



Removal of Basic Dyes from Aqueous Solution Onto H₂SO₄-modified Rice Husk



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Abstract

Rice husk, as local agricultural waste, was modified by treating it with H₂SO₄ to obtain a low-cost and an effective adsorbent. This adsorbent was investigated for the removal of basic violet 10 (BV) and basic yellow 28 (BY) dyes from aqueous solutions via batch adsorption procedure. The experiments included the initial concentration of dye, contact time and temperature. Langmuir, Freundlich, and Dubinin–Radushkevich models were studied to follow the adsorption process. The results reveal that the Langmuir model showed a better fit to the equilibrium adsorption data and the adsorption kinetics fit the pseudo-second-order model. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) were used in the course of characterization. The intraparticle diffusion model via the mass transfer was applied to examine the mechanisms of the rate-controlling step. It was found that intraparticle diffusion was mostly the rate controlling step in the adsorption of BV dye only, while the thermodynamic parameters (ΔH° , ΔS° , and ΔG°) showed that the adsorption process is a typical chemical, spontaneous, and exothermic in nature.

Keywords: Rice husk; treatment; basic dyes; adsorption; SEM and FTIR; Kinetics, Thermodynamic

1. Introduction

Dyes and pigments are widely used in various industries such as textiles, food, cosmetic, leather, plastic and paper industries. Effluents resulted from these industries are highly coloured [1] and discharged into rivers. Generally, the coloured wastewater is considered to be highly toxic to the aquatic system causing certain hazards and environmental problem such as cancer, skin irritation, dermatitis and allergy in human body [2&3].

Basic violet 10 (BV) is one of the most important water-soluble xanthenes class dyes, basic red cationic dye which is a common water tracer fluorescent. It is extensively being used in food industries as well as textile dyeing industries including textile, cotton and wool fabrics. However, cautions should be made while using BV as it is harmful to humans. Exposure to BV causes irritation of the gastrointestinal and the respiratory tracts, eye burn and irritation to skin. Accordingly, wastewater streams containing dye effluents should be pre-treated before discharge into

the receiving water bodies [4]. Basic Yellow 28 (BY 28) is cationic dye, BY 28 is among the most commonly used dyestuff to dye cotton, and thus it is also considered one of the most common industrial pollutants.

Activated carbon (AC) is commonly used as adsorbent for the efficient removal of both organic and inorganic pollutants. The intense worldwide utilization of activated carbon is attributed to its distinctive physical characteristics. For example, AC was characterized by its considerable specific surface area, porosity, pore volume and thus it possesses high sorption capacity. However, its high cost is still a major obstacle. Extensive studies have investigated the possibility of utilization of low-cost materials like coconut shell [5], corncobs [6,7], bamboo grass treated with concentrated sulfuric acid [8], orange peel [9], tea wastes [10], rice husk [11] and date stone and palm tree waste [12] and rice hull [13].

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The traditional processes of removal of dyes from wastewater include membrane technology, ion exchange, coagulation [14], adsorption [15], photocatalytic degradation [16], ozonation [17] and biological processes [18].

In the present work, the adsorption characteristics of basic violet 10 (BV) and basic yellow 28 (BY) dyes were investigated using colloidal activated carbon as adsorbent prepared from the treatment of rice husk (RH) with concentrated sulfuric acid. This study includes adsorbent characterization and the factors influencing the adsorption such as the dye concentration, temperature and contact time. Langmuir, Freundlich and D-R equations were used to determine the correlation between the isotherm models and experimental data. Pseudo-first order, pseudo-second order and intra-particle equations were used to calculate the kinetic parameters and thus to determine the adsorption mechanism.

2. Materials and Methods:

2.1. Adsorbents

Rice husk (RH) as a precursor material was collected from local rice field. It was well washed with distilled water for several times to remove all the dirt particles and dried at 110°C for 24h. The dried samples (50 gm) were soaked in different concentrations of sulfuric acid 18.4M, 12M and 8M for 24h, The samples were washed with distilled water till pH becomes 5, then dried at 110°C for 24h. These samples were designated as H1, H2 and H3, respectively. The untreated rice husk was designated as RRH.

