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Investigations of the Adsorption of Congo Red Dye from Aqueous Solution on Modified Indian Goose Grass (*Elucine indica*)

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Abstract

Adsorption of Congo red dyes on a modified leaf powder of *Eleusine indica* from aqueous solutions was studied. The potentials for adsorption of Congo red dye at different initial concentration were carried out (10mg/250ml, 30mg/250ml, 50mg/250ml, 70mg/250ml, and 90mg/250ml) using different mesh size. The experiments were carried out in a batch system to optimize variable: pH, contact time, concentration, and adsorbent size for the different adsorbent dosage of 250mg in 250ml of dye solution. The pH, contact time, concentration and adsorbent particle size are the major influencing factors for the adsorption process in all the experimental runs. At the end of the experiment, it was observed that the lower the size of the adsorbent the higher the adsorption of the dyes, the study also shows that the percentage adsorption of Congo red increase with time and decrease sharply with increase in the initial dye concentration but later became gradual. The result also shows that adsorption progress favourably in acidic medium.

Keywords

Congo Red, Eleucine indica, Adsorption, Spectrophotometer

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1. Introduction

Dye, a constituent that is widely used in textile, paper, plastic, food and cosmetics industries is an easily recognized pollutant (Onget al., 2007). Decolourizing of textile and manufacturing waste water is currently a major problem for environmental managers (Ho and Chiang, 2001). Dyes may significantly affect photosynthetic activities in aquatic life due to the presence of aromatics, metals, chlorides and others elements in them (Hammed and El-Khaiary, 2008). Many of the dye used in the industries are stable to light and oxidation, as well as resistance to aerobic digestion (Gupta et al., 2003). However, dyes usually have a synthetic origin and complex aromatic molecular structure which makes them more stable so they are not biodegradable and photodegradable; it brings some difficulties for the treatment

of these pollutants (Chen and Zhao, 2009).

Physicochemical processes are generally used to treat dye waste water. These processes include flocculation, electro flotation, precipitation, electro kinetic coagulation, ion exchange, membrane filtration electrochemical destruction, irradiation, and ozonation. However, all these processes are costly and cannot be used by small industries to treat wide range of dye waste water (Mall *et al.*, 2005). The adsorption processes provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require additional pretreatment step before its application (Janos *et al.*, 2003).

Adsorption is known to be a better technique, which has great

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importance due to ease of operation and comparably low cost of application in decoloration process (Eren and Afsin, 2007). Activated carbon is the most widely used adsorbent with great success due to its large surface area, microporous structure and high adsorption capacity. However, its use is limited because of high cost. This has led to search for cheaper substituents (Karaolu *et al.*, 2010).

Increase awareness of the pollution problem related to the discharge of toxic dye in environment with increasing stringent regulatory standard led to an increasing focus on treatment process to remove or reduce the dye content in waste stream and run offs prior to discharge to the environment. The purpose of the study is to determine the extent of the adsorption of dye of Congo red in aqueous solution by using modified leaf powder of stubborn grass. Elucineindica (Indian goose grass) is an invasive species of the grass family poaceae. It is a perennial plant that is widely distributed in Africa, Asia, America and Australia. It can easily displace desirable vegetation. It has been used in the adsorption of Zn (II) ion from aqueous solution. It was found to have potentials for removing Zn²⁺ from industrial waste water (Adeboye et al., 2009). The result from this study shall help to increase the awareness of the populace to the presences, effect and ways of removing or treating dyes in our waste water.

2. Materials and Method

Elucine indica leaves were collected from the surrounding area of Emmanuel Alayande College of Education in Oyo. The leaves were washed with distilled water to remove dirt and were dried in an oven at 100° C for 12hours to avoid thermal deactivation of the surface of the adsorbent (Schiban et al., 2006). The leave was grinded and sieved into two different particle sizes of 1.18 and 1.40millimeter. Analytical grade Congo red dye having molecular formulae $C_{32}H_{22}N_6Na_2O_6S_2$ was used as adsorbate.

2.1. Activation of the Sample

The adsorbent was activated in order to increaseits surface area so as to increasethe adsorption rate. 40gram of fine particle of leaf powder of each off the two size (1.18mm & 1.40mm) were mixed with 20ml tetraoxosulphate (VI) acid (H₂SO₄) and 20ml concentrated trioxonitrate (V) acid (HNO₃). The sample was activated in a fume cupboard in order to avoid inhaling of dangerous gas. The samplewas allowed to cool in air after whichdeionize water was used to wash it and was filtered off; the samplewas washed with deionize water several times to remove any dirty materials present and was then placed in a desiccator for three weeks to dry before use.

