Full Length Research Paper

Equilibrium and continuous flow studies on the sorption of Congo Red using ethylenediamine modified rice hulls

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The effectiveness of using ethylenediamine rice hulls (EDA-RH) to remove Congo Red (CR) from synthetic dye solution was carried out in batch and column experiments under various experimental conditions. Surface morphology analysis was carried out also using atomic force microscopy (AFM). The experimental data obtained at different initial dye concentrations fitted well to pseudo-second order kinetic model. Application of Langmuir isotherm indicated that maximum sorption capacity of EDA-RH for CR was enhanced by 2-fold as compared to natural rice hulls. Column studies revealed that the breakthrough curves of CR followed the typical S shape of packed-bed systems and it was bed-depth and influent-concentration dependent. The BDST model was used to predict the bed-depth service time data at different bed depths. A plot of BDST at 50% breakthrough yielded a straight line that, however, does not pass through the origin.

Key words: Sorption, ethylenediamine rice hulls, Congo Red, batch study, column study.

INTRODUCTION

Dyes have largely taken over around the world, interest not only in textiles, but also polymer, paint, printing, cosmetic, food and many other industries. There are over 100,000 commercially available dyes and more than 7×10^5 tonnes are produced annually (Pearce et al., 2003). However, the increasing accumulation of dyes in the aqueous environment is highly undesirable due to toxicological and environmental effects. Hence, the removal of dyes from wastewater has become a major concern.

Conventional technologies for color removal from industrial effluents include biological treatment, coagulation, ozonation, electrochemical processes, nano-filtration and activated carbon adsorption (Wang and Wang, 2008; Ong et al., 2007). Amongst all, the sorption process by

activated carbon is one of the most efficient techniques but drawback such as high capital and problems with the spent carbon limits its large-scale application. Thus, extensive research has been directed to the investigation of low cost materials as viable substitutes for activated carbon. These materials, including date pith, sawdust, corn corb, barley husk, rice hull and bagasse pith have the advantage of being inexpensive and readily available (Banat et al., 2003; Garg et al., 2003; Robinson et al., 2002; Low et al., 2000; Low and Lee, 1997).

However, a very few studies have been undertaken under the continuous flow conditions which are more useful in large scale water treatment. In this paper, we report the effectiveness of using ethylenediamine modified rice hulls in removing Congo Red because this modification has demonstrated a sorption enhancement of 2-fold as compared to natural rice hulls. The study was carried out under equilibrium and continuous flow conditions which can provide useful information on the sorption process

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before extending it to commercial systems.

MATERIALS AND METHODS

All the reagents used were of A.R. grade and purchased from Merck (Germany). The rice hull was obtained from a rice mill in the northern part of west Malaysia.

Preparation of EDA-RH and CR

The preparation of natural and EDA-RH has been reported elsewhere (Ong et al., 2007). The sorbate selected for this study was CR, which was purchased from Aldrich Chemical Company and used as received without further purification. Synthetic dye solution of CR with the concentration of 1000 mg L^{-1} was prepared as stock solution and subsequently diluted when necessary.

Equilibrium and column studies

The batch studies were carried out at room temperature (25 ± 2 °C) by mixing 0.1 g of sorbent with 20.0 ml CR solution in a centrifuge tube and shaken on an orbital shaker at 150 revolutions per minutes (rpm) for four hours unless otherwise stated. The reaction mixture was then centrifuged at 3000 rpm for phase separation. All the batch experiments were carried out in duplicate and the results given are the means with a relative standard deviation (RSD) of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. Time course experiments were investigated by shaking the sorption mixture at various predetermined intervals and analyzing the dye concentration at the end of the contact time. For sorption isotherm, the dye concentrations were varied from 30 to 150 mg L^{-1}. The percentage of dye uptake (% uptake) was calculated using the following equation:

$$\% \text{ Uptake} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Where; C_o is the initial dye concentration and C_t is the dye concentration (mg L^{-1}) at any time.

