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Removal of Congo Red from Aqueous Solutions Using Fly Ash Modified with Hydrochloric Acid

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Authors' contributions

This work was carried out in collaboration between all authors. Authors ENA and AN designed the study, performed the statistical analysis, wrote the protocol and the first draft of the manuscript and managed literature searches. Authors ASS and WD managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The adsorption of Congo Red dye onto fly ash modified with various concentrations of Hydrochloric acid (HCFA-4,HCFA-3,HCFA-2 and HCFA-1)was studied. The effect of contact time and concentration were investigated using a batch adsorption technique. The experimental data fits well with the Freundlich isotherm due to high correlation coefficients and this may be attributed to heterogeneous distribution of active sites and multilayer adsorption, while the dynamic data is best described by the pseudo-second-order kinetic model which suggests that Congo Red adsorption onto fly ash modified with Hydrochloric acid appeared to be controlled by a chemisorption process. Fly ash modified with 2 M Hydrochloric acid HCFA-2 exhibited the highest adsorption capacity (K_F=7.82) followed by HCFA-3 (K_F = 0.74), HCFA (K_F = 0.069) and HCFA-1 had the least adsorption capacity (K_F =0.004). Adsorption of Congo Red dye onto fly ash modified with various concentration of Hydrochloric acid was spontaneous since Gibbs free energy of adsorption was negative in all cases.

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Keywords: Fly ash; isotherms; hydrochloric acid; Congo Red; adsorption kinetics.

1. INTRODUCTION

Man's quest for ultimate enjoyment has led to the exploitation of the natural environment to the extent of reducing its capacity for self sufficiency [1]. It is estimated that approximately 40,000 tonnes of dyes out of about 450,000 tonnes in total production are not used but discharged into waste waters [2]. Dyes have long been used in dyeing paper and pulp, textiles, plastics, leather, cosmetics and food in industries. The effluent discharges containing dyes from the afore mentioned industrial processes are not only aesthetically displeasing but also inhibit sunlight penetration into water bodies thereby creating negative impacts within the ecosystem [3]. Dyes also have complex aromatic molecular structures which make them more stable and difficult to biodegrade [1].

Similarly fly ash, a waste from coal fired power plants contain a range of toxic constituents such as heavy metals that can leach, leak or spill out of fly ash disposal sites and cause adverse effects on humans and environmental health [4]. Among a number of strategies the adsorption based process is considered to be more efficient for the removal of various pollutants in waste water [5]. Despite the prolific use of activated carbon in adsorption processes the biggest barrier of its application by the industries is the cost implication and difficulties associated with regeneration of the adsorbent [6]. Realizing the complication, a growing exploitation to evaluate the feasibility and sustainability of natural, renewable and low cost materials as alternative adsorbents in water pollution control, remediation and decontamination processes has been exerted [7]. Fly ash is an adsorbent that is low cost and readily available and its application for the decontamination of industrial effluents is gaining recognition as a cost effective and simple means of treating discharges [1]. This paper shows reports of the removal of Congo Red dye from aqueous solutions using fly ash modified with various concentrations of hydrochloric acid as adsorbents.

2. MATERIALS AND METHODS

2.1 Preparation of Modified Fly Ash

The fly ash used for this experiment was obtained from the Sasol plant in South Africa.10.0 g of unmodified fly ash was weighed into a 250 ml conical flask. 100 ml of varied concentrations of hydrochloric acid (1 M, 2 M, 3 M and 4 M) was added into separate conical flasks containing 10.0 g unmodified fly ash respectively and each conical flask was covered with a stopper. The slurries were stirred on a magnetic stirrer for 24 hours [8,9].

The samples were filtered and the solid extracts were oven dried and latter crushed into fine powders.

2.2 Preparation of Adsorbate Solution

0.3 g of Congo Red powder was dissolved in 1000ml of distilled water (300 mg/L), this served as the stock solution for serial dilutions into 25 mg/L, 50 mg/L and 100 mg/L respectively.

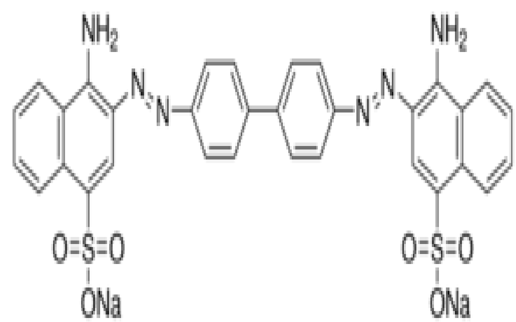

Fig. 1. Chemical Structure of Congo Red

2.3 Characterization of Fly Ash

Energy dispersive spectroscopy was applied to study the elemental components of fly ash.

