# OPTIMIZATION OF CRYSTAL VIOLET DYE REMOVAL FROM AQUEOUS SOLUTION USING AGRO WASTES

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## ABSTRACT

***Batch adsorption process involving use of groundnut shell (GS) and orange peel (OP) as adsorbents was employed for the removal of carcinogenic Crystal Violet dye from aqueous solution. Studies were carried out as function of contact time, sorbent dosage, initial dye concentration and pH of the dye solution with a view of optimizing adsorption conditions. The results obtained showed high efficiency of ≈ 98.3% and 97% using 4.5g of GS and OP respectively, showing a promising performance of the agro wastes as filters for the dye removal.***
***Keywords:*** *Crystal violet, Groundnut shell, Orange peel, % Removal, Adsorption*
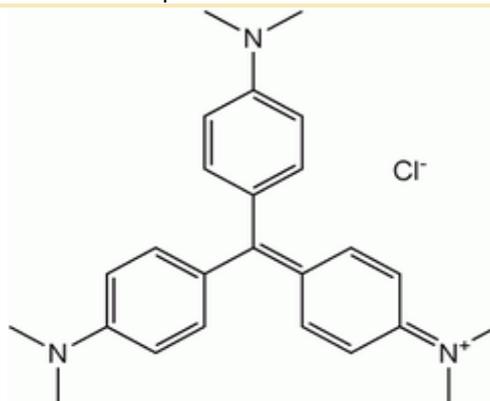
## INTRODUCTION

Water played a crucial part in the origin of life and it still has an essential role in maintaining plant and animal life (Matthews, 1996). Fresh water is already a limited resource in many parts of the world. In the next century, it will become even more limited due to increased population, urbanization, and climate change. This limitation is caused not only by increasing demand for water, but also by pollution in freshwater ecosystems from sewage, industrial waste and a wide array of synthetic chemicals (Dara, 2006).

Effluents from different industries such as textile, rubber, paper and plastics contain several kinds of synthetic dye- stuffs (Chiou and Li, 2004). The domestic, agricultural and industrial wastes significantly contribute to the pollution process (Koening *et al.,* 2003; Pedrozo and Rocha, 2007), but the textile, chemical and paper industries, and oil refineries generate huge volume of wastes (Guaratini and Zanoni, 2000; Thompson *et al.*, 2001; Wake, 2005). A very small amount of dye in water is highly visible. Further, discharging even a small amount of dye in water can affect aquatic life and food webs due to the carcinogenic and mutagenic effects of synthetic dyes (Crini, 2006).

Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart colour. Most dyes are complex organic molecules and are resistant to weather, action of detergents, etc. (Gupta *et al.*, 1992). Dyes are resistant to fading on exposure to light, water and many chemicals and therefore, are difficult to be decolourised once released into the aquatic environment. Release of these dyes in water stream is aesthetically undesirable and has serious environmental impact. It diminishes the solubility of gases, exhibits accumulative effects on the organisms and causes adverse effects on human beings (Guaratini and Zanoni, 2000). It might alter the biosynthesis process by the reduction of sunlight penetration and photosynthetic action (Amaral *et al.*, 2004). Besides, there is a concern about the interaction of these effluents in the water treatment stations, since it may provoke diverse problems of economical and public health order, given that some kinds of textile dyes can lead to allergies (Seidenari *et al.*, 2006), dermatitis (Hatch and Maibach, 1995) and tumors (Golka *et al.*, 2004).

Crystal violet or Gentian violet also known as methyl violet is used as a histological stain and in Grams method of classifying bacteria. It has anti-bacterial, antifungal and anthelmintic properties and was formerly important antiseptic. The dye has the following structure:

Chamarthy *et al.* (2001) prepared an adsorbent from peanut shell by heat treatment in the presence of phosphoric acid or citric acid and used it for the adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn (II) ions. The phosphoric acid modified shells adsorbed metal ions in larger amounts compared to citric acid modified shells. Bagasse pith, a waste product from sugarcane industry, has been studied by McKay *et al.* (1987) without any pretreatment for the removal of two basic dyes and two acid dyes. Higher adsorption capacity of 158mg/g and 177mg/g were obtained by using basic blue 69 and basic red 22 respectively. While lower capacity of 23mg/g and 22mg/g was observed for acid red 114 and acid blue 25, respectively.