Column studies were performed using a glass column of 1.0 cm internal diameter. The flow rate of the eluant was controlled by using a peristaltic pump. The effect of different influent concentrations on the breakthrough was studied using dye concentrations of 15, 20 and 25 mg L^{-1}. The column was packed to a height of about 7.0 cm using 1.0 g of EDA-RH. The flow rate was maintained and regulated at 10 ml min^{-1}. The effect of bed depth on the CR sorption was tested by packing the column to 7.0, 10.0 and 15.0 cm, corresponding to 1.0, 1.5 and 2.0 g of EDA-RH, respectively, while maintaining the influent concentration at 25 mg L^{-1} with the flow rate of 10 ml min^{-1}.

For both studies, the dye concentrations were analyzed using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption; for CR, λ_{max} = 498 nm and dilutions were carried out when measurement exceeded the linearity of the calibration curve.

Surface morphology

The AFM (Quesant Q- Scope 250) is a stylus-type instrument, in which a sharp probe, scanned raster-fashion across the sample is employed to detect changes in surface structure on the atomic scale. As the interaction force between the cantilever tip and surface varies, deflections are produced in the cantilever. These deflections are measured and used to compile a topographic image of the surface. The samples which consist of NRH and EDA-RH were sieved into size less than 105 μm before being palletized.

RESULTS AND DISCUSSION

Batch studies

The rates of CR sorption by EDA-RH at different initial concentrations are shown in Figure 1. For both concentrations studied, the initial sorption of CR was rapid in the first 60 min followed by a slower process. Equilibrium was attained in about 240 min. The fast uptake at the beginning suggests the occurrence of a rapid external mass transfer which involved the rapid attachment of the dye molecules to the surface of the sorbent. The later slow rate behavior is probably due to the slower internal diffusion process which may be the rate determining step (Banat et al., 2003; Ong et al., 2009). Similar trend was observed in the sorption of methylene blue using rattan sawdust (Hameed et al., 2007). All the plots showed the same general features; rapid uptake in the beginning due to the external mass transfer and followed by a more gradual process attributed to the intraparticle diffusion which take a relatively longer contact time.

The kinetics of sorption data can provides valuable insight into the reaction pathways and the mechanism of sorption reaction. In order to obtain some insight into the modeling kinetics of the removal of CR by EDA-RH, the experimental data were fitted into two common models, namely the Lagergren pseudo-first order model and pseudo-second order model. The pseudo-first order (Langergren and Svenska, 1898) and pseudo-second order model equation can be expressed as Equation (2) and (3), respectively (Ho and McKay, 1999:2000):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{2}$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{3}$$

Where;

q_e = the amount of dyes sorbed at equilibrium (mg g^{-1}),
q_t = the amount of dyes sorbed at time t (mg g^{-1}),
k_1 = the rate constant of pseudo-first order sorption (min^{-1}),
h ($k_2 q_e^2$) = the initial sorption rate (mg g^{-1} min^{-1}),
k_2 = the rate constant of pseudo-second order kinetics (g mg^{-1} min^{-1}).