In this study we investigate two representative samples, H2 and RRH towards the adsorption of both BV and BY dyes in addition to the evaluation of their kinetic and thermodynamic parameters. H2 sample was selected after the fast checking of the adsorption capacity for the three acid samples, and we found that although it possesses the moderate acid concentration yet it achieved the highest efficiency for the removal of both dyes investigated.

2.2. Adsorbates

Synthetic dye solution of BV and BY were used as sorbates in this study. Their structure, are illustrated in Fig. (1).

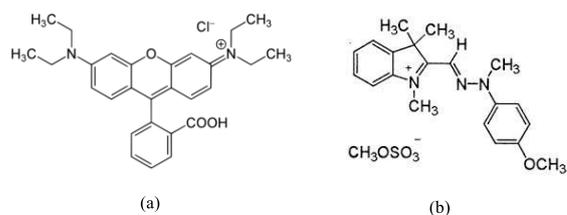


Fig.(1): structures of (a) BV and (b) BY.

BV and BY were used without further purification. All dye powders used in this study were purchased from sigma-Aldrich Ptc Ltd. (USA). Standard dye solutions of 1000 mg/L were prepared as stock solutions and subsequently diluted when necessary.

2.3. Adsorbents characterization

Nitrogen adsorption experiments at 77 K were conducted to determine the specific surface area of the test samples using BEL-Sorp, Microtrac Bel Crop, Japan [19]. The samples were outgassed overnight at 180 °C prior to adsorption measurements. The BET model was applied to fit the nitrogen adsorption isotherms and evaluate the Brunauer-Emmett-Teller surface area (SBET, m²/g), total pore volume (VP, cm³/g) and average pore diameter (\bar{r} , Å) [20].

Fourier transform infrared spectroscopy (FTIR) is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of dyes. FTIR technique is carried out by using KBr pellets (JASCO, FT-IR-460 plus).

Surface morphologies of the adsorbents (RRH and H2) were identified using scanning Electron Microscope (SEM) type JOEL JSM-6400 device at magnification = 500.

2.4 Kinetics Studies

In the kinetic experiments, 0.5g of dry sorbent was added to 100 ml of the aqueous dye solution (50, 100 and 200 ppm) at 30°C. The uptake of the adsorbate per unit mass of the sorbent was followed over time by withdrawing 1ml of sample at fixed time intervals to determine the concentration at each time which measured by using Shimadzu model Uv-Vis spectrophotometer at $\lambda = 554$ nm for BV and 418 nm for BY. The amount of dye removed by adsorbent at time t (qt) can be calculated by using the following equation:

$$q_t = (C_o - C_t)V/m \quad (1)$$

where q_t is the amount of dye adsorbed at time t (mg/g), C_o (mg/L) and C_t (mg/L) are the concentration

in the solution at time $t=0$ and at time t respectively, V is the volume of solution (L) and m is the weight of the sorbent used (g).

It is normally assumed that the overall rate of adsorption is exclusively controlled by the adsorption rate of the solute on the surface of the adsorbent, and the intra-particle diffusion and external mass transport can be neglected. Moreover, it is considered that the adsorption rate of a solute on the surface can be represented in the same manner as the rate of a chemical reaction [21]. The adsorption kinetics is commonly modeled with the pseudo-first order [22] and pseudo-second-order [23]. The equations of the two kinetics models are represented as followed. The pseudo first-order equation, describes the kinetics of adsorption process

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (2)$$

where q_e and q_t are the amounts of the dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order model can be expressed in the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

The mechanism of the diffusion of dye molecules during adsorption was studied by the intra-particle diffusion model, which is expressed as:

$$q_t = k_{id} t^{\frac{1}{2}} + C \quad (4)$$

where k_{id} is the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$).