In 1993, peanut hull was used as adsorbent by Namsivayam and Periasamy after treating with concentrated sulphuric acid, for the removal of Hg (II) ions from aqueous solutions.

Adsorbent prepared from orange peel was successfully used to remove methylene blue from aqueous solution in a batch column (Velmurugan *et al.,* 2001). The study examined the potentials of the pretreated peel for removal of methylene blue from simulated wastewater. At optimum dose (1.0g) and contact time (45min) maximum colour removal efficiencies of the peel was found to be 99% from a 12.32mg/L aqueous dye solution. The study showed that pH, contact time and adsorbent dosage play a vital role in dye removal.

Umar *et al.* (2010) employed the use of thermo chemically cracked groundnut shells for the biosorption of malachite green from aqueous solution. The dye adsorption was found to fit into Freundlich and Langmuir isotherm models. The result shows that thermally cracked groundnut shells at $600^0C$ could serve as a filter for the dye adsorption from aqueous phase. Over 80 percent adsorption was reported by each adsorbent.

**MATERIALS AND METHODS**
**Materials**
All glassware and plastic containers were washed thoroughly, rinsed with distilled water and allowed to dry in an oven. Groundnut Shell was collected from Dawanau in Dawakin Tofa local government, Kano State, while orange peel was obtained from an orange seller. The adsorbents were air dried in sunlight until almost all the moisture evaporated, and then in an oven at 80°C. The adsorbents were ground to the working size of 850μm and kept in a plastic container for subsequent use. Distilled water was used for the preparation of the Stock solution and kept in a refrigerator. Fresh working standards were prepared daily by appropriate dilutions (Ibrahim, 2011).

**Methods**
All batch adsorption experiments were carried out at room temperature as outlined below; and % removal

of the dye by each adsorbent was calculated from the relation:

$$\frac{Co - Ce}{Co} \quad x\ 100\%$$

Where $C_o$ and $C_e$ are the concentrations (mg/L) of the dye initially and at equilibrium time (Bhattacharya *et al.,* 2008; El-Nemr *et al.,* 2008; Ibrahim *et al.*, 2006; Wang and Lin, 2008).

   **a.   Effect of time**
In these experiments, 1.0g of the adsorbents were separately placed in a screw capped conical flasks and $100cm^3$ of 10mg/L dye solution was added to each and agitated on a temperature controlled mechanical shaker for 5, 10, 15, 30, 45, 60, 75 and 90minutes. The mixtures were filtered using Whatman No.1 filter paper (Abdulrahman *et al.,* 2009) and the absorbance of filtrates were taken using Jenway 6051 colorimeter at a predetermined $λ_{max}$ of 580nm.

   **b.   Effect of adsorbent dosage**
Different weights of the two adsorbents (0.5g, 1.0g, 1.5g, 2.0g, 2.5g, 3.0g, 3.5g, 4.0g, 4.5g and 5.0g) were separately contacted with $100cm^3$ of 10mg/L dye solution and agitated for their respective equilibrium contact time. The mixtures were filtered and the absorbances of the filtrates were determined as before.

   **c.   Effects of initial dye concentration**
In order to test the effect of variation in the initial dye concentration, optimal weight (4.5g) of the adsorbents were agitating in a $100cm^3$ of 10mg/L dye solution for 30 and 45min respectively. The mixtures were filtered and the absorbances of the filtrates were determined as before. The procedure was repeated with 15, 20, 25 and 30mg/L of the dye solution.

   d.   **Effect of pH**
Initial pH of the optimal concentration of the dye solution was adjusted to 4, 6, 8, and 10 using 0.5M solutions of HCl and NaOH. 4.5g each of the adsorbents were agitated with $100cm^3$ of the dye for their respective equilibrium times. Each mixture was filtratered and the filtrate was treated as before.

