

Assesment of Ground Nut Husk as a Sorbent in the Decolourization of Congo Red Contaminated Aqueous Medium

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Abstract: Groundnut husk is a common agricultural waste in Nigeria and it's used as an adsorbent for the removal of congo red (CR) from aqueous system. The present study investigated the ability of groundnut husk to abstract congo red (CR) from aqueous solution. The process of sorption of Congo red from solution was analysed using 2 different isotherm models (Langmuir and Freundlich, isotherm equations). The highest values of r^2 were obtained when the experimental data were fitted into Freundlich equation (0.984). The sorption of Congo red by groundnut husk was found to be affected by the sorbent dose, temperature, pH and initial Congo red concentration. The kinetic data showed that the sorption capacity of groundnut husk for the congo red increased with increasing initial dye concentration, while a reverse trend was observed when the effect of sorbent dosage was studied. Analysis of the data obtained from the different sorption studies revealed that the data fitted better to the pseudo-second order model than pseudo first order kinetic model, indicating that the sorption process will include chemisorptions of congo red on groundnut husk.

Key words: Congo red • Groundnut husk • Adsorption • Kinetic • Pseudo Orders • Monolayer

INTRODUCTION

Many industries, such as textile, dyestuff manufacturing, leather tanning, food preparation, paper kiproduction and printing, use dyes that produce highly colored waste effluents. These dyes can consume the dissolved oxygen required by aquatic life and some of them are directly toxic to microbial populations and can even be carcinogenic to mammals [1]. In addition, dyes are resistant to light and moderate oxidative agents, so they cannot be completely removed by conventional biological treatment processes, such as activated sludge or anaerobic digestion [2]. A wide range of methods has been developed and used for the removal of dye contaminants from wastewater. These technologies involve adsorption on inorganic matrices, decolorization by photocatalysis and/or oxidation, microbiological or enzymatic decomposition and so on [3]. Adsorption has been recognized as the most popular treatment process for the removal of non-biodegradable organics from aqueous systems, with activated carbons being the most common adsorbent for this process because of their

effectiveness and versatility [4]. However, the use of this type of adsorbent in wastewater treatment is still limited because of its high cost and difficulty in regeneration [5]. In recent years, the use of soil clay materials to replace commercially available adsorbents has become popular because of their low cost, ready availability, lack of toxicity and potential for ion exchange [6]. Their unique properties, such as a high specific surface area and surface chemistry for example, give these materials a broad range of applications [7]. In the present study, the use of groundnut husk in the attenuation of a model anionic dye (CR) in an aqueous stream shall be explored.

MATERIALS AND METHODS

Sorbate Preparation: The dye used in the present studies, CR (C.I. 2212), chemical formula = $C_{32}H_{22}N_6Na_2O$ ($\lambda_{max} = 500 \text{ nm}$) was accurately weighed and dissolved in distilled-deionised water to prepare the stock solution (500 mg L^{-1}). Different working solutions were prepared from the stock solution by serial dilution.

Sorbate Quantification: The CR concentrations in the aqueous medium were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/ Visible spectrophotometer. Standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance (λ_{\max}), as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve used in the present studies.

Sorbent Preparation: The groundnut husk was obtained from a small scale vegetable oil processing factory, situated in Owo, Ondo State, Nigeria. The groundnut husk was washed thoroughly with deionised water, to remove any attached dirt and soluble impurities, dried in the open air and then pulverized. The powder was sieved using a laboratory sieve and the 100 μ m fraction was separated. The powder was later dried in the oven at 80°C and kept in a sealed polythene bag pending usage as an adsorbent.

