Optimization and utilization of Fly ash and Orange peels for removal of safranin from aqueous solution

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***Abstract*: The present paper focuses on developing a method using combination of low cost adsorbents such as fly ash and orange peels for removal of safranin from water bodies. Parameters such as dye concentration, adsorbent dosage, pH, and temperature and contact time were optimized for adsorption using fly ash as well as the combination of both fly ash and orange peels. The experimental data showed that fly ash is a very promising adsorbent for dye removal from aqueous solution. Fly ash alone removes 83.17% dye from water. When the orange peels were added to it, the effect of adsorption was enhanced and percent removal increased to 87.94%.**

***Keywords:* Adsorption, Fly ash, Optimization, Orange peels.**

I. INTRODUCTION

Dyes are used in many industries, such as food, paper, carpet, rubber, plastics, cosmetics, and textile, in order to color their products [1]. The textile industry is one of the largest manufacturing industries. In every stage of textile industry various types of dyes are used to color their products. The dye containing wastewater is usually released directly into the nearby drains, rivers, stagnant, ponds or lagoons. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic eco-system and the biodiversity of environment [2]. Treatment of dye effluent is a major challenge, because wastewater can be complex. Not all dye effluents are the same and there is a large variety of substances present in them. In recent years there is a major focus on using low cost materials as adsorbent for the removal of various industrial dye effluents from water bodies. However, research interest into production of newer economical, easily available and highly efficient adsorbents are still under development. Common ways of wastewater treatment include adsorption, sedimentation, chemical analysis, chemicoagulation, biological methods, and advanced oxidation procedures [3]. However, these approaches are not without their disadvantages. In some of the situations various methods of separation are combined for complete removal of contaminants from wastewater. Adsorption has been extensively used in industrial processes for separation and purification. Commercially available activated carbon is frequently used for removal of dyes but it remains an expensive material. If a sorbent is inexpensive and ready for use, the adsorption process will be a promising technology. Therefore, adsorption became one of the most important technique for removal of dyes from the water bodies. There are various cheapest source of adsorbents available. The cheapest sources of preparing adsorbents include sewage treatment plant biosolids (sludge) [4], magnetically modified brewer's yeast [5], cassava peel activated carbon [9], tapioca peel activated carbon [5], soil, fly ash [6], jack fruit peel activated carbon [7], groundnut shell activated carbon activated with Zinc chloride solution [8], neem leaf powder [9], kaolinite , montmorillonite , hazelnut activated carbon [10], bagasse pith , natural clay, maize cob, orange peels [11], rice bran based activated carbon [12], guava seeds activated with Zinc chloride solution followed by pyrolysis [13],etc. Throughout the world, much research is being conducted on the use of waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilization of waste materials in new products for other applications rather than disposal in a landfill. In recent years, utilization of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit [14]. Coal is the major source of energy in India and nearly hundred million metric tons of fly ash is generated annually by burning of coal from factories and several thermal power plants. Hence, the disposal of such a huge quantity of fly ash is the major environmental concern. Ash produced from such factories and thermal power plants is dumped in landfills and ash ponds. Due to the shortage of landfill sites, increasing costs of the land and strict environmental regulations, the disposal of fly ash has become a major issue. This also creates many environmental hazards if not managed well and causes soil pollution and ground water pollution [15]. Fly ash is one of the solid wastes largely produced from power generation. Currently, its applications are only limited to civil engineering including cement and brick production and as a filling in road works. Research is therefore needed to develop new alternative environmental friendly applications that can further exploit fly ash. Recently, various kinds of fly ash have been used as low-cost sorbents for removal of heavy metals, organics and dyes from waters. Most efforts are focused on the research of adsorption property. However, an applicability of the fly ashes for the water treatment depends strongly on their origin and few research has been attempted to improve the adsorption capacity [16].

The effectiveness of orange peels is studied by various researchers in removal of dyes using its adsorption property. The agribusiness sector has increasingly grown to meet the increase in demand for food because of growing population. It contributes substantially to the generation of waste resulting from the production processes. These residues, apparently without viable application, may result in various environmental adversities due to improper disposal. Another alternative for reusing of

such orange peel waste is its conversion for use as an adsorbent material from the contaminants. Studies have shown that the activated carbon adsorption efficiency of contaminants like phenolic compounds in aqueous solution and toxic metals could be seen today as the most widely used material, despite its high cost. Therefore, the production of adsorbent materials from industrial residues, with the possibility of obtaining commercially activated carbon substitution has been studied, such as orange waste and other materials [17]. Safranin was selected as the target dye contaminant because of its wide use in dyestuff industries. The adsorption characteristics of target contaminant safranin and its removal from aqueous solution by the combination of two adsorbents and also comparative study was investigated to check the results using only fly ash and combination of fly ash with orange peels.

