EFFICIENCY OF POTATOE PEEL, RICE AND WHEAT HUSK IN THE REMOVAL OF COLOUR FROM TEXTILE WASTE WATER

[1]Omole, J. T, [1]Dauda, B. M.* & [2]Onoja, P. K.
[1]Department of Textile Science and Technology,
Ahmadu Bello University, Zaria – Nigeria
[2]Department of Chemistry,
Kogi State University, Anyigba – Nigeria

E-mail: [1]omolejt@gmail.com; [1]bendauda@yahoo.com*; [2]kimmypet2006@yahoo.com
Phone No: +234-805-700-5726

Abstract

Effectiveness of treated and untreated potato peel, rice husk and wheat husk and mixtures of any two as an adsorbent of colour from effluents containing green vat and orange reactive dyes were studied using standard methods. The results from the batch experiments showed that the ability of potato peel, rice husk, wheat husk and mixtures of any two, in removing green vat and reactive dyes from textile mill effluent are dependent on the dye structure and adsorbent concentrations. The dye removal ability of the adsorbent was in the 50 - 60 % range, with potato peel in the raw form giving the best result. It was also observed that activated samples of these adsorbents were more effective in dye removal except for potato peel. Potato peel, rice husk, wheat husk, or mixtures of any two could be employed as low-cost and effective adsorbents for the removal of vat and reactive dyes from aqueous solution. Isotherm studies showed that the adsorption followed the Langmuir Isotherm with the straight-line plot obtained for the various isotherms being steepest for potato peel, followed by wheat husk and then rice husk, indicating increasing adsorption rate in that order. Kinetic study showed that the adsorption process follows first order kinetics, the transport of the adsorbate from the bulk solution to the interior surface of the pores being the rate limiting step of the adsorption process.

Keywords: Activated adsorbent, Adsorption, Adsorption Isotherm, Dye, Low Cost Adsorbents, Textile Effluent

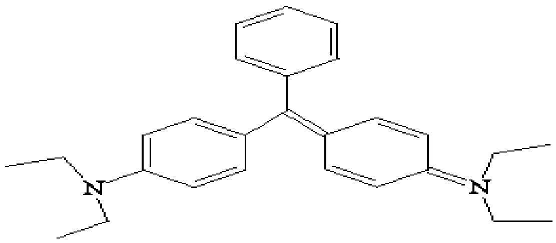
Introduction

Water has unique properties that make it possible to perform many special roles in the biosphere. It is a versatile solvent that is able to dissolve a wide range of organic and inorganic substances. It is water's versatility as a solvent that enables it to serve as a solvent for so many materials. The use of water for domestic purposes covers consumption, washing and flushing away waste (Edmund and Max, 1976). The control of water pollution has become of increasing importance in recent years. The release of textile effluents containing dyes and other toxic substances into the environment constitutes only a small portion of water pollution but its dangerous effects have necessitated the need for immediate solution (Dauda et al., 2012). The major component of textile effluents is the dye, which even in small quantities are visible due to their brilliance.

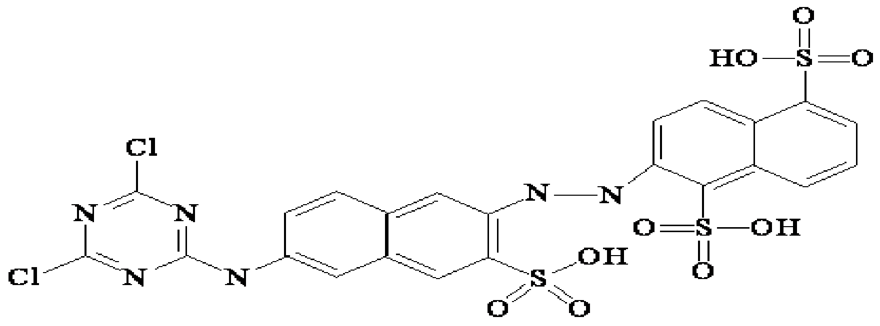
Textile industries are amongst the largest generators of effluent due to the very large quantities of water required in various textile wet processes. For example, a wool textile industry requires about 400 million litres of water each day for the operations of scouring, dyeing and washing off (Nkeonye, 2009).