Characterisation of Groundnut Husk: The point of zero charge (PZC) of the groundnut husk was determined by solid addition method⁸ viz. to a series of 100 mL conical flasks, 45 mL of 0.1 M KNO₃ solution was transferred. The pH₀ values of the solution were roughly adjusted from 2 to 12 by adding either 0.1 N HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO₃ solution. The pH₀ of the solutions were then accurately noted. Groundnut husk (1 g) was added to each flask and securely capped immediately. The suspension was then agitated intermittently for 24 hours to equilibrate. The pH values of the supernatant liquid were noted. The difference between the initial pH (pH₀) and final pH (pH_f) values (Δ pH) (pH₀ - pH_f) was plotted against the pH₀. The point of intersection of the resulting curve at which Δ pH = 0 gave the PZC.

Evaluation of Groundnut Husk Sorption Capacity Using Adsorption Isotherm: The sorption isotherm capacity was investigated using different initial concentration (mg/L) of congo red (25, 50, 100, 150, 200 and 300). A typical experiment was conducted by weighing 0.1g of the groundnut husk sample into 50ml of known concentration of congo red and then agitated at a constant speed of 200 rpm using magnetic stirrer. Samples were withdrawn after the agitation period, diluted and centrifuged for

10 min at 12,000 rpm and the absorbance of the supernatant solution was measured and analyzed for the residual congo red concentration in the aqueous solution by UV/Visible spectrophotometer at λ_{\max} of congo red (500nm).

Effect of Groundnut Husk Dosage: On the effect of groundnut husk dosage, the equilibrium uptake of congo red was studied at 309 K with sorbent dosage of 0.1, 0.2, 0.4, 0.6 and 0.8 g of groundnut husk in contact with dye solution of concentrations ranging from 50-300 mg L⁻¹. The flasks were agitated at 200 rpm for 2 h and the equilibrium concentration of the residual dye was determined spectrophotometrically.

Thermodynamic Studies: Effect of temperature was performed at temperatures ranging from 150 K to 600 K, at a fixed sorbent dosage (0.1 g) and initial congo red concentration from 25-300 mg L⁻¹. The flask was shaken at 200 rpm for 2 h and the equilibrium concentration of the residual dye was determined spectrophotometrically.

Effect of pH: The effect of pH on the uptake of CR by groundnut husk was studied by measuring 50mls of 200mg/L of CR prepared in four different conical flasks. The pH of the solutions in the five conical flasks were adjusted to 3, 5, 8, 10 and 12 using either dilute HCl or NaOH. Accurately weigh 0.1g of the sample were added to each of the solution, previously adjusted to the desired pH. It was agitated at 200rpm for 120 minutes at ambient temperature. Samples were withdrawn after the agitation period and analyzed for the residual CR concentration.

Effect of Initial Concentration on Sorption Kinetics: The kinetics of the sorption of Congo red unto groundnut shell sample was studied at different initial Congo red concentration (25, 50, 100, 150, 200 and 300mg/L) for 240minutes. A typical experiment procedure was conducted by measuring accurately a litre of Congo red solution of a known concentration into a beaker and 2g of groundnut husk sample was added and agitated at 200rpm for 240 minutes. The experiment was carried out at room temperature (36°C). Samples were withdrawn at fixed time intervals viz: (2, 10, 20, 30, 60, 90, 120, 180 and 240 mins), centrifuged and the supernatant was analyzed for residual Congo red concentration using UV/spectrophotometer.

RESULT AND DISCUSSION

Characteristics of Groundnut Shell: The point of zero charge (PZC) was obtained at pH value of 6.4 (Figure 3.1). The point of zero charge (PZC) describes the condition when the electrical charge density on a surface is zero. In other words, the PZC is usually the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface. The value of pH is used to describe the PZC only for system in which H^+/OH^- are the potential-determining ions. Below the point zero charge, the surface of the groundnut husk is predominantly positive while above the point zero charge the surfaces is negatively charged [9]. This also affects the protonation and deprotonation of surfaces which is common with oxides and hydroxides surfaces.