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II. MATERIALS AND METHODS:

Adsorbents collection and preparation:

1. Fly ash collected from Thermal Power Plant (FA): Fly ash was sieved through ASTM 45 mesh, treated with distilled water to remove all adhering dust particles and organic matter, dried in an oven at 110^{0}C and stored in labelled polyethylene terephthalate (PET) bottles at room temperature.
2. Orange peels collected from local juice centre (OP): Orange peels were shade dried, grounded and stored in labelled polyethylene terephthalate (PET) bottles at room temperature.

Adsorbate preparation:

A cationic dye viz, Safranin was procured from Molychem, India. A stock solution of 1000 mgL^{-1} was prepared using distilled water as diluent and various concentrations were made by diluting the stock solution with suitable volume of distilled water. All the reagents used were of analytical grade.

Batch adsorption study:

To analyze adsorption property of fly ash and combination of fly ash and orange peels, a representative batch adsorption study was performed by considering safranin dye as an adsorbate. The parameters such as dye concentration, amount of adsorbent, pH, temperature and contact time were optimized for fly ash and combination of fly ash and orange peels using the One-Factor At A-Time approach. Known amount of adsorbents with 25 cm^3 of known concentration of dye solution was taken in 50 cm^3 of Erlenmeyer flasks. These flasks were agitated in orbital shaker. (Scigenics Biotech ORBITEK Model number: 400LJ6). The pH of the solution was adjusted by 0.1 N NaOH or HCl. Once the equilibrium was established, supernatant liquid was filtered off using Whatman filter paper no. 41 and the filtrates were analyzed for the residual (unadsorbed) dye, spectrophotometrically. (Shimadzu UV-1650 PC). The amount of dye adsorbed at time t, qe (mg/g), was obtained by calculating the difference between the initial and the final dye concentration as shown in equation 1:

$$qe=(C0-Ce) \times V/W \qquad \text{(Equation 1)}$$

Where qe is the amount of dye adsorbed (mg/g) and C0 is the initial dye concentration (mg/L), while Ce is the concentration of dye in solution at equilibrium (mg/L), V is the volume (L), and W is the weight of adsorbent(g).

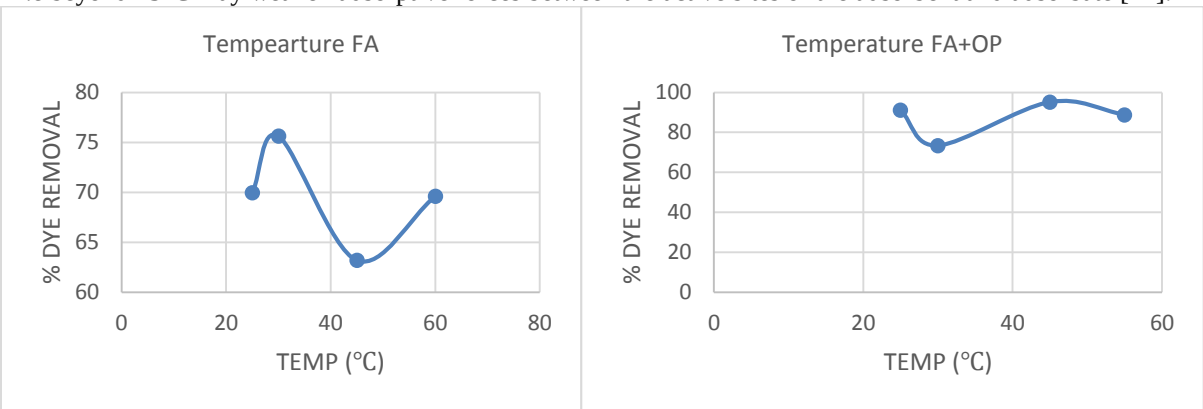
The percentage removal of the dye was computed using the following equation:

$$\text{Percentage of removal (\%)} = (C0-Ce)\times 100/C0 \qquad \text{(Equation 2)}$$

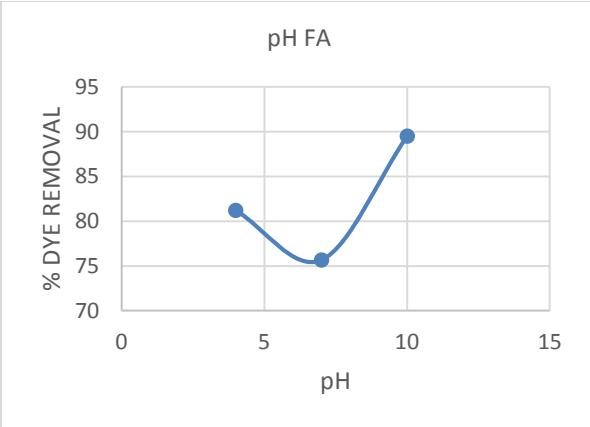
Where C0 and Ce are the initial and equilibrium concentration of dye (mgL^{-1}) in solution [14,15]