It has been estimated that about 9 % of the total amount (45,000tons) of dye stuff produced in the world are discharged in textile waste waters (Allen and Koumanova, 2005). Growing concern about environmental issues has prompted the textile industry to resort to environmentally friendly treatment technologies. Many non–conventional and low–costs adsorbents have been proposed by several workers. The most frequently used adsorbent for the removal of the coloured and toxic pollutants in waste water is currently activated carbon. A wide variety of carbons have been prepared from agricultural and wood wastes such as coir pith, banana pith, date pith, maize cob, rice husk, rice hulls, fruit seeds, nutshell, pine wood, sawdust, coconut tree, bamboo, cassava peel, etc. Aloko and Adebayo (2007) used raw and carbonized rice husk as adsorbent to adsorb colour from waste water, and from their study discovered that raw rice husk have the higher colour removal efficiency than the chemically activated sample. According to Kushhawa et al (2008), the method used to modify rice husk strongly affects the adsorption efficiency. The study by Itodo and Itodo (2002), revealed the feasibility of shea nut shells as an effective biomass for dye uptake with relatively high percentage removal.

The objective of this work is to use some locally sourced agricultural wastes namely, potato peel, rice husk and wheat husk to remove colour of textile waste water through their equilibria and. adsorption equilibrium and kinetic studies using brilliant orange and brilliant green dyes (Figure 1) with the objective of determining the effect of structure of dye on ease of removal of such dye.



Brilliant Green Vat Dye



Brilliant Orange Reactive Dye

Figure 1: Brilliant orange reactive and brilliant green vat dye

Materials and Methodology

Sample Collection

The materials used as adsorbents were agricultural wastes. These were rice husk and wheat husks both obtained from an irrigation farm in Kadawa, Zaria and potato peel form the student dining hall of Ahmadu Bello University, Zaria. These were chosen because of their chemical stability, non-catalytic activity and local availability at very low cost.

Dyes and Chemicals

Two commercial dyes of known chemical structure; brilliant orange reactive dye and brilliant green vat dye were used. Concentrated sulphuric acid and formaldehyde were also used. All chemicals used were of analytical reagent grade.

Sample Preparation and Pre Treatment

Rice husk, wheat husk, and potato peel were washed repeatedly with distilled water followed by filtration so as to remove dust and soluble impurities. The washed samples were oven dried at 110^{o}C to constant weight. The cleaned samples were then ground into powder and sieved to 250 – 500 µm particle size. Each fraction was washed again to remove colour and turbidity. Each waste sample was divided into two parts; one part was processed to obtain chemically treated waste and the other part remained untreated.

The chemically activated samples were prepared by soaking the samples in 0.6M H_2SO_4 for two hours at 25^{o}C. The acid waste slurries were then heated to 120^{o}C. The acidified material was washed with distilled water to remove any excess acid and then dried at 100 – 130^{o}C until constant weight was achieved.

The untreated samples were then soaked in distilled water for about 10 – 15 minutes and treated with formaldehyde to prevent any further colour interference during adsorption process. The material was then dried in an oven at 100^{o}C to a constant weight and the dried material was used as the raw sample. The treated and untreated samples were then preserved in glass bottles and kept in a dessicator for further use.

Preparation of Dye Solutions

Two commercial dyes – brilliant orange reactive dye and brilliant vat green dye (figure 1) were used. A stock solution of each dye was prepared by dissolving 1 g of the dye in 1000 ml distilled water to make a stock solution of 1000 mg/l. Other concentrations were prepared by serial dilution. For absorbance measurements, a UV-Visible Spectrophotometer (Jenway, 6405 UV-Vis Spectrophotometer) was employed using silica cells of path length 1 cm. These measurements were taken at the maximum λmax of each dye. Supernatant concentrations were determined from standard calibration curve.

Batch Adsorption Experiments

To evaluate the efficiency of adsorbent, laboratory batch mode experiments were conducted. 2.5 g, 5.0 g and 7.5 g of the adsorbent (adsorbent dose) were taken separately and placed in a set of 250 ml beakers containing aqueous solution of the dye for varying contact time period, at room temperature and neutral pH. The contents were shaken on a rotary shaker at a speed of 150 rpm for 2 hours and allowed to settle. At the end, the adsorbents were removed by centrifugation at 150 rpm for 10 minutes and the supernatants were analyzed for the residual concentration of the dye. All experiments were carried out in duplicate with respect to each condition and mean values are presented. The maximum deviation was less than 6 %. The two different adsorbents' were also combined by mixing and adsorption efficiencies determined.

The adsorption behaviours of the samples were studied by evaluating the percentage removal efficiency of the dyes given by the relation:

$$\%\ \text{removal efficiency} = \frac{C_o - C}{C_o} \times 100$$

Where;

C_o = the initial concentration of dye before adsorption.
C= the final concentration of dye after adsorption.