The rate constants and the correlation coefficients of the
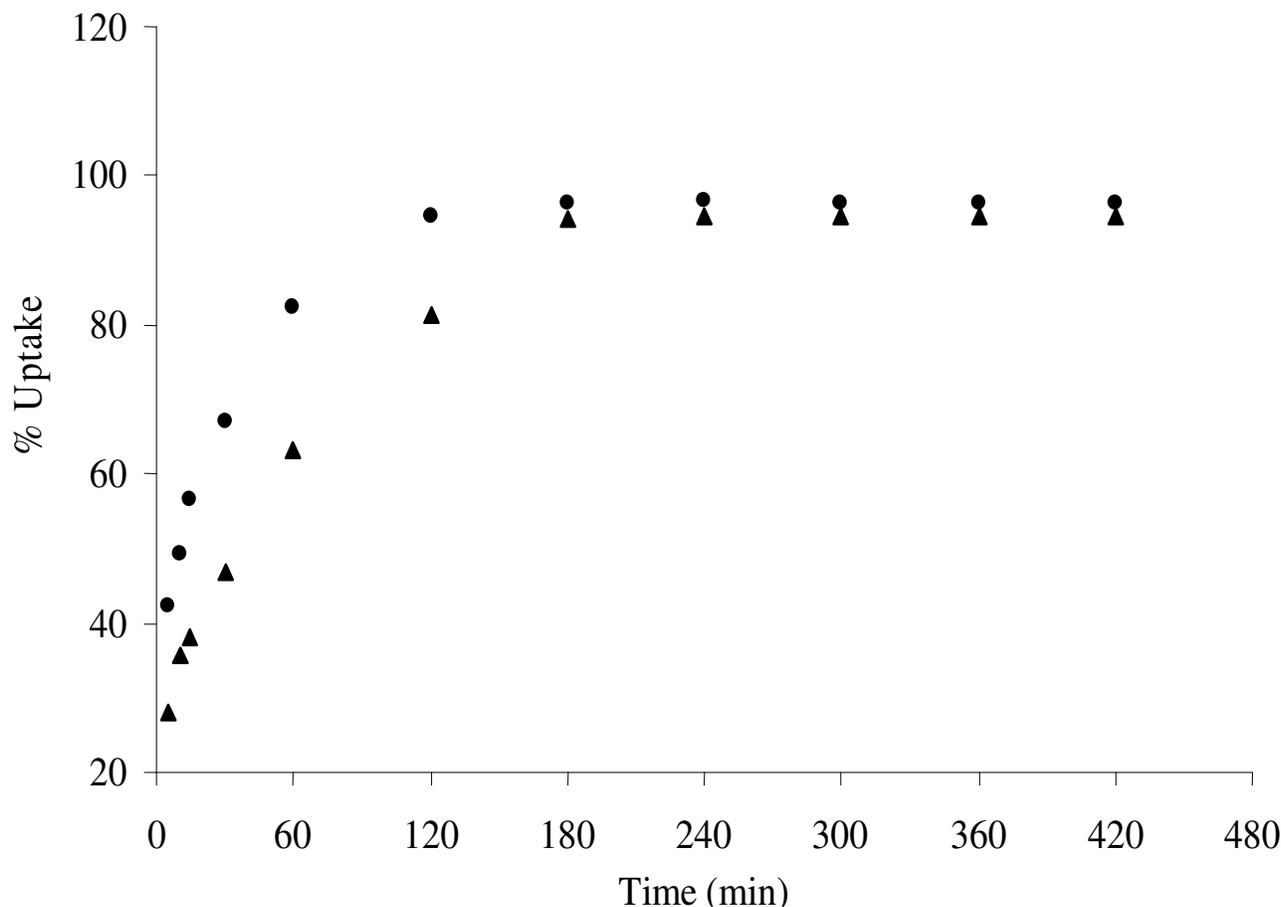
Figure 1. Effect of initial concentration and contact time on the sorption of CR by EDA-RH (●, ▲- 50 and 200 mg/L of CR).

Table 1. Sorption capacities and correlation coefficients based on pseudo-first and pseudo-second kinetics.

Initial concentration (mg L^{-1})	Pseudo-first order		Pseudo-second order		Experimental
	Sorption capacities (mg g^{-1})	R[2]	Sorption capacities (mg g^{-1})	R[2]	Sorption capacities (mg g^{-1})
50	3.85	0.5479	10.27	0.9991	9.66
100	13.78	0.5125	19.80	0.9893	18.88

two kinetic models are shown in Table 1. It was observed that the experimental data showed a better compliance with the pseudo-second order model than the pseudo-first order model, suggesting that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate (Ong et al., 2007; Ho and McKay, 2000; Lakshmi et al., 2009; Gong et al., 2008). Similar result was reported for the sorption of CR from aqueous solution onto surfactant-modified montmorillo-nite (Wang and Wang, 2008).