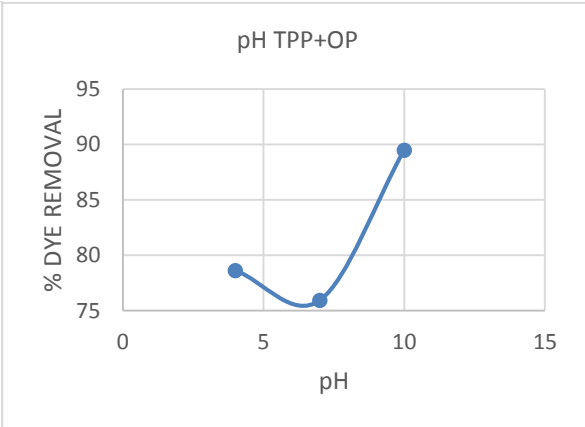
III. RESULT AND DISCUSSION:

Effect of temperature: The temperature range of 25℃ to 60^{0}C was studied. Temperature of 30℃ was found favorable when only FA as an adsorbent was used whereas 45 ℃ was effective when FA+ OP was used for adsorption. A very high temperature i.e beyond 45^{0}C may weaken adsorptive forces between the active sites of the adsorbent and adsorbate [14].

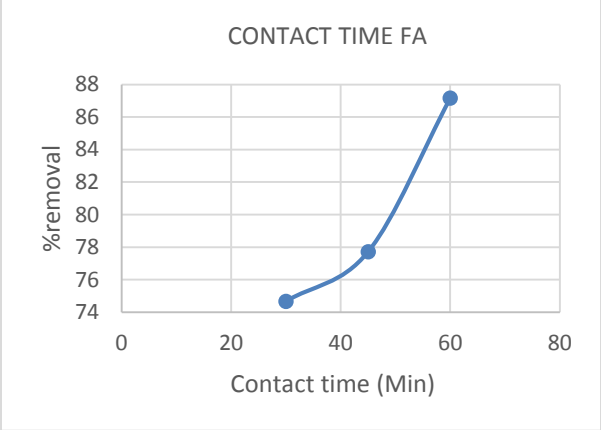


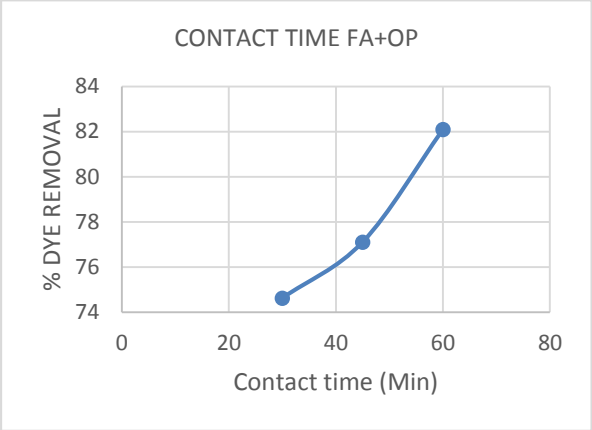
Effect of pH: A range of 3.0 to 10.0 was selected for the optimization of pH and it was adjusted using 0.1 N HCl or 0.1N NaOH. The dye removal efficiency of adsorbent increased with increase in pH and it was found to be maximum at pH 10 in both the cases. The presence of excess of H^+ ions at acidic pH can compete with the dye cations for adsorption site. As the pH increases, the acidic sites start getting neutralized and negative surface charge of adsorbents increase. These negatively charged sites on the adsorbent result in the increased percentage of dye removal [18].