2.4 Adsorption Studies

Equilibrium and kinetic adsorption experiments were conducted in batches at room temperature with a Stewart Reciprocating Shaker at 100 rotations per minute [10].

The contact time was evaluated on samples of 0.2 g of fly ash modified with various concentrations of HCl (i.e. fly ash modified with 4 M HCl, fly ash modified with 3 M HCl, fly ash modified with 2 M HCl and fly ash modified with 1 HCl) in 10 ml of dye solution, each sample was tested with 25 mg/L, 50 mg/L and 100 m/L of Congo Red solution for 60 minutes.

100 mg/L of Congo Red was tested on all modified forms of fly ash for 10, 30, 60 and 90 minutes respectively. The substrates were separated from supernatant with use of a centrifuging machine, operated for 10 minutes at 30 revolutions per minute [11,12]. Equilibrium concentrations of the supernatant were analyzed with Jenway 6,300 Spectrophotometer at λ_{max} = 665 nm after calibration.

2.5 Adsorption Isotherms

Congo Red adsorption on fly ash modified with HCl was analyzed using Langmuir type II, Freundlich and Florry – Huggins Isotherms.

The Langmuir Isotherm is used to characterize the monolayer adsorption, which is represented by the equation [13].

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abc_e} \qquad (1)$$

Where,

q_e = amount of dye adsorbed at equilibrium (mg/L),

$c_e = equilibium\ concentration\ of\ dye\ (mg/L,\ a\ and\ b\ are\ Langmuir\ constants$

The Freundlich Isotherm is generally applicable to adsorption that occurs on heterogeneous surfaces. The linear form is shown below:

$$lnq_e = lnk_f + \frac{1}{n} lnc_e \qquad (2)$$

Where, k_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Flory–Huggins Isotherm considers the surface behavior of the adsorbates and adsorbents, the surface covered by the adsorbate can be calculated from the equation;

$$Log\frac{\theta}{c_e} = Logk_a + nLog(1-\theta) \qquad (3)$$

Where k_a = equilibrium constant of adsorption, n = number of adsorbates occupying adsorbent site, and θ = degree of surface coverage.

2.6 Adsorption Kinetics

In order to investigate the mechanism of adsorption, kinetic models such as the zero-order, first order, second-order, pseudo-second order and third-order kinetic models were applied to study the adsorption dynamics [14,15].

$Zero-order\ kinetic\ model.$

$$q_t = q_o + k_o t \qquad (4)$$

$First-order\ kinetic\ model.$

$$lnq_t = lnq_o + k_1 t \qquad (5)$$

$Second-order\ kinetic\ model. \frac{1}{q_t} =$

$$1/q_o + k_2 t \qquad (6)$$

$pseudo-second-order\ kinetic\ model.$

$$\frac{t}{q_t} = \frac{1}{h_o} + \left(\frac{1}{q_t}\right)t \qquad (7)$$

$Third-order\ kinetic\ model.$

$$\frac{1}{q_t^2} = \frac{1}{q_0^2} + k_3 t \qquad (8)$$

3. RESULTS AND DISCUSSION

3.1 EDS

The elemental analysis (Figure. 2 EDS Spectrum of Fly Ash) indicates that the fly ash used for this study is a class C fly ash (the sum major elements Si, Al, O and Fe is less than 70%) [16]. Carbon (43.4%), Oxygen (33.4%), Silicon (9.3%), Aluminum (8.1%), Calcium (4.8%), Iron (0.2%), Potassium (0.2%), Magnesium (0.2%), and Sulphur (0.2%).

3.2 Effect of Initial Concentration

To study the effect of different concentrations of dye on adsorption behavior three concentrations (25, 50 and 100 mg/L) were used and the amounts adsorbed were calculated and given in Table 1 [17,18].

Table 1 shows the effect of adsorbate dose on percentage of dye adsorbed, there is a gradual increase in the percentage of dye adsorbed for all modified forms of adsorbate. The observed increase in the adsorption of Congo Red may be ascribed to the presence of sufficient adsorption sites at the adsorbent [19]

3.3 Adsorption Isotherms

The Adsorption Isotherms were studied using initial concentrations of 25 mg/L, 50 mg/L and 100 mg/L of adsorbate with an adsorbent dosage of 0.2 g/L. Three adsorption Isotherms (Langmuir, Freundlich and Florry-Huggins) were adopted to investigate Congo Red behavior on HCFA-4, HCFA-3, HCFA-2 and HCFA-1. The parameters of the three adsorption Isotherms are listed in Table 2.