2.2. IR Characterization of the Leaf Plant

The IR characterization (Table 1) was done using infrared spectrophotometer. The possible functional groups present in *Elucine indica* are shown in Table. This shows that the most abundant functional group present are sulfonyl, S-O, amine N-H, carbonyl C-O and hydroxyl O-H

Table 1. IR Characterization (cm⁻¹).

Functional Group	IR Frequency	
Carbonyl	C-O	1718-1735 cm ⁻¹
	C-O	1107-1300 cm ⁻¹
Amine	N-H	3400-3600 cm ⁻¹
Hydroxyl	О-Н	1159-1384 cm ⁻¹
Aromatic	С-Н	590-890 cm ⁻¹
Alkane	С-Н	1380-1470 cm ⁻¹
Carboxyl	СООН	3400 cm ⁻¹ - Broad
Sulfonvl	S-O	592 cm ⁻¹

2.3. Adsorption Equilibrium Experiment

The batch adsorption technique was used because of its simplicity. Batch adsorption studies were carried out by observing the effect of experimental parameters namely pH, size of adsorbent, contact time and concentration. 0.25g (250mg) of modified leaf powder was added to 250ml of dye solution in a conical flask. The mixture was agitated continuously for 1hours as the equilibrium time. uptake of Congo red were determine from the difference of Congo red concentration ranging from 10mg/250ml, 30mg/250ml, 50mg/250ml, 70mg/250ml, 90mg/250ml respectively. The suspension was filter off and the filtrates were analyzed for residual Congo red (CR) concentration by UV-Visible spectrophotometer at 498nm. The amount of Congo red uptake by modified leaf powder of the goose grass (Eleusine indica) in each flask was calculated using the mass balance equation.

$$q = (C_0 - C_1) \left[\frac{V}{W} \right]$$

Where q is the amount of Congo red adsorbed by leaf powder of stubborn grass

C₀is the initial concentration of dye

C₁ is the final concentration of dye

V is the volume of solution (L) = 250ml

W is the adsorbent weight - dosage = 250mg

The dye percentage (%) removal was calculated using the equation below

Percentage of dye removed =
$$\frac{C_0 - C_1}{C_0} \times 100$$

2.4. Adsorption Kinetic Experiment

For kinetic studies of 10mg/250ml, 30mg/250ml,

50mg/250ml, 70mg/250ml, 90mg/250ml Congo red as the initial concentration each were treated with 250mg (0.25g) of the adsorbent (modified leaf powder of a goose grass). The mixtures were then subjected to agitation using shaker at 180rpm. Mixture were taken from the thermostated shaker at appropriate time interval (20minutes, 30minutes, 40minutes, 50minutes, and 60 minutes) and the left out concentration in Congo red solution were analyzed by UV-Visible spectrophotometer at 498nm. The amount of Congo red uptake by the modified goose grass leaf powder was calculated using the mass balance equation

$$q = (C_0 - C_1) \left[\frac{V}{W} \right]$$

Where q is the amount of Congo red adsorbed by leaf powder of stubborn grass

 C_0 is the initial concentration of dye

 C_1 is the final concentration of dye

V is the volume of solution (L) = 250 ml

W is the adsorbent weight - dosage = 250mg

The dye percentage (%) removal was calculated using the below equation

% of Congo red removed =
$$\frac{C_0 - C_1}{C_0} \times 100$$

Where C_0 is the initial concentration of Congo red and C_1 is the final concentration of Congo red respectively.

2.5. Effect of pH On Experiment

To study the effect of pH on Congo red adsorption, 250 mg of leaf powder of stubborn grass (adsorbent) was added to solution containing 30mg/250ml of Congo red. The initial pH values were adjusted to 3, 4, 5, 10, 11, 12 by adding 0.1M HCl and NaOH. The flasks were shaken for the specified time (60 minutes) in a thermostated shaker. The flasks were withdrawn from the shaker after the desired time of reaction and analyzed for residual Congo red concentration.

3. Result and Discussion

3.1. Effect of Contact Time

Adsorption of Congo red on modified goose grass, *Elucine indica* was studied for about 1 hour (20, 40 and 60minutes)using two different particle sizes of adsorbent (1.18mm and 1.40mm). Tables 2-4 showed the effect of contact time, different adsorbent size and concentration on the rate of adsorption of Congo Red. It indicated that as the concentration of Congo red increases, the percentage of Congo red adsorbed decreases. Hence the rate of adsorption decreases progressively (Figure 1), this result is related to adsorption of basic dyes on activated carbon prepared from Polygonumorientale Linn by (Wang *et al.*, 2010) and adsorption kinetics for the removal of hazardous dye Congo red by biowaste materials as adsorbents by (Sumanjit *et al.*, 2013).

