UNDER PEER REVIEW

Original Research Article

REMOVAL OF CONGO RED FROM AQUEOUS SOLUTIONS USING FLY ASH MODIFIED WITH HYDROCHLORIC ACID

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 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). The Gibbs free energy of adsorption values reveal that only adsorption of Congo Red dye onto fly ash modified with 1M Hydrochloric acid (HCFA-1) was spontaneous.

Keywords: congo red, thermodynamics, adsorption, equilibrium, kinetics, fly ash

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

UNDER PEER REVIEW

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.

Material and Methods

Preparation of Modified fly ash: The fly ash used for this experiment was obtained from the Sasol plant in South Africa.10.0g of unmodified fly ash was weighed into a 250ml conical flask.100ml of varied concentrations of hydrochloric acid (1M, 2M,3M and 4M) was added into separate conical flasks containing 10.0g unmodified fly ash respectively and each conical flask was covered with a stopper. The slurries were stirred on a magnetic stirrer for 24 hours.
The samples were filtered and the solid extracts were oven dried and latter crushed into fine powders.

Preparation of Adsorbate solution

0.3 g of Congo Red powder was dissolved in 1000ml of distilled water (3000mg/L), this served as the stock solution for serial dilutions into 25mg/L, 50mg/L and 100mg/L respectively.

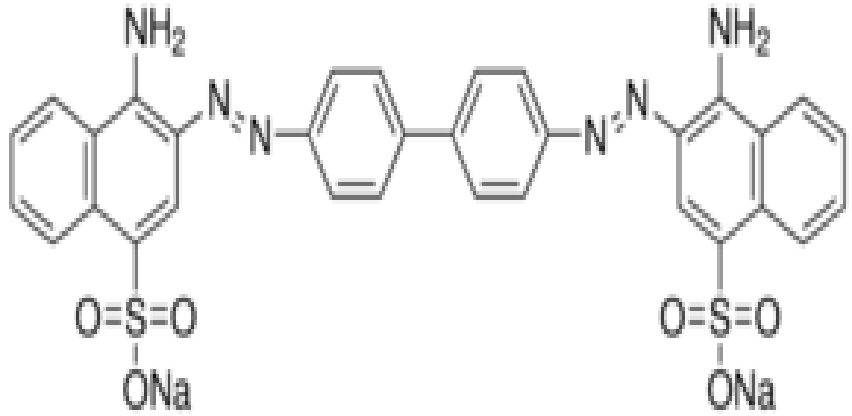

Figure 1. Chemical Structure of Congo Red

Characterization of Fly ash

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

Adsorption Studies

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

UNDER PEER REVIEW

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

100mg/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. Equilibrium concentrations of the supernatant were analyzed with Jenway 6,300 Spectrophotometer at λ_{max} =665nm after calibration.

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

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

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 Florry – 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.

Adsorption Kinetics

UNDER PEER REVIEW

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.

$$Zero - order\ kinetic\ model. \qquad q_t = q_o + k_o t \qquad (4)$$

$$First - order\ kinetic\ model. \quad lnq_t = lnq_o + k_1 t \qquad (5)$$

$$Second - order\ kinetic\ model. \quad 1/q_t = 1/q_o + k_2 t \qquad (6)$$

$$pseudo - second - order\ kinetic\ model. \qquad \frac{t}{q_t} = \frac{1}{h_o} + \left(\frac{1}{q_t}\right) t \qquad (7)$$

$$Third - order\ kinetic\ model. \qquad \frac{1}{q_t^2} = \frac{1}{q_0^2} + k_3 t \qquad (8)$$

RESULTS AND DISCUSSION

EDS

The elemental analysis (figure 2) indicated that the fly ash used or this study had the following composition; 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%).

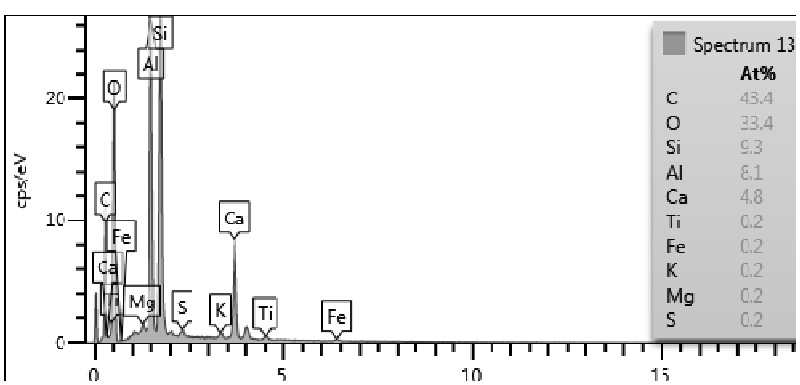

Figure 2: EDS Spectrum of fly ash

UNDER PEER REVIEW

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.