If the adsorption mechanism follows the intra-particle diffusion process a plot of q_t against $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C [24].

2.5 Batch adsorption Studies

Batch sorption techniques were done by shaking 0.2g of investigated adsorbent with 50ml aqueous dye solution in 250ml Erlenmeyer flasks placed in a temperature controlled shaking water bath at different concentrations between 10-200 mg/L, temperatures between 30 to 50°C at a constant shaking rate of 150 rpm. The amount of dye adsorbed q_e can be calculated by the following equation:

$$q_e = (C_0 - C_e) V/m \quad (5)$$

where C_e is the concentration of dye at equilibrium.

Three models were applied for the equilibrium of RB and RY, the Langmuir, Freundlich and Dubinin-Radushkevitch (D-R) models.

Langmuir Adsorption Isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [25]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (6) into linear form.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (7)$$

Where q_m is the maximum monolayer coverage capacity (mg/g) and K_L is the Langmuir isotherm constant (L/mg).

The values of K_L and q_{max} were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ [26].

Freundlich Adsorption Isotherm: This is commonly used to describe the adsorption characteristics for the heterogeneous surface [27]. These data often fit the empirical equation proposed by Freundlich:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

Where K_f is Freundlich isotherm constant (mg/g), n is the adsorption intensity.

The linear form of equation 8 is:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process [28]. If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption [29].

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [32]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$q_e = q_s \exp(-K_{ad} \varepsilon^2) \quad (10)$$

The linear form

$$\ln q_e = \ln q_s - K_{ad} \varepsilon^2 \quad (11)$$

Where q_s is theoretical isotherm saturation capacity (mg/g); K_{ad} is the Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and ε is Dubinin–Radushkevich isotherm constant. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [31&32]:

$$E = \sqrt{\frac{1}{2B_{DR}}} \quad (12)$$

Where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be calculated as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (13)$$

where R , T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. One of the unique features of the Dubinin–Radushkevich (DRK) isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed ($\ln q_e$) vs ε^2 the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve [33]. The constant such as q_s , and K_{ad} were determined from the appropriate plot using equation 11 above.

3. Results and Discussion:

3.1 Adsorbents characterization

Figure (2) shows the adsorption-desorption isotherms of RRH and H2. Surface parameters of RRH and H2 are listed in Table (1). The rice husk treated by H_2SO_4 (H2), possesses higher porosity when compared to that of the raw rice husk. This is due to the removal of some inorganic species like silica and carbonate at the adsorbent's surface. Similar observations were reported in literature [34] where modifications of adsorbents using sulfuric acid were found to increase their specific surface area and micropore areas.

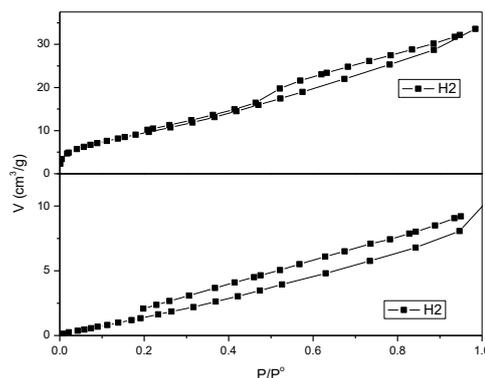


Fig. (2): the adsorption-desorption isotherms of RRH and H2.

Table (1): Surface parameters of RRH and H2

Adsorbent	V_m (cm^3/g)	C	Mean pore radius (nm)	Total pore volume (cm^3/g)	S_{BET} (m^2/g)
H2	8.559	33.308	2.91	0.05448	37.40
RRH	1.7103	5.6585	4.16	0.01556	7.47

In this study, FTIR technique is used as an important tool to define the characteristic functional groups on the adsorbent surface which are involved thereafter in dyes adsorption process. The FTIR spectra of RRH and H2 were used for the sake of comparison to determine the changes in the vibrational frequency of the functional groups on the adsorbent surface before and after the acid treating process. It is well-known that useful information about these changes could be achieved through the FTIR measurements [35]. The FTIR spectra of RRH and H2 samples are shown in Fig. 3. [35].