**RESULTS AND DISCUSSION**
Fig. 1(a & b) shows the effect of contact time on % removal of the dye. With increased agitation, the external mass transfer coefficient increases resulting in higher adsorption of the dye molecule. In this process, the dye molecules have to first encounter the boundary layer effect, then adsorption from the surface and finally, diffusion into the porous structure of the adsorbent.

The reaction is a heterogeneous equilibrium process and may reach saturation after some time, which according to Malik (2003) will take a relatively longer contact time. From the figures, the removal of crystal violet by GS and OP increases with time up to a maximum of 95% and 90% respectively for 30min and 45min period.

This is followed by a region where there is no noticeable change in percentage removal with increase in agitation period, a process that signifies attainment of adsorption equilibrium. Based on this, 30 and 45mins were taken as equilibrium times for GS and OP respectively. This region was followed by a third region, from 75 and 90min respectively, where there is gradual decrease in percentage removal with increase in agitation period, signifying possibility of desorption after saturation of the adsorbent. This desorption may be due to the system's constant stirring and weak interactions between the dyes and bioadsorbents (Namasivayam and Arasi, 1997). The results suggested that where speed of treatment is required, GS may preparably be employed over OP. Also that GS have higher affinity for the dye compared to OP. Similar results have been reported by Weber (1972); Kannan and Sundara (2001); Velmurugan *et al.* (2001); Sarioglu and Atay (2006) and Madhavakrishnan *et al.* (2009) for the removal of Methylene blue using biosolid.

The mass quantity of adsorbent material to be used is of great importance in order to have an efficient dye removal. The effect of sorbent dosage on the removal of crystal violet dye is shown in Fig 2 (a & b). The percentage removal of the dye on GS increased up to approximately 97%. However, on OP the percentage removal increased to a value of 91%. This also confirms the higher affinity of the dye by GS in comparison to OP. The general trend of increase of % removal with increase in sorbent dose has been reported by Malik *et al.* (2006) in physico-chemical

and surface characterization of adsorbent prepared from groundnut shell by $ZnCl_2$ and its ability to absorb colour.

Using optimal sorbent dose of 4.5g, Fig.3 showed an increase in the % removal of the dye with increase in adsorbate concentration from 5 to 30mg/L. On GS, the percentage removal increased from 97 to 98.3%, while on OP the percentage removal increased from 90 to 97.7%. This observation has been supported by the work of Velmurugan *et al.* (2001) on the variation of adsorption efficiency of Crystal violet dye with increase of initial dye loading concentration.

The pH of the dyes solution plays an important role in the adsorption process, particularly on the adsorption capacity. In this work the pH of the dye solution was varied from 4 to 10 in order to determine the optimum pH value for the dye removal. Fig. 4 shows an increase in the % removal from pH 4 to 8 ranging from 97 to 98.3% followed by a decrease at pH 10 with 96% removal efficiency for GS, a pattern simply referred to as adsorption envelop. However, on OP the % removal shows an average increase of 94 to 96.4% from pH 4 to 10 signifying that the optimum pH is likely yet to be reached. The lower removal of the dye at acidic pH range may be associated with the competition that sets in between the excess concentration of $H^+$ ion and the cationic part of the dye for the active site on the adsorbents. A similar trend of adsorption was observed by Namasivayam and Periasamy, (1993) for the adsorption of Acid violet 17 by waste banana pith.
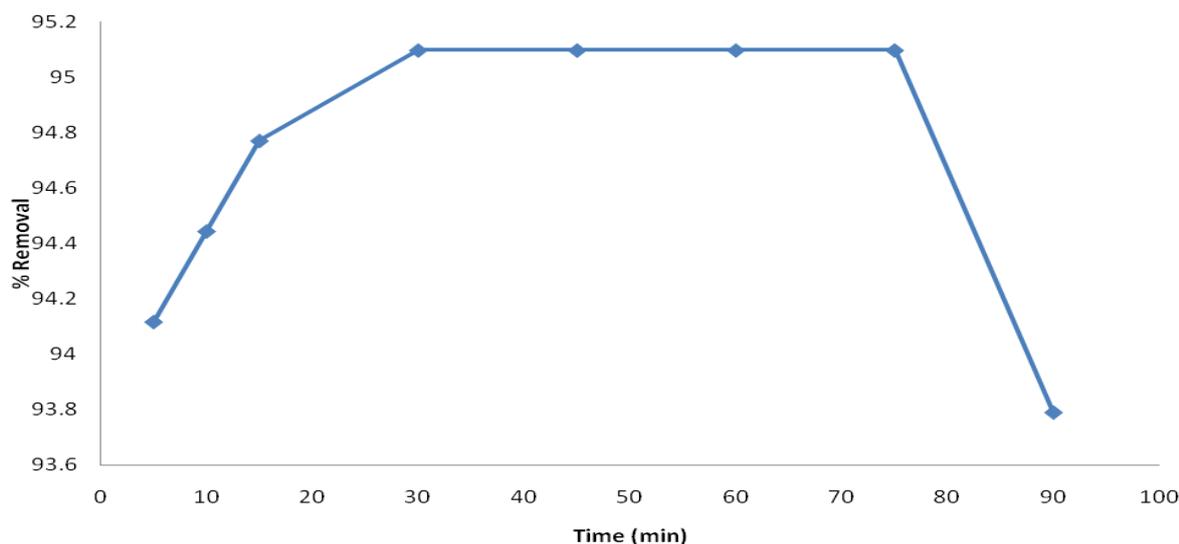