Although Langmuir isotherm gives high correlation coefficients (R^2) however, the sorption factor (S_F) for fly ash modified with 4 M HCl[HCFA-4] (-3.076), fly ash modified with 2M HCl[HCFA-] and fly ash modified with 1M HCl[HCFA-1] were less than zero (0) while that of fly ash modified with 3 M HCl[HCFA-3] is greater than one (1) therefore this isotherm type is unfavorable [20]. Freundlich isotherm fit the experimental data due to high correlation coefficients (R^2) and this may be attributed to the heterogeneous distribution of active sites and multilayer adsorption on fly ash modified with HCl [8] however, fly ash modified with 2 M HCl (HCFA-2) exhibited a high adsorption capacity (K_F =7.82) followed by HCFA-3(K_F =0.74), HCFA-4 (K_F =0.069) and HCFA-1 (K_F =0.004).

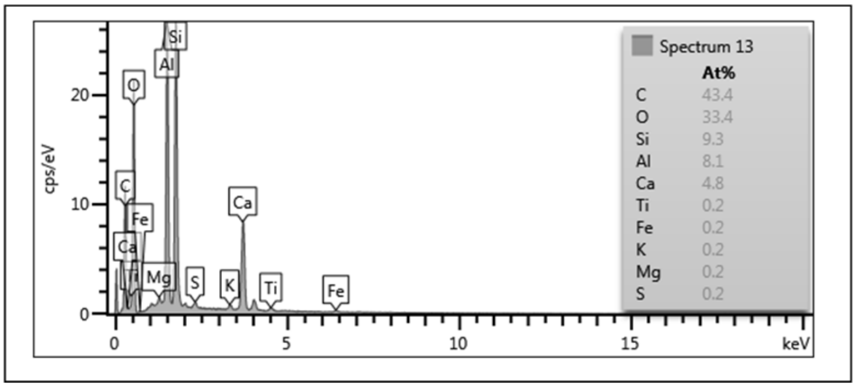

Fig. 2. EDS Spectrum of fly ash

Table 1. Amount (mg/g) and percentage of dye adsorbed

Initial concentration of Congo Red	Fly ash modified with 4 M HCl		Fly ash modified with 3 M HCl		Fly ash modified with 2 M HCl		Fly ash modified with 1 M HCl	
	mg/g	% adsorbed	mg/g	% adsorbed	mg/g	% adsorbed	mg/g	% adsorbed
25 mg/L	15	60	16.5	66	23.3	93.3	19	76
50 mg/L	38	76	36.5	73	47	94	44	88
100mg/L	83	83	82.5	82.5	96	96	93	93

Table 2. Parameters of three adsorption isotherms for Congo Red adsorption on modified fly ash samples

Isotherm model	Parameter	HCFA-4	HCFA-3	HCFA-2	HCFA-1
Langmuir	S_F	-3.076	3.50	-0.59	-0.46
	R^2	0.874	0.9728	0.9878	0.5052
Freundlich	K_F (mg/L)	0.069	0.74	7.82	0.004
	R^2	0.951	0.9715	0.9715	0.951
Florry-Huggins	K_a	1.96	7.318	4.409	1.5503
	R^2	0.5501	0.8836	0.7821	0.8766

3.4 Effect of Contact Time

The effect of contact time on the percentage of Congo red adsorbed was done by carrying out badge adsorption studies for ten (10) minutes, thirty (30) minutes, sixty (60) minutes and ninety (90) minutes respectively. The result are shown on Table 3.

For HAFA-4 maximum adsorption was achieved after ten minutes (85%) after which slight desorption is observed as percentage adsorption gradually reduce from 85% - 81% after sixty minutes. HAFA - 3 showed maximum adsorption after ten minutes (94%) and gradual desorption occurred for sixty minutes. For HAFA - 2 maximum adsorption was achieved only after minutes and no desorption was observed, as there was gradual increase in percentage adsorption with time. HAFA - 1 showed maximum adsorption after ten minutes and marginal desorption occurred after sixty minutes.

In summary, available adsorption site on the adsorbents were fully occupied after ten minutes in HAFA-4, HAFA-3 and HAFA-1 after which marginal desorption occurred. In the case of HAFA-2 available adsorption sites were fully occupied after ninety minutes and no desorption was observed.