The following batch experiments were conducted. The batch experiments conducted the effect of contact time, adsorbent dose and adsorbent mixture.

Adsorption Isotherm Test

The Langmuir equation has been successfully applied to many adsorption systems (Malik 2003, Namasivayan and Kavitha 2003) and is given by the equation:

$$qe = (K_L \times S_M \times Ce) \div (1 + K_L \times Ce) \ldots\ldots\ldots\ldots\ldots(1)$$

where: K_L is the equilibrium adsorption coefficient (l/mg)
S_M is the maximum adsorption capacity (mg/g)
Ce is the adsorbate equilibrium concentration

Equation (1) can be written in the following linear form:

$$Ce \div (X \div M) = [1 \div (K_L \times S_M)] + (Ce \div S_m) \ldots\ldots\ldots(2)$$

where: X = amount of solute adsorbed per unit weight of adsorbent
M = adsorbent dosage required to reduce the initial concentration Co.

Kinetics of Adsorption Test

The kinetics of adsorption of brilliant orange dye on potato peel, rice husk, and wheat husk, was studied by applying the Lagergeren first order rate equation (Lee et al, 1996; Trivedi et al 1973).

$$\text{Log } (qe - q) = \text{Log } qe - (Kt \div 2.303) \ldots\ldots\ldots\ldots\ldots(3)$$

Where q (mg/g) is the amount of dye adsorbed at time t, qe (mg/g) is the amount of dye adsorbed at equilibrium, and K is the equilibrium rate constant of sorption.

Results and Discussion

Effects of initial adsorbent concentration and contact time on the rate of adsorption by the raw, activated and combined potatoes, rice and wheat wastes are presented in Tables 1 & 2 and presented graphically for both dyes in figures 2 & 3.

Table 1: Effect of adsorbent dose and time on % dye removal for brilliant green dye

ADSORBENT	ADSORBENT DOSE (g/100ml)	%	DYE	REMOVAL
		20 min	40 min	60 min
Raw Rice	2.5	34.05	29.95	30.05
	5.0	44.22	40.32	37.62
	7.5	53.95	55.24	56.86
*Act'd Rice	2.5	38.92	38.81	39.58
	5.0	47.68	49.30	54.16
	7.5	52.11	60.11	61.08
Raw Potato	2.5	48.76	42.81	43.03
	5.0	54.16	53.73	55.68
	7.5	63.68	62.27	63.89
Act'd Potato	2.5	29.10	20.11	21.30
	5.0	31.57	29.62	31.03
	7.5	38.70	35.68	38.70
Raw Wheat	2.5	25.94	25.62	27.03
	5.0	29.73	38.81	40.11
	7.5	37.62	45.95	47.03

Act'd Wheat	2.5	26.27	32.43	32.76
	5.0	33.51	42.38	45.41
	7.5	40.86	51.57	54.70

*Act'd = activated

Table 2: Effect of adsorbent dose and time on % dye removal for brilliant orange dye

ADSORBENT	ADSORBENT DOSE (g/100ml)	% DYE REMOVAL		
		20 min	40 min	60 min
Raw Rice	2.5	30.64	39.29	44.66
	5.0	35.03	48.63	49.95
	7.5	40.44	52.60	53.02
*Act'd Rice	2.5	36.31	41.64	46.11
	5.0	40.76	50.20	50.76
	7.5	56.17	54.91	59.72
Raw Potato	2.5	45.15	49.02	51.20
	5.0	50.56	54.98	54.16
	7.5	64.33	65.97	67.00
Act'd Potato	2.5	34.17	38.74	30.24
	5.0	42.64	43.64	38.68
	7.5	49.03	49.96	46.08
Raw Wheat	2.5	39.21	34.92	40.91
	5.0	44.94	40.74	44.89
	7.5	60.42	50.89	52.86
Act'd Wheat	2.5	41.08	30.97	43.85
	5.0	48.81	35.92	49.01
	7.5	59.51	44.77	65.79

*Act'd = activated

Effect of Contact Time on Dye Removal

For both raw and chemically activated adsorbents, figure 2 showed that the adsorption rates for brilliant green dye liquor increased with time but eventually stabilized at some point when all the adsorption sites in the adsorbent had been filled i.e. at equilibrium exhaustion. For the first 20 minutes, the adsorption rates were very rapid due to the presence of large amount of the adsorption sites that the dye molecules could anchor on. However, after twenty minutes, the rate of adsorption of the dye reduced and after about 30 minutes the amount of colour adsorbed remained constant even if the experimental time was prolonged which then brought the whole system to a state of equilibrium, that is, the rate at which the dye molecules (colour) were absorbed by the adsorbents had reached their peaks (Nkeonye, 1987). Similar trend was observed for the brilliant Orange dye solution as shown in figure 3 to the extent that potato showed the highest % dye removal. On the average, dye exhaustion was higher for the brilliant orange dye than the green dye (see figure 10) due probably to the more linear structure of the orange dye which allows easier penetration into the pores of the adsorbent.