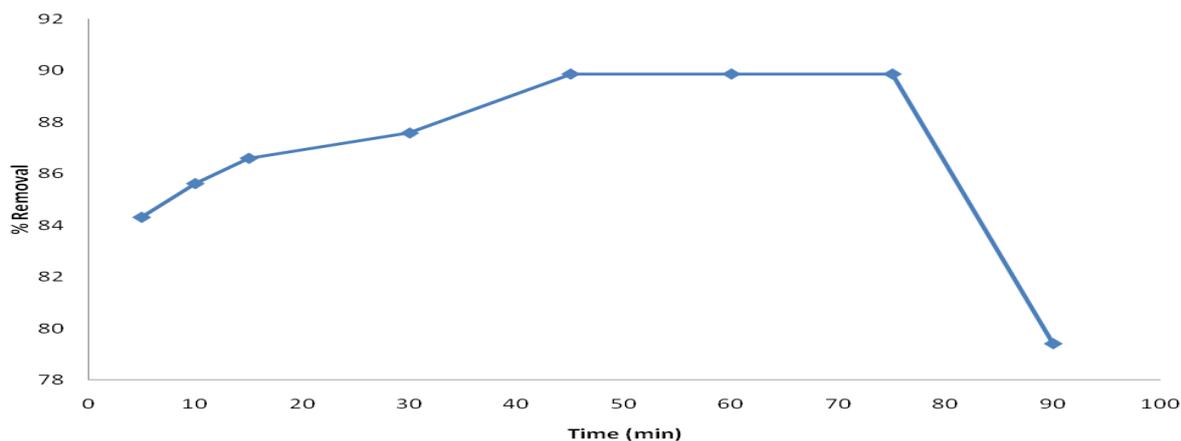**Fig. 1a: Estimation of Adsorption Equilibrium Time using Groundnut Shell**