3.5 Adsorption Kinetics

Adsorption kinetics is an effective method to evaluate the mechanism of CR adsorption on modified forms of fly ash [21]. Here, five adsorption kinetic models (zero-order model, first- order model, second-order model, pseudo-second-order model and third-other model) were applied to analyze the experimental data. Table 3 reveal that the adsorption data of HCFA-4, HCFA-3,HCFA-2 and HCFA-1 fit the pseudo-second –order model accurately due to the high correlation coefficients (R^2), which suggests that CR adsorption onto fly ash modified with various concentrations of Hydrochloric acid appeared to be controlled by a chemisorption process [22,23].

3.6 Gibbs Free Energy of Sorption ($\Delta \boldsymbol{G}^{\boldsymbol{O}}_{\boldsymbol{ads}}$)

The apparent Gibbs free energy of sorption $\Delta \boldsymbol{G}^{\boldsymbol{O}}_{\boldsymbol{ads}}$ is a fundamental criterion of spontaneity. Thus, adsorption occurs spontaneously at a given temperature if the Gibbs free energy of adsorption is negative. The Gibbs free energy of sorption of Congo Red by HCFA-4, HCFA-3, HCFA-2 and HCFA-1 were evaluated at room temperature (303 K) using the following equation.

$$\Delta \boldsymbol{G}^{\boldsymbol{O}}_{\boldsymbol{ads}} = -\, RT\ lnK_a \qquad (9)$$

Where,

R = Universal gas constant (8.314 $JK^{-1}mol^{-1}$)

T = Absolute temperature (303 K)

K_a= Equilibrium constant of sorption obtained from Florry-Huggins plot

Gibbs free energy of adsorption values shown in Table 4. Reveals that the adsorption of Congo Red dye onto the adsorbents (HCFA-4, HCFA-3, HCFA-2 and HCFA-1) were all spontaneous.

Table 3. Effect of contact time on % adsorption

Time (minutes)	HAFA - 4 % adsorption	HAFA - 3 % adsorption	HAFA - 2 % adsorption	HAFA - 1 % adsorption
10	85.0	94.0	92.0	96.5
30	84.2	93.9	95.0	96.0
60	81.5	93.5	95.8	95.5
90	81.0	90.5	97.0	91.5

Table 4. Correlation coefficients for kinetic models of adsorption of Congo Red onto fly ash modified with HCl

Kinetic model	HCFA-4 R^2	HCFA-3 R^2	HCFA-2 R^2	HCFA-1 R^2
Zero-order	0.9305	0.7693	0.8325	0.0508
First-order	0.9301	0.7809	0.8281	0.0508
Second-order	0.7571	0.7450	0.8573	0.0710
Pseudo-second-order	0.9998	0.9993	0.9998	0.9901
Third-order	0.9327	0.7693	0.8182	0.0540

Table 5. Gibbs free energy of sorption of Congo Red by HCFA-4, HCFA-3, HCFA-2 and HCFA-1

Modified fly ash sample	K_a	ΔG^{O}_{ads} Jmol^{-1}
HCFA-4	1.96	- 1695.2
HCFA-3	7.318	-5013.94
HCFA-2	4.409	-3737.52
HCFA-1	1.5503	-1093.60

4. CONCLUSION

In this study, the adsorption of Congo Red dye onto fly ash modified with various concentrations of Hydrochloric acid was investigated and the following conclusions can be drawn.

1. An increase in the concentration of Congo Red increases the % adsorption for constant amount of adsorbent and this may be ascribed to sufficient adsorption sites on the adsorbent.
2. Fly ash modified with 2M Hydrochloric acid HCFA-2 exhibited the highest adsorption capacity (K_F=7.82) followed by HCFA-3 (K_F = 0.74), HCFA (K_F = 0.069) and HCFA-1 had the least adsorption capacity (K_F =0.004).
3. The Freundlich isotherm fits the experimental data best due to high correlation coefficients and this may be attributed to heterogeneous distribution of active sites and multilayer adsorption [24].
4. The adsorption data of HCFA-4, HCFA-3, HCFA-2 and HCFA-1 fit the pseudo-second –order model accurately due to the high correlation coefficients (R^2), which suggests that Congo Red adsorption onto fly ash modified with Hydrochloric acid appeared to be controlled by a chemisorption process.
5. The Gibbs free energy of adsorption values reveals the adsorption of Congo Red dye onto all four forms of modified fly ash were spontaneous.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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