Sorption isotherms are of fundamental importance for the description of how molecules of sorbate interact with the sorbent surface. Hence, two different sorption models are compared for the fitting of experimental data, namely Langmuir and Freundlich isotherms. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogenous sites within the sorbent whereas the Freundlich model is generally found to be better suited for the characterizing multi-layer process. In order to establish the maximum dye sorption capacity, the Langmuir equation (Equation 4) was applied to the sorption equilibria at different initial concentrations:

$$\frac{C_e}{N_e} = \frac{1}{N^* b} + \frac{C_e}{N^*} \qquad (4)$$

Table 2. Isotherm constants for the sorption of CR by EDA-RH.

	Langmuir				Freundlich		
	N^*(mg g^{-1})	b (L mg^{-1})	R^2	R_L	K_f	n	R^2
NRH	13.26	0.0187	0.9663	0.276-0.646	0.7861	1.9051	0.9359
EDA-RH	26.39	0.4427	0.9980	0.016-0.274	9.0532	2.7894	0.9565

Whereas the linear form of Freundlich can be represented as:

$$\log N_e = \frac{\log C_e}{n} + \log K_f \qquad (5)$$

Where;

C_e = equilibrium concentration of the dye (mg L^{-1});
N_e = amount of dye sorbed at equilibrium (mg g^{-1});
N^* = maximum sorption capacity (mg g^{-1});
b = constant related to the energy of the sorbent (L mg^{-1});
n= Freundlich constant for intensity and
K_f = Freundlich constant for sorption capacity.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is defined by the following equation:

$$R_L = \frac{1}{(1 + bC_o)} \qquad (6)$$

Where; b and C_o are the same as defined before. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The sorption isotherm constants and coefficients for the linearised forms of the isotherm models for the sorption of dyes on EDA-RH are listed in Table 2. Both Langmuir and Freundlich models appeared to provide reasonable fittings for the sorption data of CR on EDA-RH. This is indicative of both the monolayer adsorption and heterogeneous surface conditions which exist under the experimental conditions. Notwithstanding, this Langmuir model allows the calculation of limiting sorption capacities that could be useful for the comparison of the sorption efficiency of materials studied. The maximum sorption capacity of NRH for CR is included in Table 2 for comparison. It is clear that the maximum sorption capacity for CR was enhanced by 2-fold as compared to NRH. The R_L values for the sorption of CR onto EDA-RH are in the range of 0.016 - 0.274 which shows that the sorption process is favorable.

Column studies

The results obtained from batch studies are important in providing information on the effectiveness of the sorbent-dye sorption system. However, this process is usually limited to the treatment of small volumes of effluent under equilibrium conditions which do not give accurate scale-up data for industrial treatment systems where a continuous flow system is normally employed. Besides, uneven flow patterns throughout the column and the problems of regeneration cannot be meaningfully studied in batch experiment. Therefore, it is necessary to carry out flow tests using columns to obtain design models which would be applicable to commercial systems.

The breakthrough curves of CR from synthetic dye solutions at various influent concentrations (15 to 25 mg L^{-1}) followed the typical 'S' shape of the packed bed sorption system. The percentage removal of dye decreased with increasing dye concentrations whereby a sharper breakthrough curve was obtained at a higher dye concentration. Similar phenomenon were observed in the removal of BB3 using modified rice husk (Lee et al., 2008) and biosorption of methylene blue by rice husk (Han et al., 2007)

The effect of bed depth on the sorption characteristics of CR was studied. Breakthroughs at $C_t/C_o = 0.5$ occurred at 110, 300 and 450 ml of dye solutions for bed depths of 7, 10 and 15 cm, respectively. The breakthrough curves exhibit a phenomenon where the higher the bed depth, the longer the service time before breakthrough occurred. This was attributed to the increase in binding sites on the sorbent. Similar result was reported in the removal of dyes by rice husk (Han et al., 2008).