Table 2. Showing Result for 20minutes Contact Time.

Initial Congo red (CR)	For 1.18mm Particle size			For 1.4mm Particle size		
conc. (mg/250ml(Co)	Final Congo red conc(C _i)	Amount of Congo red adsorbed(q)	% of dye adsorbed	Final Congo red conc (C_l)	Amount of Congo red adsorbed(q)	% of dye adsorbed
10	8.047	1.953	19.53	8.220	1.780	17.80
30	28.078	1.916	6.41	28.237	1.763	5.88
50	48.182	1.818	3.64	48.493	1.507	3.01
70	68.262	1.738	2.48	68.736	1.264	1.81
90	88.300	1.700	1.88	88.888	1.192	1.24

Table 3. Showing Result for 40minutes Contact Time.

Initial Congo red (CR)	For 1.18mm Particle size			For 1.4mm Particle size		
conc. (mg/250ml(Co)	Final Congo red conc(C _i)	Amount of Congo red adsorbed(q)	% of dye adsorbed	Final Congo red conc(C _i)	Amount of Congo red adsorbed(q)	% of dye adsorbed
10	8.072	1.928	19.28	8.310	1.690	16.90
30	28.091	1.909	6.36	28.551	1.449	5.07
50	48.223	1.777	3.55	48.800	1.164	2.40
70	68.293	1.707	2.44	68.973	0.988	1.46
90	88.383	1.617	1.80	89.244	0.690	0.84

For 1.18mm Partic		le size For 1.4mm Particle size				
Initial Congo red (CR)	Final Congo red	Amount of Congo	% of dye	Final Congo	Amount of Congo	% of dye
conc. (mg/250ml(C)	conc(C1)	red adsorbed(q)	adsorbed	red conc(C1)	red adsorbed(q)	adsorbed
10	8.108	1.892	18.92	8.371	1.629	16.29
30	28.174	1.826	6.09	28.579	1.421	4.74
50	48.270	1.730	3.46	48.852	1.148	2.30
70	68.384	1.616	2.31	69.059	0.943	1.35
90	88.489	1.511	1.68	88.379	0.621	0.69

Table 4. Showing Result for 60minutes Contact Time.

As the contact time increases (Table 5), the percentage removal of Congo red decreases (Figure 1), these also compare favourably with the use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution reported by Mane *et al.*, 2007 and Nakbanpote *et al.*, 2002. Also it was noted that the smaller the particle size, the higher the percentage of dye adsorbed.

Table 5. Percentage of Congo red dye adsorbed with time.

Time (min)	% adsorbed with 1.18mm particle size	% adsorbed with 1.4mm particle size
20	6.78	5.95
40	6.68	5.33
60	6.49	5.07

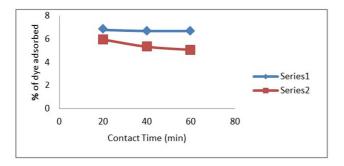


Figure 1. Plot showing the effect of contact time on the percentage of congo red dye adsorbed.

3.2. Effect of Dye Concentration

The adsorption capacity decreases with increase in the initial dye concentration (Table 6). Initially there was a sharp decrease (Figure 2) but at about 50mg/L it became gradual. This was obtained when Elucine indica was used in the adsorption of zinc ion from solution (Adeboye et al., 2009). This is an indication that there is increase in the dye/biomass ratio which leads to a decrease in the efficiency of adsorption and as reported (Babarinde et al., 2008) it may be due to the saturation of the available binding site on the biomass. However, the amount of dye adsorbed per unit mass of the modified Elucine indica increased with increase in the dye concentration. This simply shows that adsorption is independent on the initial concentration of the dye because at very low concentration, the ration of the initial number of dye molecule to the available surface area is low, this makes the adsorption independent of the initial concentration but at high concentration the binding site is fewer, and this thus makes the adsorption dependent on the initial concentration.

Table 6. Effect of dye concentration of the Percentage adsorbed with different particle adsorbent sizes.

Conc	% adsorbed with1.18mm	% adsorbed with 1.40 mm
(mg/L)	Particle size	Particle size
10	19.24	16.99
30	6.28	5.28
50	3.55	2.57
70	2.41	1.54
90	1.78	0.59

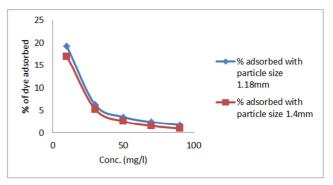


Figure 2. Effect of initial dye concentration on adsorption.