Determination of Sorption Capacity of Groundnut Husk Using Adsorption Isotherm: In order to understand the mechanism of CR sorption by groundnut husk and evaluate the relationship between the CR on the groundnut husk and in solution, the experimental data were fitted into two different isotherm equations; the Langmuir and Freundlich isotherms equations. The constant parameters of the isotherm equations for this adsorption process were calculated by regression using the linear form of the isotherm equations. The Langmuir and Freundlich parameters and their correlation coefficients (r^2) were calculated and presented in Table 3.1. An error function is required to evaluate the fitness of each isotherm equation to the experimental data obtained from the optimization process employed. In the present study, the linear coefficient of determination (r^2) was used. The highest value of r^2 was observed when the experimental data obtained from the sorption of CR by groundnut husk samples were fitted into Freundlich isotherm equation (0.984). The description of the sorption of CR on groundnut husk by the Freundlich isotherm equation is a pointer to the heterogeneity of the surface with a non-uniform distribution of heat of adsorption over the surface of the groundnut husk. These heterogeneous adsorption sites are very much similar to each other in respect of adsorption phenomenon [10]. The values of the reciprocal of n (i.e $1/n$), (0.0562) which is less than unity is an indication of the favorable nature of adsorption of the CR on groundnut husk. Also the capacity for the adsorbability of the solute (K_1) on groundnut husk is high.

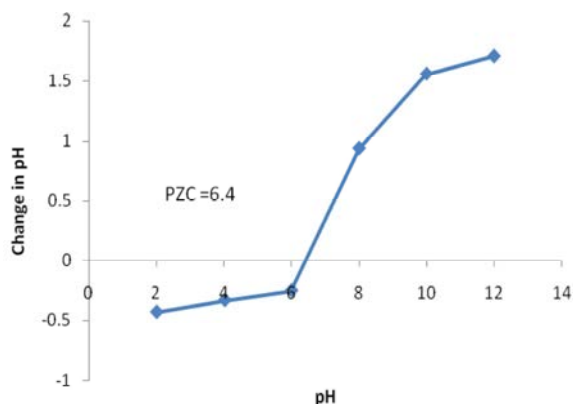


Fig. 3.1: Point of zero charge

Table 3.1: Freundlich and Langmuir parameters.

Langmuir	Freundlich
$q_m = 76.24$	$K = 10.321$
$b = 0.0367$	$1/n = 0.0562$
$r^2 = 0.955$	$r^2 = 0.984$

The Langmuir sorption capacity ($q_m = 76.24$) obtained from the present study were compared with the values obtained by other researchers from the use of other sorbents for the removal of some anionic dyes from aqueous solution (Table 3.2). The result presented in Table 3.2 showed that the groundnut husk compared favorably with the other adsorbents that have been used and the Langmuir sorption capacity was higher than the other adsorbents.

Effect of Groundnut Husk Dosage : The results presented in Table 3.3 show that as the groundnut husk dose was increased from 0.1 to 0.8g/50mL, a reduction was observed in the values of the monolayer sorption capacities, q_m , from 80.52 to 19.66 $mg\ g^{-1}$. The reduction in the sorbent capacity, i.e. the amount of congo red sorbed per unit weight of sorbent with increase in ground nut husk dose could be ascribed to two reasons: the increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process [19, 20] and secondly may be due to particulates interactions. Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length¹⁹. The value of the sorption equilibrium constant, b , increased with increase in the sorbent dose.

Thermodynamic Studies: The amounts of CR adsorbed on the groundnut husk increased with the increasing temperature of adsorption (Figure 3.2). This is because the

Table 3.2: Comparison of Monolayer Equilibrium Capacity for Some Anionic Dyes with Other Biosorbents.