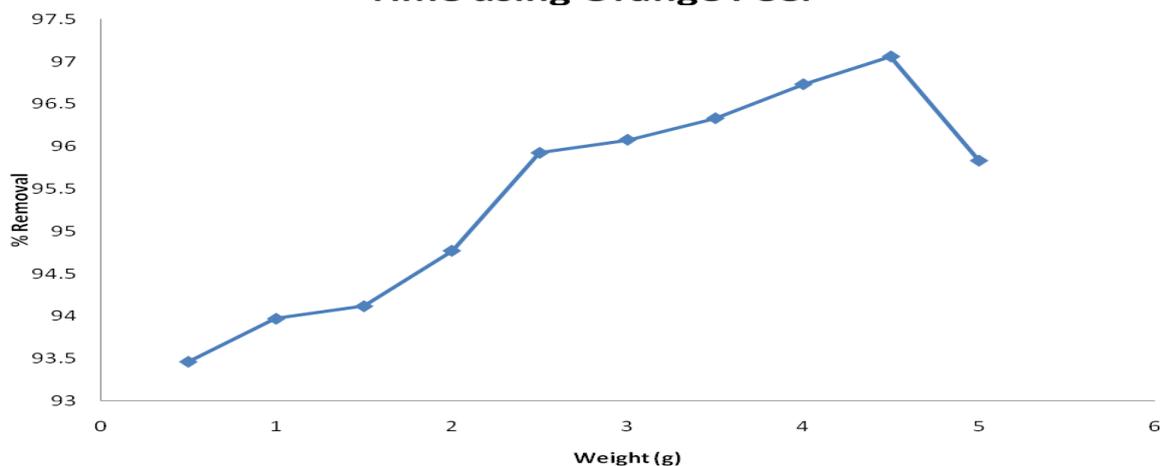**Fig. 1b: Estimation of Adsorption Equilibrium Time using Orange Peel**



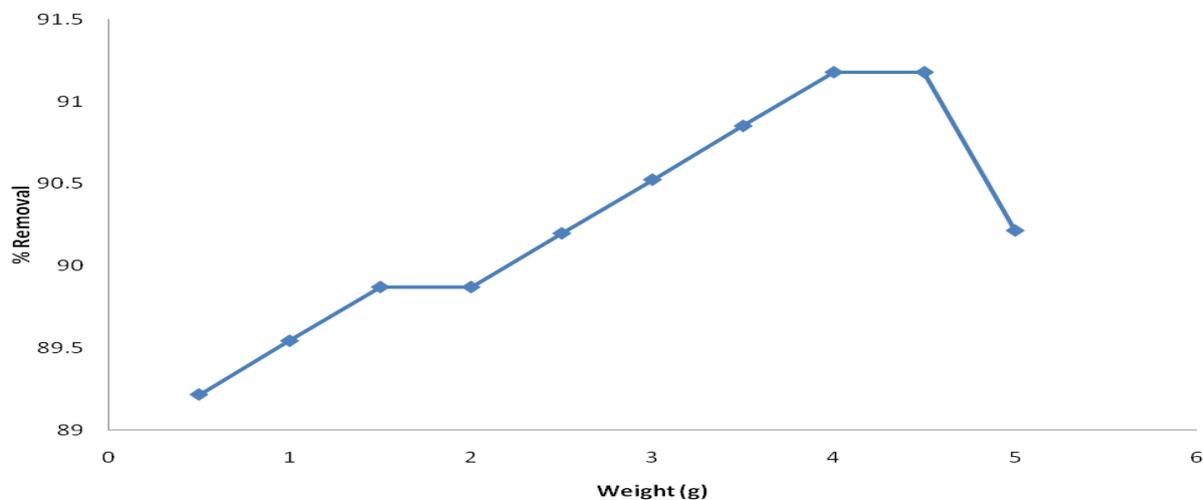**Fig. 2a: Variation of % Removal with Increase in Weight of Groundnut Shell**