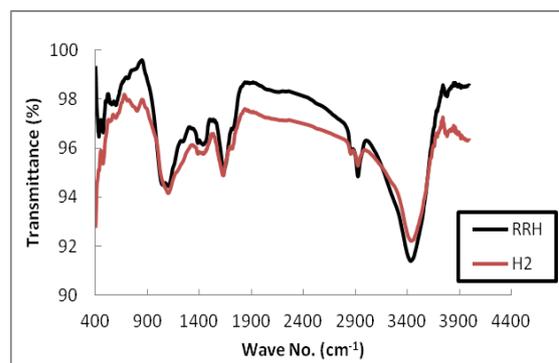


Fig.(3): FTIR spectra of RRH and H2.

In the spectra of RRH sample, the characteristic peak at 3404.31 cm⁻¹ is due to the existence of free hydroxyl groups. In addition, the peaks at the region (3100-2800 cm⁻¹) are attributed to the stretching of C-H bonds. Further, the C-H stretching vibration peaks at 2925.81 cm⁻¹ reveal the presence of alkane functional group.

The C=O stretching peaks around 1641.31-1737.74 cm⁻¹ may be ascribed to the hemicelluloses and lignin aromatic groups [36]. The peak between 1546.80-1652.88 cm⁻¹ corresponds to C=C stretching vibrations indicative of alkenes and aromatic functional groups. The peaks around 1380 cm⁻¹ refer to CH₃, while those at 1461.94 cm⁻¹ denote the existence of CH₂ and CH₃ groups [37]. A peak at 1379.01 cm⁻¹ ascribed to carboxyl-carbonate structures and the aromatic CH. The peaks between 1153.35 and 1300 cm⁻¹ correspond to vibration of CO group in lactones. The peaks around 862.12- 476.38, 1080.06 and 1238.21 cm⁻¹, correspond to Si-H, Si-O-Si stretching and CHOH stretching groups, respectively. The polar groups on the surface are likely to provide a considerable cation exchange capacity to the adsorbent [37].

In H₂ spectra, the intensity of free hydroxyl groups and C-H bonds at 3404.31 and 3100-2800 cm⁻¹, respectively decreases and the intensity of Si-H groups at 862.12 cm⁻¹ increases. This is related to protonation by sulfuric acid. Also, the peak at 1238.21 cm⁻¹ becomes broader than RRH confirming the presence of the CHOH group with high content. The previous results confirm that the change in functional groups on the surface of adsorbent affects the dye sorption.

Scanning electron microscopic analysis (SEM) for RRH and H₂ samples were selected as two representative samples for the sake of comparison and to identify the impact of sulfuric acid on the surface of

the raw material. Both SEM images are shown in Fig. 4 (a & b).

For the raw rice husks (RRH), the surface is relatively organized without any pits or pores and still intact, Fig. 3a. While for the sulfuric acid-treated sample, as we can clearly see, Fig. 3b, there are many pits, pores and cracks indicating the aggressive attack of this strong acid with the botanical structure of the raw material during the impregnation. Those pores and cracks might result from both the oxidation and the dehydration processes that can be expected to occur for the lignocellulosic material as a consequence of the severe interaction of the chemical reagent with the husks during impregnation [38,39]. These findings were confirmed in their surface chemistry by FTIR and by their surface area studies as discussed before.