Several models have been proposed to predict the relationship between a fixed sorption bed and service time and the most commonly quoted model for this correlation is perhaps the Bed-Depth-Service-Time (BDST) model (Bohart and Adam, 1920) that states that the service time for a column is given by

$$t = \frac{N_o}{C_o U} H - \frac{1}{kC_o} Ln\left(\frac{C_o}{C_t} - 1\right) \qquad (7)$$

Where:

t = service time to breakthrough (min);
N_o = sorption capacity (mg g^{-1});
C_o = initial dye concentration (mg L^{-1});
C_t = effluent concentration (mg L^{-1}) ;
U = linear flow rate (cm min^{-1});
H = bed depth (cm);
k = rate constant of sorption (L mg^{-1} min^{-1}). At 50% break-
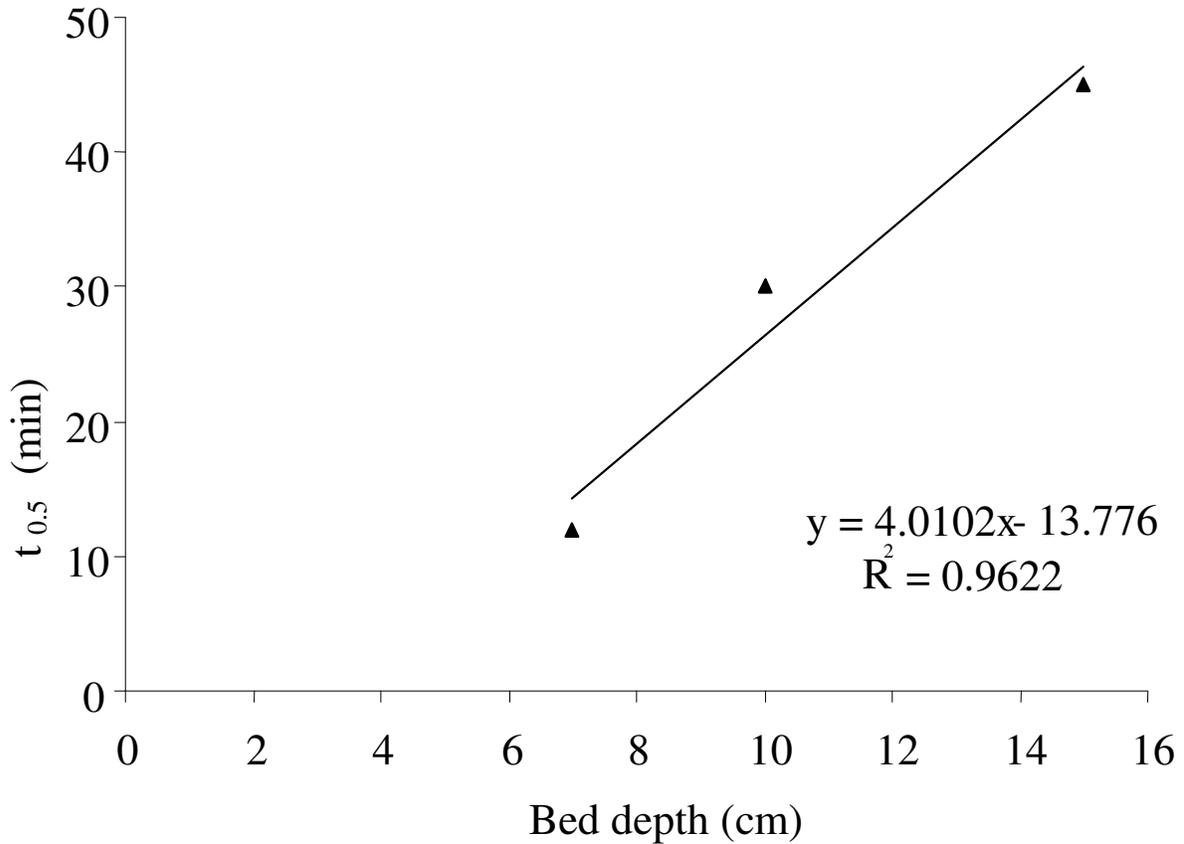
Figure 2. BDST plot of CR-EDA-RH system.