Table 1 shows a gradual increase in the percentage of dye adsorbed from 60% to 83% for fly ash modified with 4M HCl, 66% to 82.5% for fly ash modified with 3M HCl, 93.3% to 96% for fly ash modified with 2M HCl and 76% to 93% for fly ash modified with 1M HCl. The observed increase in the adsorption of Congo Red with increase in concentration(25g/L, 50g/L and 100g/L) may be ascribed to the presence of sufficient adsorption sites at the adsorbent [7]

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

Initial Concentration of Congo Red	**Fly ash modified With 4M HCl**		**Fly ash modified With 3M HCl**		**Fly ash modified With 2M HCl**		**Fly ash modified With 1M 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

Adsorption Isotherms

The Adsorption Isotherms were studied using initial concentrations of 25mg/L, 50mg/L and 100mg/L of adsorbate with an adsorbent dosage of 0.2g/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.

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	0.196	0.7318	0.4409	1.5503
	R^2	0.5501	0.8836	0.7821	0.8766

Although Langmuir isotherm gives high correlation coefficients (R^2) however, the sorption factor (S_F) for HCFA-4 (-3.076), HCFA-2 (-0.59) and HCFA-1 (-0.46) were less than zero(0)

UNDER PEER REVIEW

while that of SHFA-3 (3.50) is greater than one(1) therefore this isotherm type is unfavorable. 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 2M 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) had the least adsorption capacity.

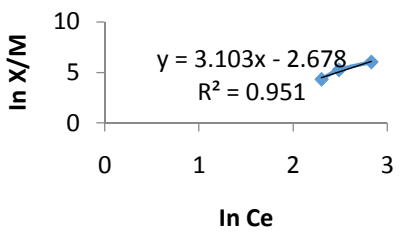

Figure 3. Freundlich plot for the sorption of CR on HCFA-4

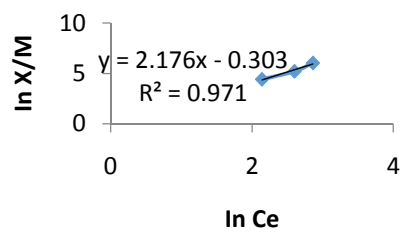

Figure 4. Freundlich plot for the sorption of CR on HCFA-3

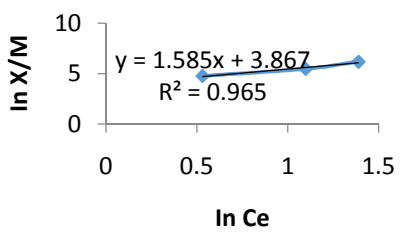

Figure 5. Freundlich plot for the sorption of CR on HCFA-2

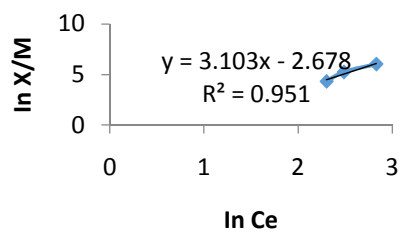

Figure 6. Freundlich plot for the sorption of on HCFA-1

Adsorption kinetics is an effective method to evaluate the mechanism of CR adsorption on modified forms of fly ash. 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.

UNDER PEER REVIEW

***Table 3**. Correlation Coefficients for kinetic models of adsorption of Congo Red onto fly ash modified with HCl*

Kinetic model	HCFA-4 $\mathbf{R^2}$	HCFA-3 $\mathbf{R^2}$	HCFA-2 $\mathbf{R^2}$	HCFA-1 $\mathbf{R^2}$
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

Gibbs free energy of sorption (ΔG^{O}_{ads})

The apparent Gibbs free energy of sorption ΔG^{O}_{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.

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

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

***Table 4.** 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	0.196	4064.7
HCFA-3	0.7318	778.8
HCFA-2	0.4409	2042.6
HCFA-1	1.5503	-1093.6

The Gibbs free energy of adsorption values shown in table 4. Shows that only the adsorption of Congo Red dye onto fly ash modified with 1M Hydrochloric acid (HCFA-1) was spontaneous.

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.

UNDER PEER REVIEW

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.
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 that only the adsorption of Congo Red dye onto fly ash modified with 1M Hydrochloric acid (HCFA-1) was spontaneous

