At first the reading for water is taken this is blank reading. Then colorimeter reading taken for all sample solution. This is reference reading same procedure repeated for $K_2Cr_2O_7$ solution. The colorimeter optical density mode is set for 0.0 for the pure water and 100 for opaque the corresponding values of the % transitivity's are 100 and 0.

Experimental Flow Steps



Results and Discussion

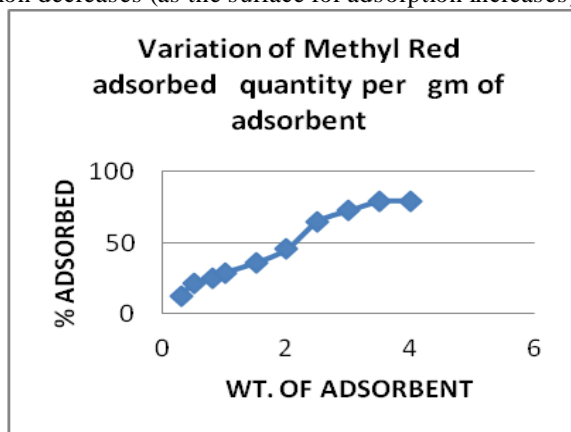
1. Calculation of Surface Area: The Surface Area is found to be $217\text{m}^2/\text{gram}$.

2. Colorimeter Readings of Batch studies with Adsorbent of Methyl Red Solution

The solution of Methyl red after adsorption shows following colorimeter reading using various amounts of adsorbent.

Sr. No	Weight in gms of Adsorbent	Methyl Red Solution	Final (gm/lit)
1	0.3	100 ml	1.75
2	0.5	100 ml	1.56
3	0.8	100 ml	1.5
4	1	100 ml	1.42
5	1.5	100 ml	1.28
6	2	100 ml	1.09
7	2.5	100 ml	0.7
8	3	100 ml	0.55
9	3.5	100 ml	0.42
10	4	100 ml	0.41

The fig. shows the behaviour of amount of adsorbent and the concentration of solution. It can be concluded that as the amount of adsorbent applied increases the concentration of resultant solution decreases (as the surface for adsorption increases).



Colorimeter Readings of Batch studies with Adsorbent of $\text{K}_2\text{Cr}_2\text{O}_7$ Solution

The solution of $\text{K}_2\text{Cr}_2\text{O}_7$ after adsorption shows following colorimeter reading using various amounts of adsorbent.

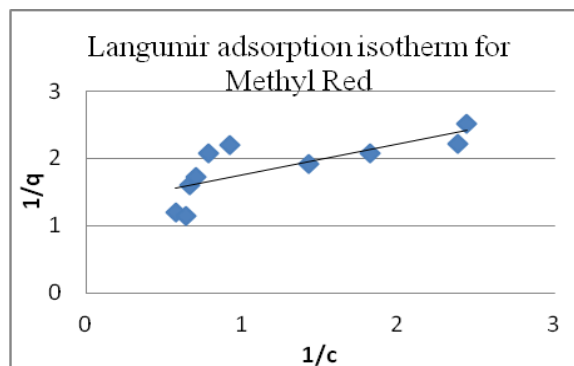
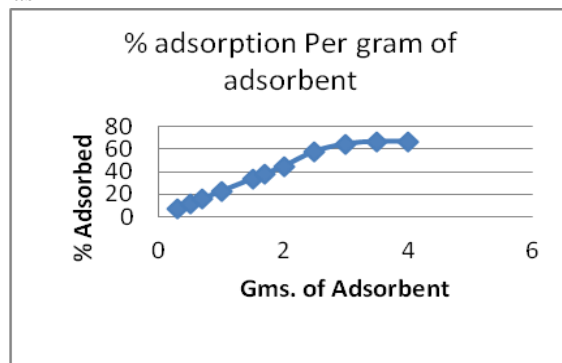
Sr. No.	Weight in gms of Adsorbent	Chromium Solution volume	Final (gm/lit)
1	0.3	100 ml	4.21
2	0.5	100 ml	4
3	0.7	100 ml	3.8
4	1	100 ml	3.5
5	1.5	100 ml	3
6	1.7	100 ml	2.8
7	2	100 ml	2.5
8	2.5	100 ml	1.9
9	3	100 ml	1.6
10	3.5	100 ml	1.5

The fig. shows the behaviour of amount of adsorbent and the concentration of solution. It can be concluded that as the amount of adsorbent applied increases the concentration of resultant solution decreases (as the surface for adsorption increases).

Langumir Adsorption Isotherm equation for Methyl Red Solution:

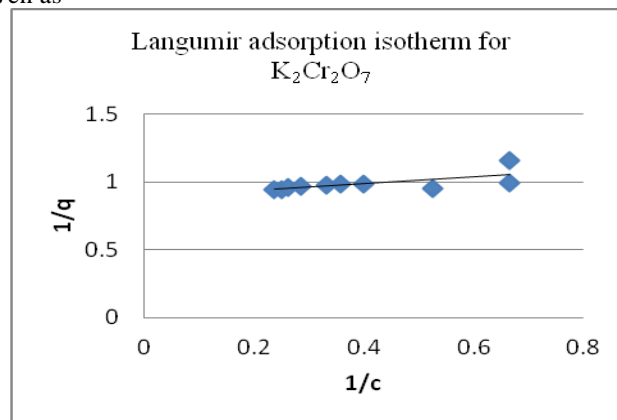
Langumir isotherm is used for fitting the experimental data in adsorption studies to understand the extent and degree of favourability of adsorption. The isotherm depend upon

temperature and the constants each in the general form can be given as



Langumir Adsorption Isotherm equation for $\text{K}_2\text{Cr}_2\text{O}_7$ Solution:

Langumir isotherm is used for fitting the experimental data in adsorption studies to understand the extent and degree of favourability of adsorption. The isotherm depend upon temperature and the constants each in the general form can be given as



The equation for Langumir Isotherm for the adsorption of $\text{K}_2\text{Cr}_2\text{O}_7$ is

$$(1/q) = 0.9 + (0.625 / c)$$

The Langumir Adsorption Isotherm is found to fitted to Methyl red and $\text{K}_2\text{Cr}_2\text{O}_7$ data sets

Conclusion:

Adsorbent is developed from fly ash by alkali fusion, followed by hydrothermal treatment. The main crystalline phase of fly ash is converted into different types of adsorbent by suitable treatment condition. The properties of adsorbent material formed strongly depended upon the treatment conditions and composition of the raw materials. Adsorbent of varying surface area, silica/alumina ratio and crystallinity may be obtained by changing the reaction parameters such as aging time, fusion temperature and fly ash/NaOH ratio. The cost of the developed adsorbent is low as compared to commercial adsorbents.

The present study showed that the coal fly ash based adsorbents were effective in removing heavy metal ion Chromium and Methyl Red solution from aqueous solutions. It showed that the selectivity sequence of metal ions by the adsorbents was dependent on the system employed, and was mainly dependent on the initial concentrations of the metal ions.

The Langmuir Adsorption Isotherm is found to fit in the data points for the adsorption of Chromium and Methyl Red.

The developed adsorbent can be applied to waste water treatment and ion exchange applications. This work therefore shall be very much useful to synthesis adsorbent at low cost and apply it to commercially important fields.

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