Q_m (Mg/g)	Adsorbent	Adsorbate	Reference
76.24	Groundnut husk	Congo red	This work
38.60	Palm kernel fiber	4-bromoaniline-azo-1,8-dihydronaphthalene -3,6-disodium sulfate	11
30.50	Spent brewery grains	Acid Orange	7 12
22.40	Orange peel	Congo Red	13
19.88	Orange peel	Acid Violet	17 14
14.40	Peat	Acid Blue	15
4.42	Banana pith	Acid Brilliant Blue	16
4.26	Sugar cane dust	Rhodamine B	17
3.23	Orange peel	Rhodamine B	17
1.33	Orange peel	Procion Orange	13
66.23	Palm kernel seed coat	Congo Red	18

Table 3.3 : Effect of groundnut husk dosage

m_s (g/50mL)	q_m (mg g ⁻¹)	b (Lmg ⁻¹)	r^2
0.1	80.52	0.033	0.9753
0.2	60.74	0.052	0.9923
0.4	46.77	0.061	0.9936
0.6	25.83	0.098	0.9941
0.8	19.66	0.175	0.9958

diffusion of CR molecules in the aqueous phase is gradually faster with an increased temperature of adsorption and this thereby promotes the exchange interaction between the CR molecules and cations on the groundnut husk surface.

Effect of pH: The CR solution pH optimization (Fig 3.3) revealed a monotonic reduction in the magnitude of CR sorbed with increase in pH value and the amount of

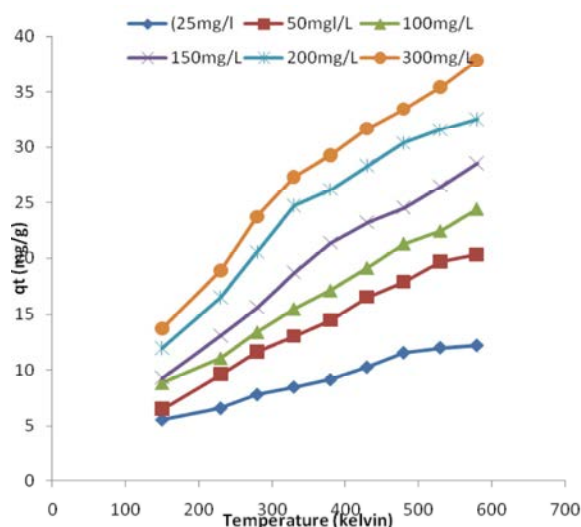


Fig. 3.2: Effect of temperature on the adsorption of CR on groundnut husk

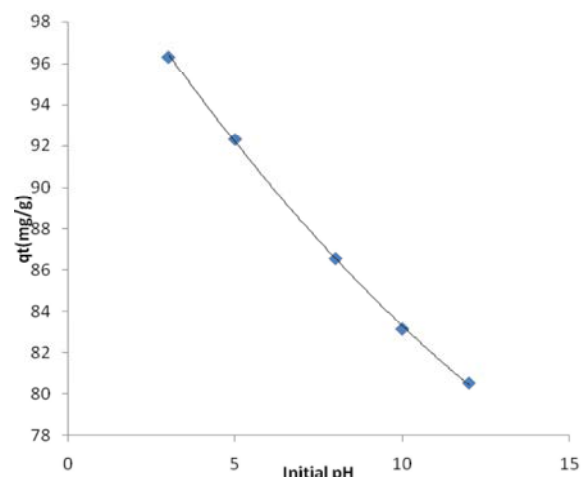


Fig. 3.3: Effect of pH on the uptake of CR by groundnut husk

sorbate sorbed became negligible at the highest pH studied. Lower pH values favoured the removal of the CR moieties than higher pH values. The curve shows that CR adsorption on groundnut husk could be linked to a simple anion/ OH^- exchange reaction on the groundnut husk surface. In the case of a simple anion exchange, anion uptake decreases monotonically with pH due to the increase of OH^- concentration and the change of surface charge to negative [21]¹.