3.3. Effect of pH on Percentage Adsorption

Table 7 and 8 shows the percentage of dyes adsorbed at different pH on the adsorbent with the two different particle sizes. The result obtained showed that as the acidity increases from 5-3, the percentage of adsorption of Congo red dye from aqueous solution also increases but the table of values of the adjusted alkalinity of the two adsorbent particle sizes shows that as the alkalinity increase from 10-12 and the rate of adsorption of Congo red decreases (Figure 3). The change in the percentage removal over this pH range 3-12 is and indication that a strong force exist between the dye and the modified adsorbent and this shows that H⁺ and OH⁻ ions could influence the adsorption capacity (Figure 3). The interaction is larger at pH 5 due to the effect of the H⁺ ion with dye cation for the sorption sites. The percentage of adsorption increases above this pH value due to the presence of COOH groups and it also shows that adsorption of dyes on the modified leaf powder involves ion exchange mechanism. This result is comparable with the result obtained from removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid

waste by Namasivayam and Kavitha, (2002) and Namasivayam *et al.*, 1996 and on acid activated carbon (Hema and Arivoli, 2006.

Table 7. Showing the effect of pH on the adsorption of 1.18mm particle size of Congo Red Dye.

pН	Initial Congo red (CR) conc. (mg/250ml(Co)	Final Congo redconc(C ₁)	Amount of Congo red adsorbed(q)	% of dyeadsorbed
3	30	29.02	0.980	3.26
4	30	29.01	0.990	3.30
5	30	28.99	1.010	3.37
10	30	29.50	0.500	1.67
11	30	29.58	0.420	1.40
12	30	29.62	0.380	1.26

Table 8. Showing the effect of pH on the adsorption of 1.40mm particle size of Congo Red Dye.

pН	Initial Congo red (CR) conc. (mg/250ml(Co)	U	Amount of Congo red adsorbed(q)	% of dye adsorbed
3	30	28.23	1.770	5.90
4	30	28.16	1.840	6.13
5	30	28.14	1.860	6.20
10	30	28.82	1.180	3.93
11	30	29.08	0.920	3.06
12	30	29.23	0.770	2.57

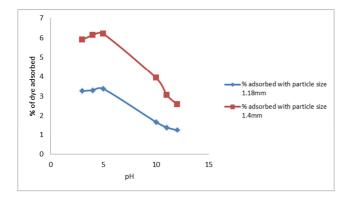


Figure 3. Plot showing the effect of pH on the % Congo red adsorbed.

3.4. Comparison of Adsorption Capacity of Congo Red on *Elucine indica* with Other Low Cost Adsorbent

Adsorption capacity of congo red on low cost adsorbent Table 9 showed that adsorption of *Elucine indica* is very low compared with other adsorbents. It can be observed that *Grewia asiatica* leaves, Cashew nut Shells, Guava (*Psidium guajava*) leaf powder and Waste banana pith exhibited high adsorption capacity. This may be due to the activation process, initial carbon content and pore development which may be as result of the morphology of the low cost materials (Garg *et al.*, 2004).

 Table 9. Comparison of adsorption capacity of congo red with other low cost adsorbent.

Adsorbents	pН	% Adsorption	References
Altemanthera bettzichiana plant	5	80.5	Patil and Shrivastara, 2010
Cashew nut Shells	3	93	Kumar et al., 2010
Guava (Psidiumguajava) leaf powder	1	93	Naidu et al., 2010
Waste banana pith	2	92	Namasvayam and Kanchana, 1993
Ball-milled sugar cane	5	84.70	Zhang et al., 2011
Raphaussativa peels	3	87.26	Rehman et al.,2012
Grewiaasiatica leaves	7	96.35	Rehman et al., 2012
Activated Carbon	2	95.6	Rehman et al., 2012
Elucineindica (Indian goose grass)	3	19.24	Present Study

4. Conclusion

The adsorption of Congo red on modified leaf powder of stubborn grass (Elucine indica) was examined at different experimental condition. The result showed that the rate of adsorption increases with decrease in concentration. Increase in the contact time decrease the rate of adsorption. Also, the adsorption of dyes is pH dependent and this study showed that the adsorbent adsorbed better in acidic medium than in alkaline medium. Effect of particle size showed that there is increase in the removal efficiency with decrease in particle sizes. this is as a result of the presence of more surface area which becomes readily available for the dye to make attraction with the modified Elucine indica. So modified grass of mesh size 1.18 mm should be used. Though the adsorption capacity of the Elucine indica is very low compared with other low cost adsorbent, it is very cheap, readily available and eco-friendly. So it can be substituted for expensive activated carbon for economical treatment process for dye removal from industrial effluent

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