through $\left(\dfrac{C_o}{C_t}\right) = 2$ and $t = t_{0.5}$, the equation is reduced to:

$$t_{0.5} = \left(\dfrac{N_o}{C_o U}\right) H \qquad (8)$$

or

$$t_{0.5} = \text{constant} \times H \qquad (9)$$

Thus, a plot of BDST at 50% breakthrough against bed depth using Equation (7) should be a straight line passing through the origin provided the sorption data follow the model. The plot of t against H at 50% breakthrough for CR-EDA-RH systems (Figure 2) is a straight line that, however, does not pass through the origin. This deviation from the BDST model is similar to that reported in the sorption of Cr (VI) using coconut coir pith (Parinda et al., 2008), the sorption of Cu and Pb by tartaric acid modified rice hull (Wong et al., 2003) and the sorption of Cr(VI) using quaternized rice husk (Low et al., 1999). The nonconformity of the BDST model may be due to the pre-

sence of more than one rate limiting step in the sorption process (Lee et al., 2008; Wong et al., 2003; Lee et al., 1998) and the complex sorption mechanism as suggested and observed in the batch study.

Surface morphology

The surface morphology of natural rice hull (NRH) and EDA-RH were studied using the contact mode by AFM on a 20×20 μm^2 area is shown in Figures 3 and 4, respectively. The contact mode where the tip scans the sample in close contact with the surface is the most commonly used in AFM as it can provide information on the cross-section analysis, bearing analysis and roughness analysis.

From Figures 3 and 4, it is apparent that both NRH and EDA-RH exhibit spherical like structures. The section analysis obtained through the selection of the transect line across the sample shows that the grain size in NRH has a broad distribution ranging from 0.718 - 2.364 µm, whereas, EDA-RH exhibits a smaller range, 1.324 - 2.521µm. The AFM image when analyzed in terms of average surface roughness (R_a), increases from 169.5 nm (NRH) to 330.0 nm in EDA-RH. This is most probably
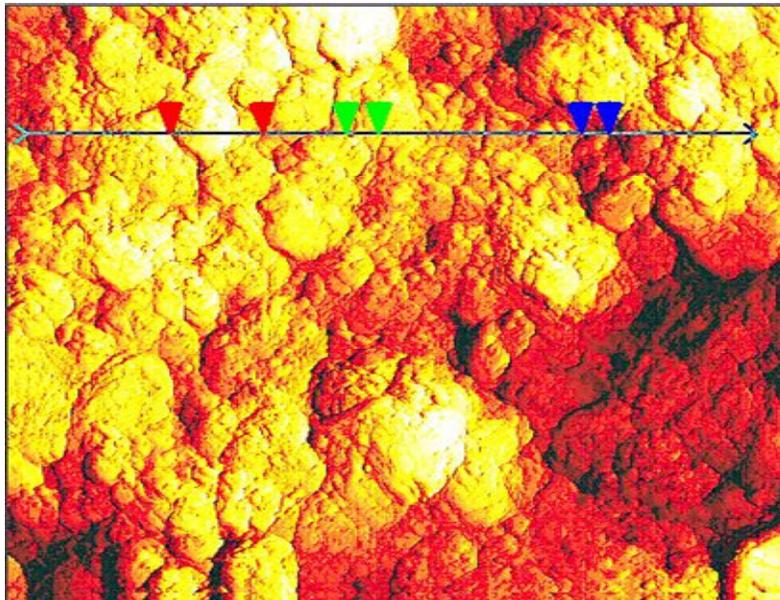
Figure 3. AFM image of NRH with transect line for cross-sectional analysis.
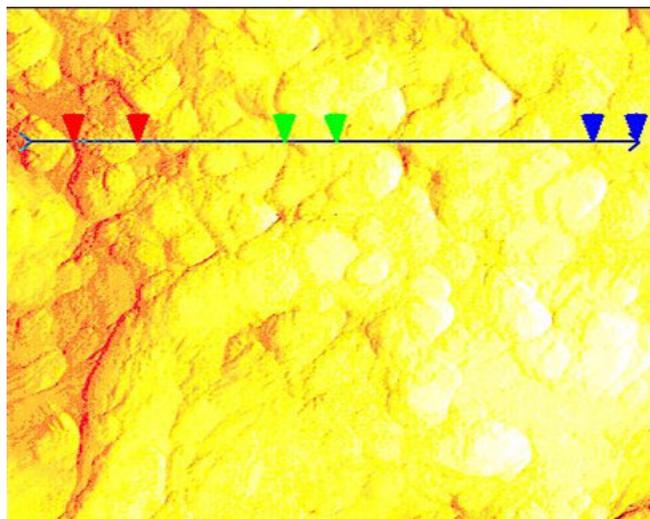
Figure 4. AFM image of EDA-RH with transect line for cross-sectional analysis.

caused by the eruption during EDA modification.