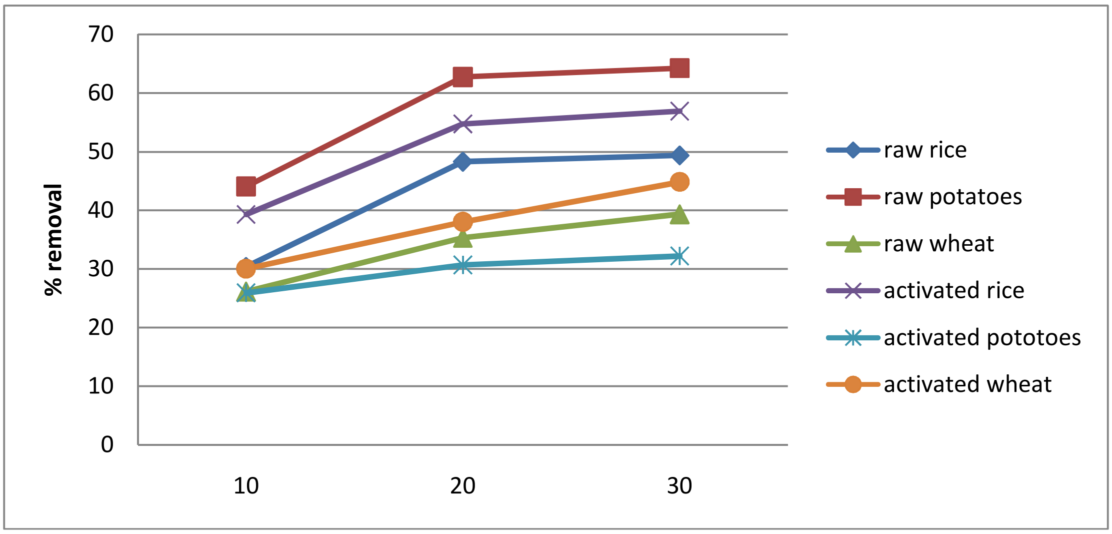


Figure 2: Effect of contact time on % dye removal (brilliant green)

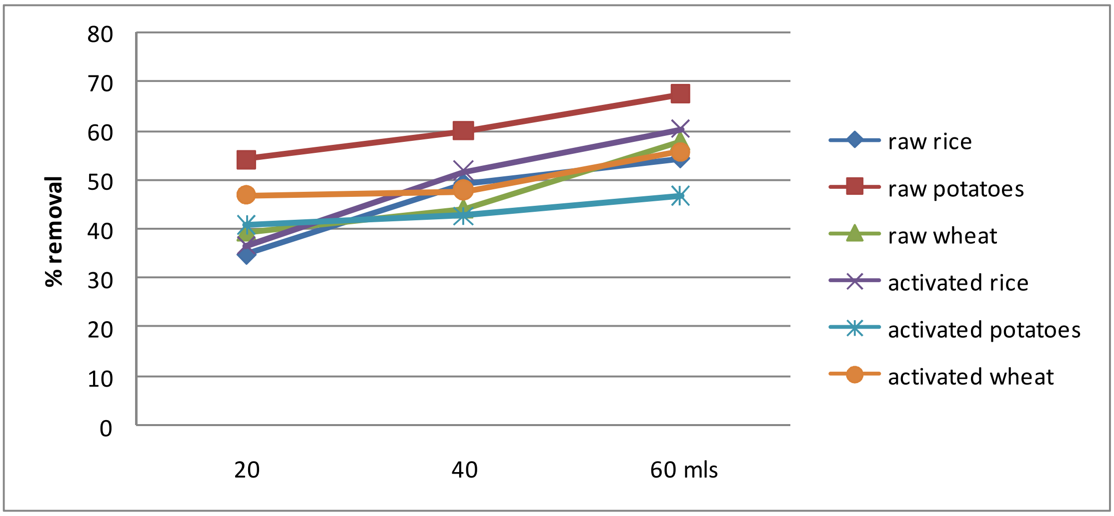


Figure 3: Effect of contact time on % dye removal (brilliant orange)

Another observation from figures 2 and 3 is that activated samples showed higher equilibrium exhaustion compared to the raw adsorbents. While this is true in the raw form, activated potatoes gave a slightly different result; the activated potato adsorbent displayed lower equilibrium exhaustion compared to the raw potato sample. This was probably due to water and acid up-take during the acidification process with 0.6M sulphuric acid at 25^0C. The potatoes waste's sites might have almost been filled up with the solution as the particles were swollen. Therefore very little adsorption sites were available to pick-up the colour from the prepared dye solution.