Effect of Initial Concentration on Sorption Kinetics:

The results presented in Figure 3.4 show the effects of initial concentration on the time-concentration profile of congo red adsorption on groundnut husk. It was observed that the amount of Congo red (mg/g) adsorption by the groundnut husk increased with increase in the congo red concentration. The amount of the congo red uptake also increased with contact time and at some point

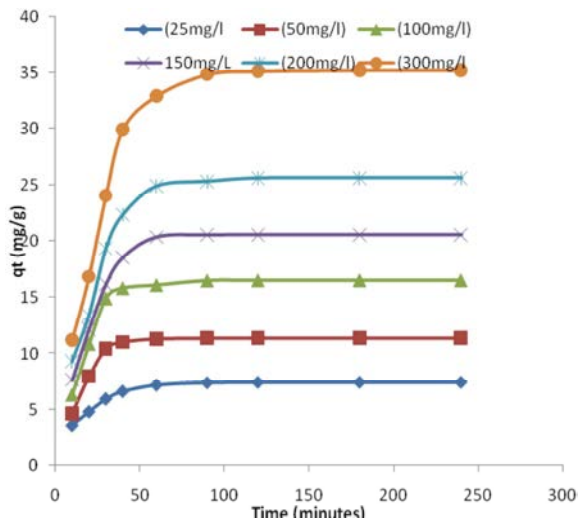


Fig. 3.4: Results of the effects of initial congo red concentration on the sorption of congo red by groundnut husk.

in time reached an almost constant value where the amount of dye being removed from aqueous solution onto the ground nut husk is in a state of dynamic equilibrium with the amount of dye desorbed from the groundnut husk. For each of the concentrations of congo red used in the present study, the greater amount of dye was removed within the first 30 min of study. This shows that the sorption of congo red onto ground nut husk is an extremely rapid reaction process. The rapid reaction rate could be ascribed to a large number of vacant sites available at the initial stage; as a result an increased concentration gradient exists between the congo red molecules in solution and on the adsorption surface. As the congo red ion loading increases, on the groundnut husk, this gradient reduces and gives way to slower uptake

Pseudo First Order and Pseudo Second Order Kinetics:

The result obtained, when the Pseudo first and pseudo second order kinetic model was used to test the data obtained from the sorption of congo red by groundnut husk sample, are presented in Fig. 3.5 and 3.6 respectively

The parameters derived from the pseudo first order kinetic model and the correlation coefficient (r^2) of the sorption of congo red on groundnut husk at different initial congo red concentration are presented in Table 3.4.

The values of the correlation coefficients of the pseudo first order were lower (0.013 - 0.435). The experimentally determined equilibrium congo red sorption capacity $q_{e(\text{exp})}$ was compared with the predicted values,

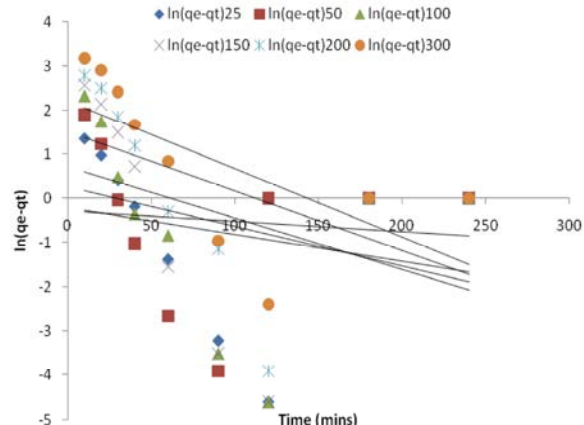


Fig. 3.5: Results of the pseudo first order kinetic plot of the sorption of congo red by Groundnut husk at different initial congo red concentration.