The surface topography of NRH and EDA-RH are illustrated by the colour of the images (Figures 5 and 6). Colour mapping is the usual method used for displaying the data where light colour indicates high features or high topography and lower topography is shown by darker color. With the introduction of amine groups on the surface of rice hull, the material becomes more intense; this explains the higher topography shown after modification. Br, Bruening and Cohen (2005) evaluated the changes in coal macerals by taking AFM measurements before and after oxidation process. They attributed the larger area of

lower topography in oxidized coal macerals to the loss of material.

Conclusions

In this study, EDA-RH has demonstrated its potential to be an economical and efficient sorbent for the removal of CR from aqueous solutions. The equilibrium sorption was achieved in 240 min and sorption kinetics obeyed preferably the pseudo second-order kinetics. The isotherm study showed that equilibrium sorption data of CR on
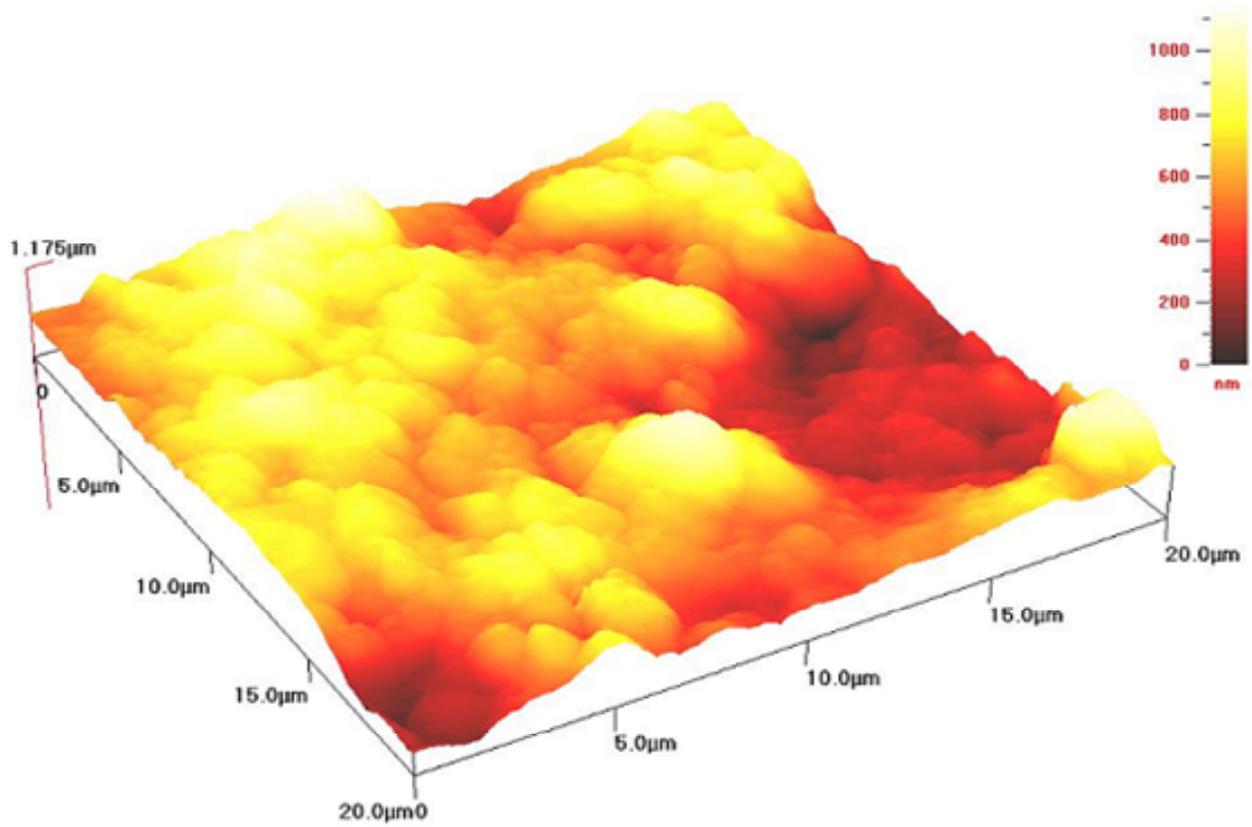