Effect of Adsorbent Dose on Dye Removal

The effect of varying the adsorbent concentration in brilliant orange aqueous dye solutions is as presented in Figures 4 and 5. The result for both dyes gave an initial rise in adsorption probably due to larger driving force and smaller surface area. Large surface area of the adsorbent and smaller size of the adsorbate favors adsorption. The rate of adsorption is high at the beginning as sites are available and unimolecular layer increased. Adsorption and desorption occurred simultaneously and the rates became equal at a stage called the *adsorption equilibrium*, when isotherms were applied.

As the adsorbent dose increased, more adsorption sites wer present and available for colour up-take hence the percentage removal increased.

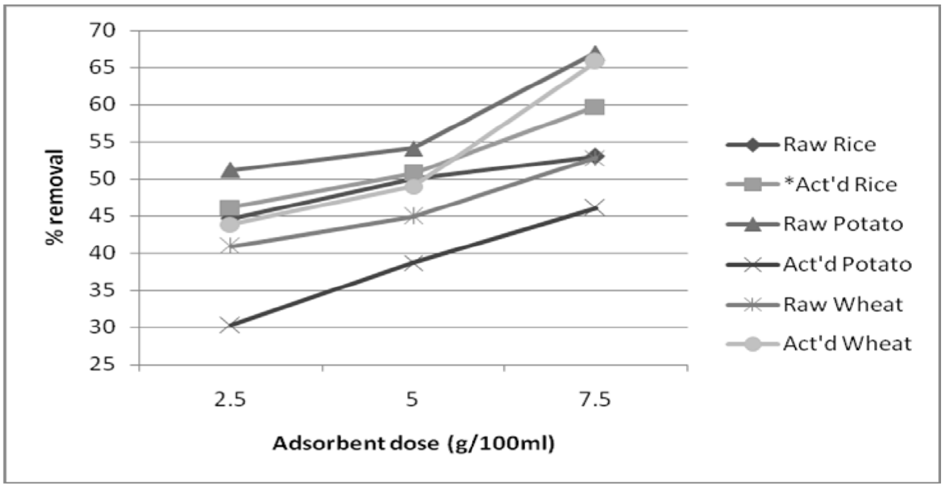


Figure 4: Effect of adsorbent dose on % dye removal (brilliant orange)

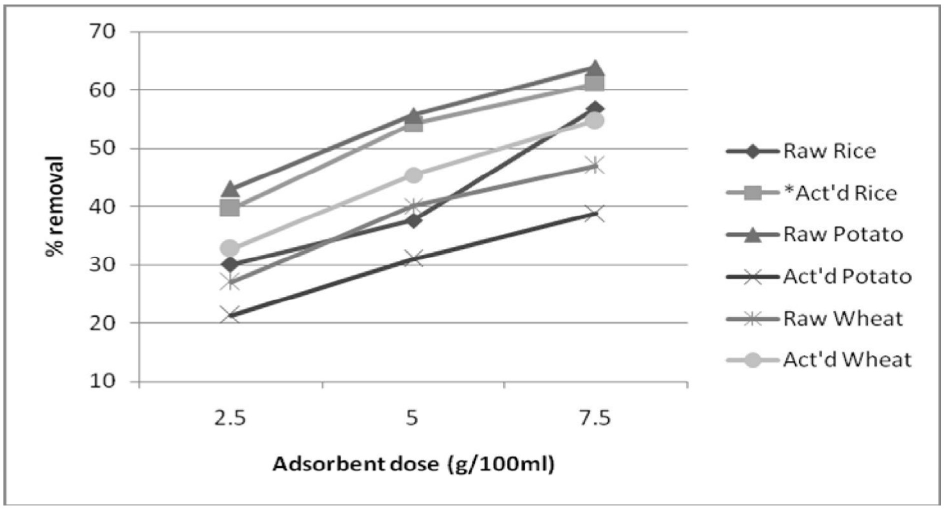


Figure 5: Effect of adsorbent dose on % dye removal (brilliant green)

Effect of Combination

This effect was as shown in figure 6 (brilliant green dye liquor) and figure 7 (brilliant orange dye liquor) for raw adsorbents. Both figures show that for potato/rice the percentage removal was highest, this also buttresses the high efficiency of raw potatoes as adsorbent in its raw form. From both figures 75/25 (weight ratio) potato/rice combination had the highest efficiency of dye molecule removal. Interestingly, the 75/25 combination gave the highest dye uptake at equilibrium irrespective of the adsorbent types mixed together.