REFFERENCES

1. EBELEGI,N.A.,(2015), Studies on the Adsorption Capacity of Modified Fly Ash Using Synthetic Dye solutions as Adsorbates. M.Sc Thesis Submitted to the Post Graduate School, Niger Delta University, Wilberforce Island, P.M.B 071 Yenagoa, Bayelsa State.
2. SEEY,T.L,(2012), Equilibrium,Kinetic and Thermodynamic Studies on the Adsorption of Direct Dye on Novel Adsorbent Developed from Uncaria Gambir Extract, Journal of Physical Science. Vol 23(1), 1-13.
3. FUNGARO D.A, LUCA G. C., ALESSANDRO P.S., IZDORO J.C, SUELI B. J., 2010, Adsorption of Methylene blue from aqueous solution on Zeolite material and improvement as toxicity removal to living organisms, Orbital, The Electronic Journal of Chemistry,Vol.2,No.3,pp 236-247.
4. TSIRIDIS, V.,SAMARAS,P.,KUNGOLOS,A.,SAKELLAROPOULOS,G.P.,(2006),application of Leaching Tests for Toxicity Evaluation of Coal Fly Ash, Wiley Inter science, doi 10,1002/tox 20187,pp. 409-416.
5. XUNJUN,C.,(2015), Modeling of Experimental Adsorption Isotherm Data, Open Access Information, ISSN 2078-2489.
6. FOO,K.Y.,HAMEED,B.A.,(2009), Recent Developments in the Preparation and Regeneration of Activated Carbons by Microwaves, Advance Colloid Interface Science. 149, 19-27.
7. FOO,K.Y.,HAMEED,B.A.,(2010), Insights into the Modeling of Adsorption Isotherm Systems, Chemical Engineering Journaal 156(2010), 2-10.
8. GOSWAMI,A.K., KURLKARNI,S.J., DHARMADHIKARI,S.K., PATIL,P.E. (2013), Fly Ash as Low Cost Adsorbent to Remove Dyes, International Journal of Scientific Research and Management (IJSRM), Vol. 2, Issue 5, pp 842-845.

UNDER PEER REVIEW

9. KHAN, T.A., ALI I., SINGH, V.V., SHARMA, S. (2009), Utilization of Fly ash as Low –Cost Adsorbent for the Removal of Methylene Blue, Malachite Green and Rhodamine B Dyes from Textile waste water, Journal of Environmental Protection Science, Vol.3, pp112-22.
10. WOOLARD,C.D., PETRUS, K., M Van der HORST. (2000), The Use of Modified Fly Ash as an Adsorbent for Lead, ISSN 0378-4738=Water S.A,Vol.26, pp531-536
11. PAGGA .U and BRAUN D., (1986). The degradation of dye stuffs: part II, Behavior of dye stuffs in aerobic biodegradation tests. *Chemosphere*, 15, pp,479.
12. BADA,S.O. and POTGEITER-VERMAAK, S. (2008), Evaluation and Treatment of Coal Fly Ash for Adsorption Application, Leonardo Electronic Journal of Practices and Technologies, Issue 12, pp 37-48
13. SRIDEVI V.,LAKSHMI,C.M.V.V.,AND YADLA,S.V.,(2013), Adsorption Isotherm Studies of lead from Aqueous solution using Fly Ash, International Journal of Innovative Research in Science, Engineering and Technology, ISSN No.2319-8753, 2(11),:7022-7030.
14. POOTA,V.J.P., MCKAY, G., HEALY,J.J. (1976),The removal of Acid Dye from Effluent Using Natural Adsorbents, Peat.Water Res; 10:1067-1670.
15. SONG, C., WU, S. CHENG, M.,TAO,P.,SHAO,M. and GAO, G.,(2014), Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation for Removal of Lead(II) From Aqueous Solutions, Sustainability, 6,86-98; doi:10.3390/su6010086
16. HUNG,P.A AND HAI,N.X.(2014), Mineral Composition and Properties of Modified Fly Ash, ARPN Journal of Agricultural and Biological Sciences,Vol.9, pp 51-54.
17. ISREAL,A.A.,UDUOK,U.,UMOREN, S. and OKON,O. (2013), Kinetic and Equilibrium Studies of Adsorption of Lead (II) Ions from Aqueous Solution Using Coir Dust (*Cocos nucefera* L) and its Modified Extract Resins, The Holistic Approach to Environment 3(2013)4, 209-222
18. SHARMA, A., SRIVASTAVA., DEVRA,V. and RANI,A. (2012), Modification in the Properties of Fly Ash through Mechanical and Chemical Activation, American Chemical Science Journal, 294):177-187
19. WANKASI D., 2013, Adsorption a Guide to experimental Data Analysis, Ano Publication Company, Port Harcourt, Rivers State.
20. SHABEIG, S., BAGGERI,N.,GHORBANIANS.A., HALLAJISANI,A., and POORKARIMI,S.(2013), Anew Adsorption Isotherm Model of Aqueous Solutions on Granular Activated Carbon, World Journal of Modeling and Simulation, Vol. 9 no.4, pp 243-254
21. KNAEBEL,K. S., (2014), Adsorption Research, Inc, Dublin, Ohio.
22. MAHLABA,J.S.,KEARSLEY,E.P. AND KRUGER,R.A.(2011), Physical, Chemical and Mineralogical Characterization of Hydraulically disposed fine coal ash from SASOL Synfuels, Fuel, doi:10.1016/j.fuel.2011.03.022.
23. PETRIK,L.F.,WHITE,R.A.,KLINK, M.J.,SUMERSET, V.S.,BURGERS,C.L. AND FEY, M.V.,(2013), Utilization of South African fly ash to treat Acid Coal Mine Drainage and Production of high quality Zeolite from residual solids, International ash utilization symposium, centre for applied energy research, University of Kenturcky, Paper No. 61.