Figure 5. Surface topography of NRH.
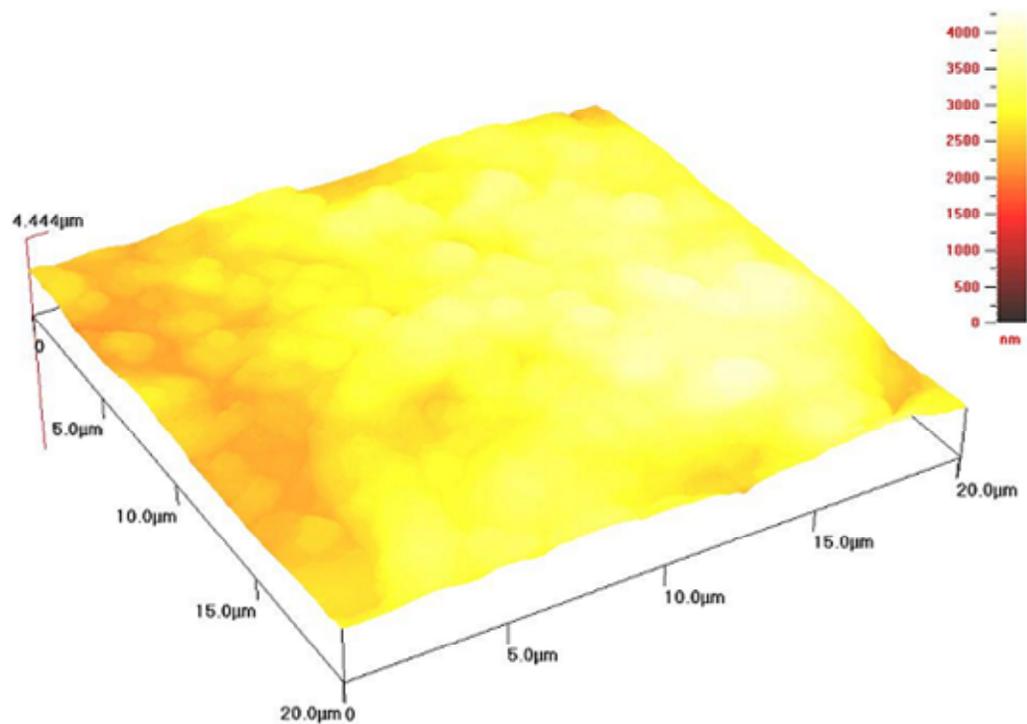
Figure 6. Surface topography of EDA-RH.

EDA-RH conform to both Langmuir and Freundlich isotherm models. Based on the Langmuir isotherm analysis, the maximum sorption capacity was determined to be 26.4 mg g^{-1}. Column studies revealed that the breakthrough times of CR was a function of bed depths and initial concentration. Generally, decreasing influent concentrations and increasing bed depths increased the service time of the column. The column capacity was evaluated using BDST model and the plot of BDST at 50% breakthrough generated a straight line but with some deviation. EDA-RH has been demonstrated to be a useful sorbent for the removal of CR under batch and column studies. In order to utilize its full potential as commercial sorbent, more parameters should be carried out and uptake of this dye from industrial waste water must be evaluated. Currently, such investigations are underway in our laboratory.

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