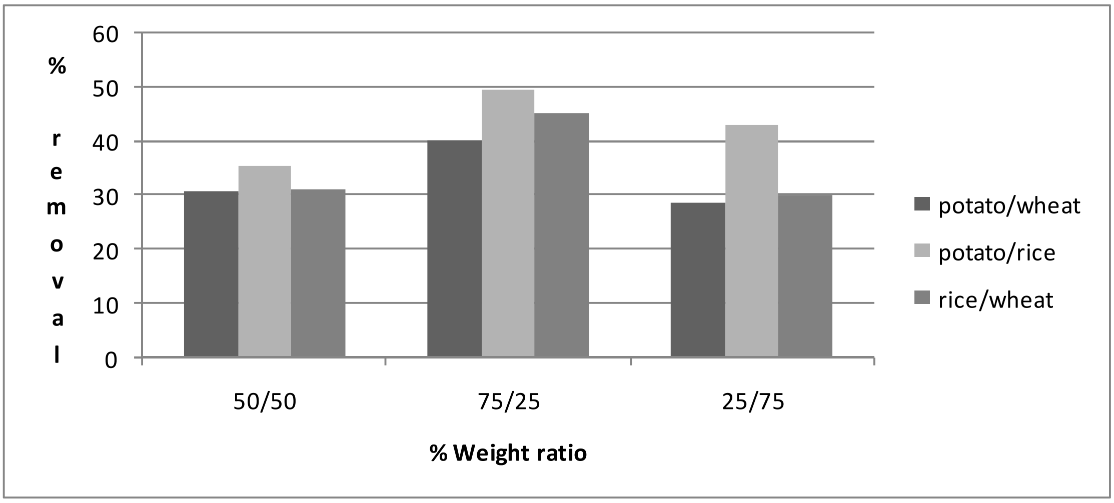


Figure 6: Equilibrium exhaustion for adsorbent mixtures (brilliant green dye)

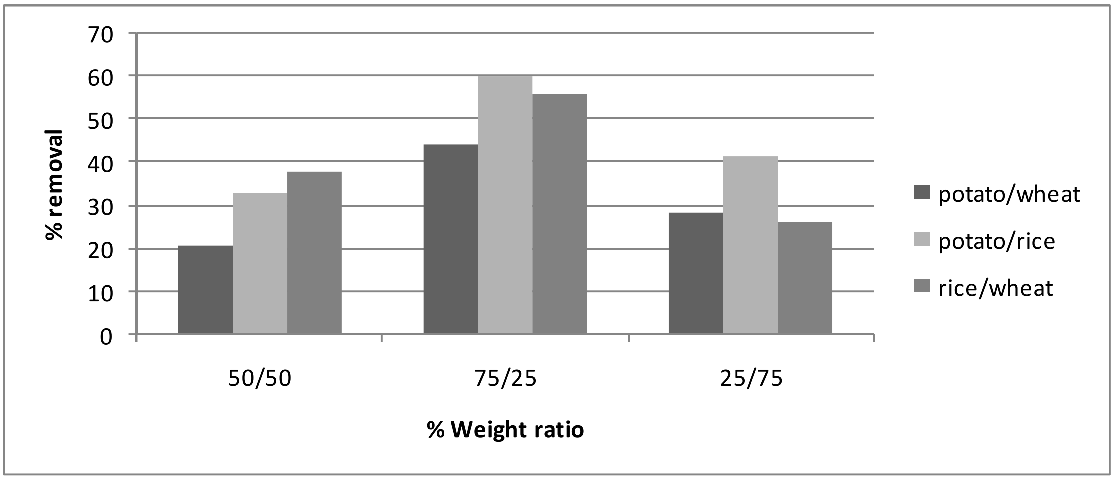


Figure 7: Equilibrium exhaustion for adsorbent mixtures (brilliant orange dye)

Adsorption Isotherms

Based on the equilibrium exhaustion plot obtained in Figure 2, which seem to indicate the presence of a finite number of sites for dye adsorption, the adsorption data were analysed according to Langmuir model for the adsorbents. The dye adsorption data were plotted according to Langmuir equation. A linear plot of Ce/(X/M) versus Ce was obtained for the three samples as shown in Figure 8.