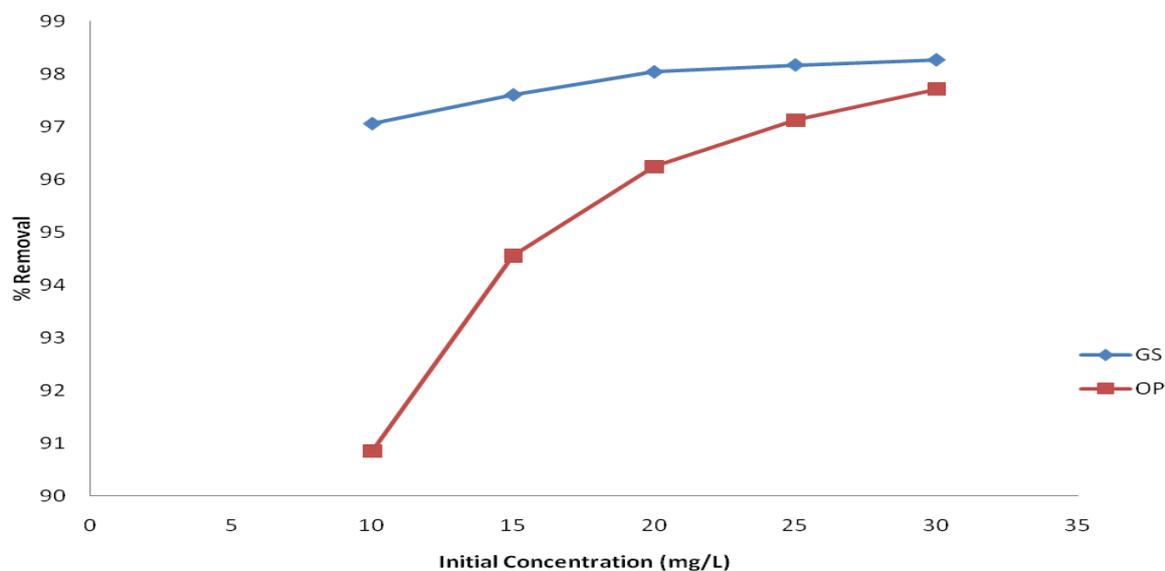**Fig. 2b: Variation of % Removal with Increase in Weight of Orange Peel**

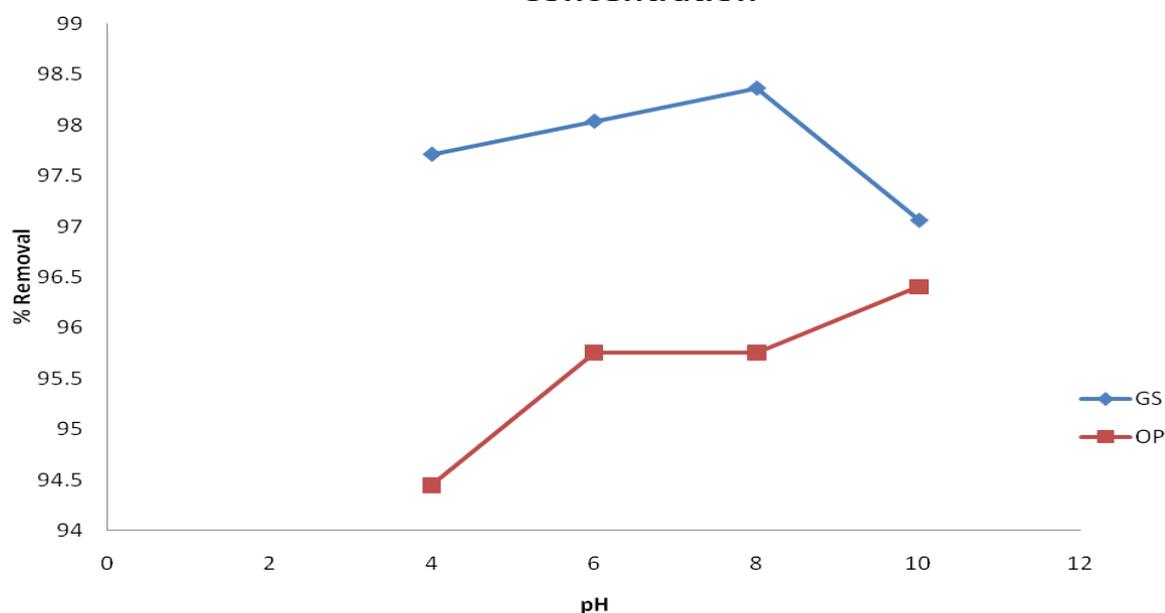**Fig.3: Variation in % Removal with Initial Dye Loading Concentration**



**Fig. 4: Variation of % Removal with pH of the Dye Solution**

**CONCLUSION**

The work shows the possibility of using Groundnut Shell and Orange peel for the uptake of crystal violet dye. Effects of contact time, adsorbent dosage, initial dye concentration, and pH on the % removal of the dye suggested an equilibrium adsorption time of 30 and 45min respectively for GS and OP, optimum weight of $4.5g/100cm^3$ of the dye and a pH of 8.

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