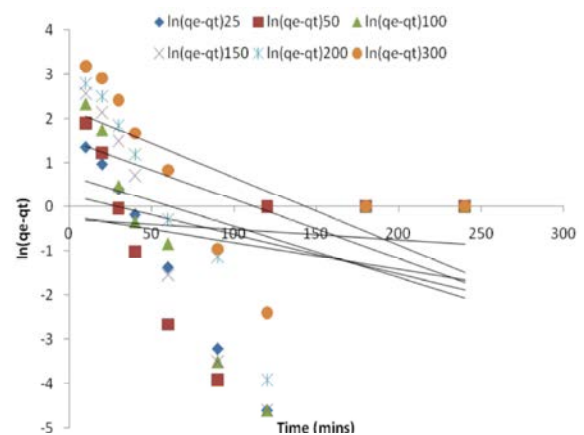


Fig. 3.6: Results of the pseudo second order kinetic plot of the sorption of congo red by Groundnut husk at different initial congo red concentration.

Table 3.4: Pseudo First Order Kinetic Parameters of the Sorption of congo red by groundnut husk at Different Initial congo red Concentration.

Initial conc.(mg/L)	q_{exp}	q_{cal}	K_1	r^2
25	5.49	0.994	0.213	0.069
50	9.40	0.998	0.299	0.013
100	14.57	0.991	0.230	0.109
150	18.58	0.989	0.684	0.156
200	23.68	0.987	1.455	0.282
300	33.25	0.985	2.081	0.435

from the pseudo first order plot q_e and a large disparity between the $q_{e(\text{exp})}$ and $q_{e(\text{cal})}$ values are pointers to the inability of the pseudo first order model to successfully describe this sorption process. The non fitting of the data to the pseudo first order kinetic model is an indication that

Table 3.5: Pseudo Second Order Kinetic Parameters of the Sorption of congo red by Groundnut husk at Different Initial congo red Concentration.

Initial conc.(mg/L)	q _{exp}	q _{cal}	K ₂	h	r ²
25	5.49	5.75	0.023	0.069	0.999
50	9.40	9.71	0.021	1.854	0.998
100	14.57	15.15	0.013	2.760	0.998
150	18.58	19.61	0.008	2.762	0.998
200	23.68	25	0.005	2.804	0.998
300	33.25	35.71	0.003	3.317	0.998

$k_1(q_e - q_t)$ does not represent the number of available sites and $\ln q_e$ is not equal to the intercept of the plot of $\ln(q_e - q_t)$ against t .

The pseudo second order parameters and the correlation coefficient values for the sorption of congo red by groundnut husk is shown in Table 3.5. The correlation coefficients for the pseudo second order kinetic plot ranged between 0.998 and 0.999. The linearity of the plots were very high when compared with pseudo first order. This extremely high value of r^2 for the sample confirmed that the sorption process followed a pseudo second order mechanism [22]. A similar phenomenon has been observed in the adsorption of nitrate onto various materials [23], arsenic (v) by modified calcined bauxite [24] and phosphate on dolomite [25]. The value of h and q_e increased with an increased in initial congo red concentration.

CONCLUSION

The result from the equilibrium adsorption studies showed that the capacity of the groundnut husk was 76.24 and when the data was tested, the data fitted the freundlich isotherm model than Langmuir which implies that the sorption of congo red by groundnut husk took place on the heterogeneous surface with a non uniform distribution of heat over the surface of the groundnut husk than monolayer coverage. The effects of sorbent dose, temperature and pH on the congo red uptake and initial congo red concentration on the rate of sorption were examined in the present studies. Increase in the sorbent dose leads to a reduction in the values of monolayer sorption capacity due to an increase in the number of binding sites on the surface of the sorbent as its dosage increased. The thermodynamics studies revealed that, increase in temperature leads to an increase in the amount of congo red sorbed by the groundnut husk due to an increase in the diffusion of congo red molecules in the aqueous phase. The result obtained from the optimization of the initial Congo red solution pH showed

that the congo red sorption by groundnut husk increased as the solution pH reduced. The sorption process was characterized by an initial rapid congo red uptake which slows down with time as the sorption process proceeds. The pseudo-second-order kinetic model was found to best fit the experimental data within the time range of sorption.

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