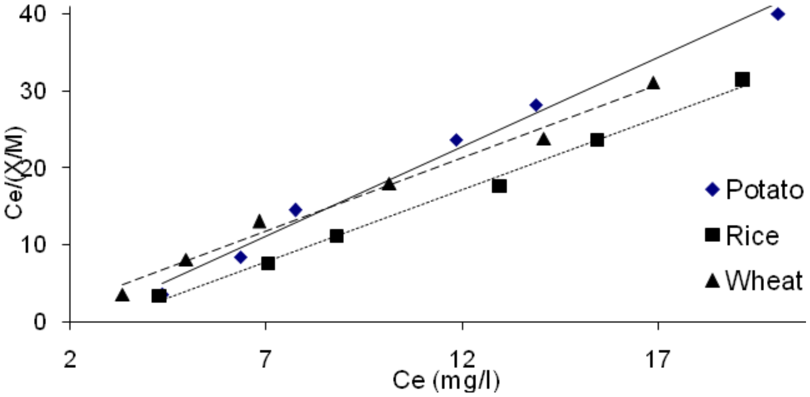


Figure 8: Langmuir isotherm showing adsorption behaviour of adsorbents (brilliant green)

The straight-line plots obtained for the various isotherms was steepest for potato peel, followed by wheat husk and then rice husk, indicating increasing adsorption rate in that order. Due to the presence of limited adsorption sites, a time was reached when all sites were completely occupied and adsorption of colour ceased, irrespective of increasing contact time. At this time, when all adsorption sites in the adsorbent were completely occupied, equilibrium been reached.

Kinetics of Adsorption

The straight line plots of Log (qe – q) versus t for dye at different biomasses under the used condition indicated the validity of equation (3) and the process followed first order kinetics. The transport of the adsorbate from the bulk solution to the interior surface of the pores being the rate limiting step of the adsorption process.

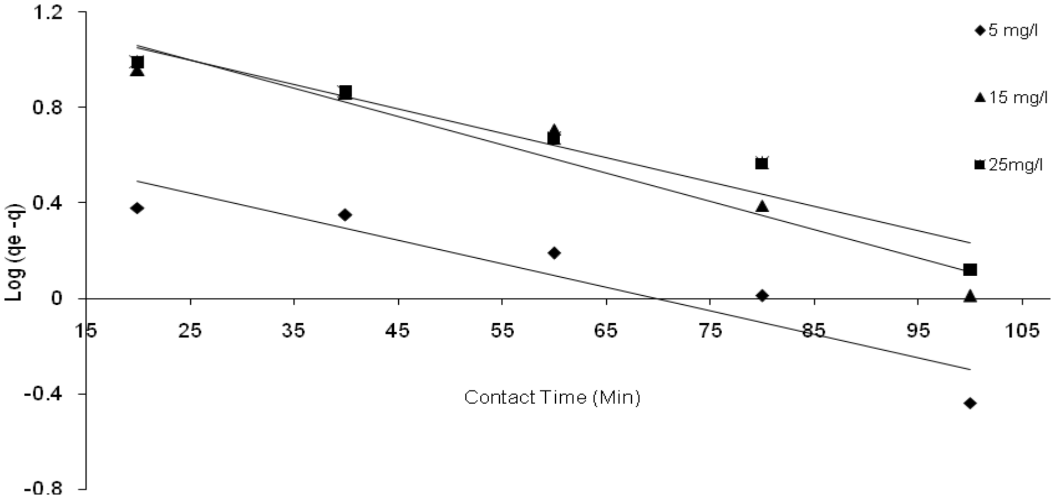


Figure 9: Lagergeren first order plot showing the kinetics of adsorption of adsorbents

The rate-determining step was mainly controlled by intra-particle diffusion. This is buttressed by figure 10 which shows that brilliant orange dye having more linear structure diffuses faster into the adsorbent compared to the brilliant green dye that has a more ranked structure.