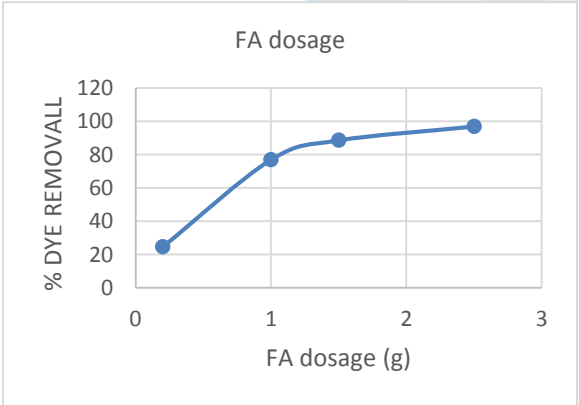


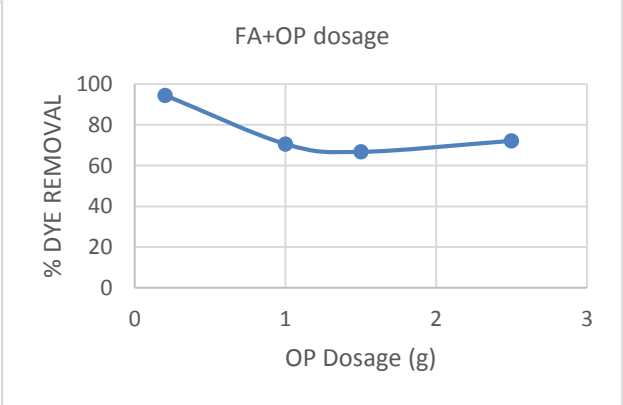
Effect of contact time: Contact times ranging from 30 to 60 minutes were considered to study the effect of contact time. As the contact time increases the % dye removal increases in both the cases [19].



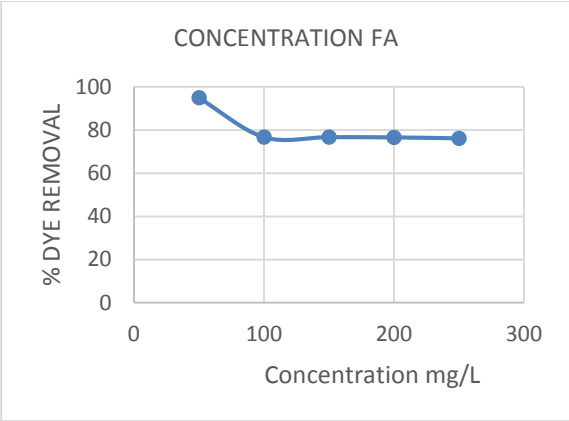


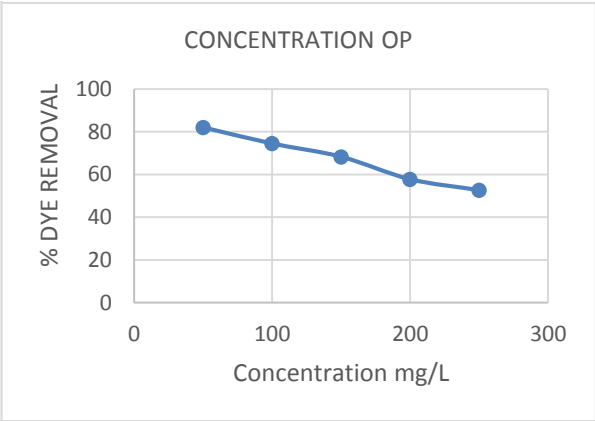
Effect of adsorbent dosage: Adsorbent dose is the important parameter in the adsorption studies which determines the capacity of an adsorbent for a given initial concentration of the dye. To investigate the effect of mass of adsorbent on the adsorption of dye 0.2g to 2.5g of FA was taken in the first case and optimized FA dosage was found to be 1g. In the second case 1g FA was kept constant and 0.2g to 2.5g of OP was chosen for optimization. 0.2g of OP along with 1g FA results in maximum % dye removal [15,18,20].





Effect of concentration: Concentrations ranging from 50 to 250 mgL^{-1} were selected and it was observed that with the increase in concentration, there is a decrease in the % removal of the dye. However, 50 mgL^{-1} was chosen as the optimized concentration of the dye as the amount of dye adsorbed on to the adsorbent was maximum at that concentration [21].





Optimized parameters:

Sr.No	Parameters studied	Optimized Parameters
1	Contact time	60 minutes
2	pH	10
3	Adsorbent dosage	1g
4	Dye concentration	$50mgL^{-1}$
5	Temperature	30^0C

Table: Optimized parameters for FA

Sr.No	Parameters studied	Optimized Parameters
1	Contact time	60 minutes
2	pH	10
3	Adsorbent dosage	0.2g
4	Dye concentration	$50mgL^{-1}$
5	Temperature	45^0C

Table: Optimized parameters for FA+OP

Percentage dye removal: The % dye removal was found to be 83.17% when only FA was used as adsorbent. The % dye removal was increased to 87.94% when the combination of FA and OP was used.

IV. CONCLUSION

The adsorption behaviour of the two adsorbents was evaluated by considering dye concentration, adsorbent dosage, solution temperature, pH and contact time. The study of adsorption of safranin infers that percentage dye removal from aqueous solution using FA was found to be 83.17%. FA is a potent adsorbent but when its combined with OP, the adsorption of dye increased to 87.94%. Hence, such new technologies will extend and enhance the usefulness of wastes such as FA and OP as renewable resources for value added products. There is a good scope of research to extend the applications of such wastes as potent adsorbents for pre-clean up treatment of various samples while protecting nature which will lead to sustainable development.

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