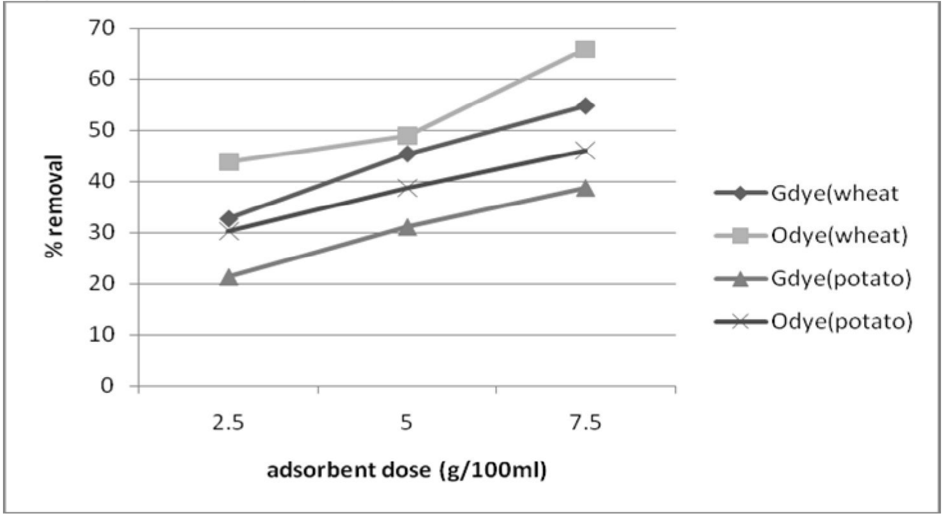


Figure 10: Effect of dye structure on dye removal

Conclusions and Recommendations

The results obtained revealed that the use of agricultural wastes such as potato peel, rice husk and wheat husk in treating vat and reactive dye effluents was highly efficient, with maximum adsorption occupying between 50 – 60 % range. While other workers had reported higher % dye removal using other agricultural wastes, the high abundance of the agricultural wastes investigated in this work and makes them potentially attractive at virtually no cost. Furthermore, the fact that these wastes can be put to good use and not left to rot away, creating environmental pollution and hazard, makes them potential alternatives to commercially activated carbon. An interesting observation was the fact that activated potato adsorbent showed poorer equilibrium exhaustion compared to the raw form. The results also showed that adsorption was dependent on the contact time (Figures 2 & 3), adsorbent dose (Figures 4 & 5), and dye structure (Figure 10). The efficiency percentage removal also showed that the combination or mixture of two adsorbent is sometimes better than the individual effect.

These agricultural wastes especially the raw potato and activated rice husk are therefore recommended for the removal of colour from waste waters containing dyes, since they are locally available and cheap.

References

Abdulwahab, O. et al. (2005). Use of rice husk for adsorption of direct dyes from aqueous solution from the journal of aquatic research, Egypt.

Allen, S. J. & Koumanova, B. (2005). Decolourization of water / wastewater using adsorption (review). *Journal of the University of Chemical Technology and Metallurgy*, 40(3), 175-192.

Aloko, D. F. & Adebayo, G. A. (2007). Production and characterization of activated carbon from agricultural waste (rice husk and corn-cob). *Journal of Engineering and Applied Sciences*, 89, 440-444.

Dauda, B. M., Kolawole, E. G. & Abegunde, T. T. (2012). Use of agricultural waste in colour removal form textile mill effluent containing direct and vat dyes. *Nigerian Journal of Material Science and Engineering*, 3 (1), 64-70.

Edmund, B. B. & Max, S. (1976). *The treatment of industrial wastes*, second edition. London: Mc Graw Hill Inc., pp. 242-259.

Itodo, A. U. & Itodo, H. U. (2002). Activation chemistry and kinetics of shea nut shell biosorbents for textile waste water treatment. *Journal of Pure and Applied Sciences*, 68, 51-60.

Kushwaha, S., Suparna, S. & Padmaja, P. (2008). Equilibrium, kinetics and thermodynamic studies for adsorption of Hg (II) on palm shell powder. *Water Resources Journal*, 43,600-606.

Lee, C. K., Low, K. S. & Chow, S. W. (1996). Chrome sludge as adsorbent for colour removal. *Environmental Technology,* 17, 261-266.

Malik, P. K. (2003). Use of activated carbons prepared from sawdust and rice husk fro adsorption of acid dyes: A case study of acid yellow 36. *Dyes and Pigments*, 4, 56-59.

Namasivayam, C. & Kavitha, D. (2003). Adsorption removal of 2-chlorophenol by low cost coir pitth carbon, *Journal of Hazardous Materials,* 1, 16-23.

Nkeonye, P. (1987). *Fundamental principles of textiles dyeing, printing and finishing*. Zaria: Ahmadu Bello University press.

Nkeonye, P. (2009). *Textile preparatory processes and waste liquor treatment*. Zaria: Asekome & Co publishers.

Trivedi, H. C., Patel, V. M. & Patel, R. D. (1973). Adsorption of cellulose triacetate on calcium silicate. *European Polymer Journal,* 9, 28-37.