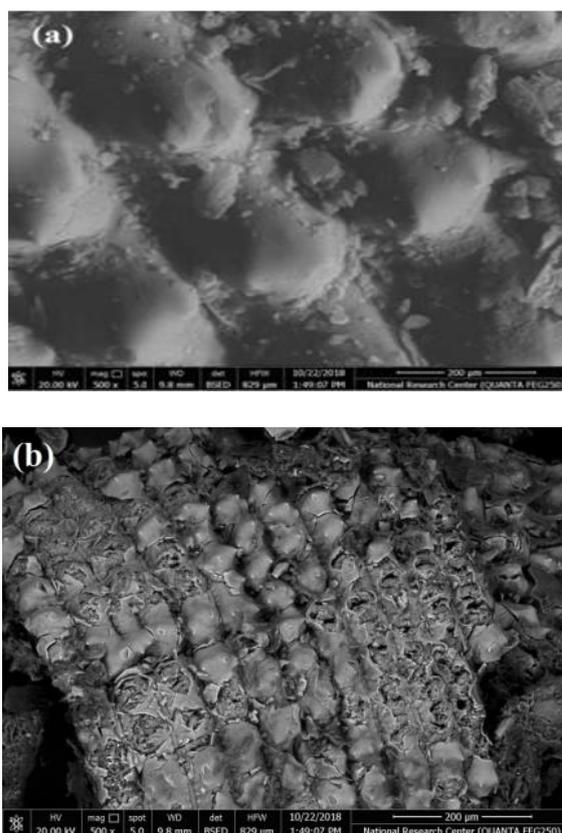


Fig. (4) SEM images for the surfaces of (a) RRH and (b) H₂ samples at x = 500 magnification.

3.2 Adsorption Kinetics:

Figure (5) illustrates the influence of contact time on adsorption behavior of BV and BY dyes by modified RH (H2) at different dyes concentrations.

The rate of BV and BY removal was very rapid during the 30 min and 20 min, respectively and thereafter, it remained constant. No significant increase is shown in adsorption after about 60 min as in Fig. 5 (a,b). The rate of dye adsorption increases with the increasing of dye concentration and the adsorption rate of BV is higher than the rate of BY.

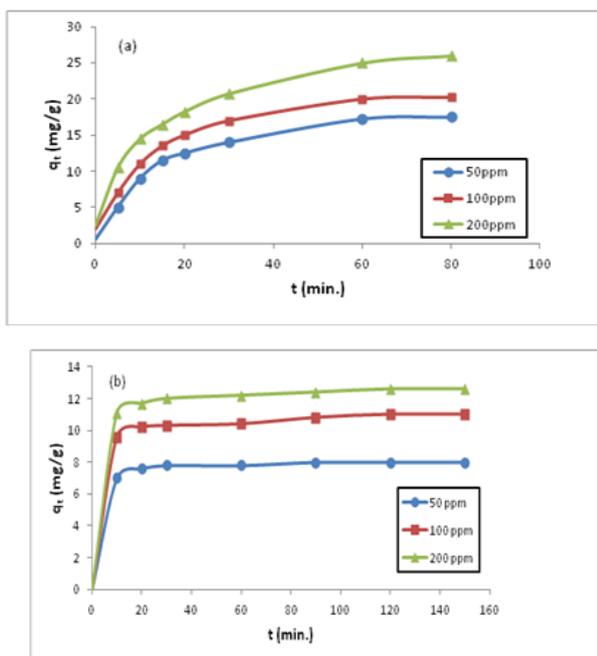


Fig. (5) Effect of contact time on adsorption of (a) BV and (b) BY dyes onto H2 at different dyes concentrations

The initial high rates of removal are due to the existence of a large number of vacant active binding sites in H2. These active sites promote large amounts of dye species to bound rapidly onto H2 surfaces. The number of binding sites then shortly becomes limited causing difficulty for the remaining vacant surface sites to be occupied by cationic ions. This is due to the repulsive forces between the positive ions on the solid surface and the liquid phase [40-42]. Consequently, the driving force of mass transfer between the liquid and solid phase in an aqueous adsorption system decreases with time elapse.

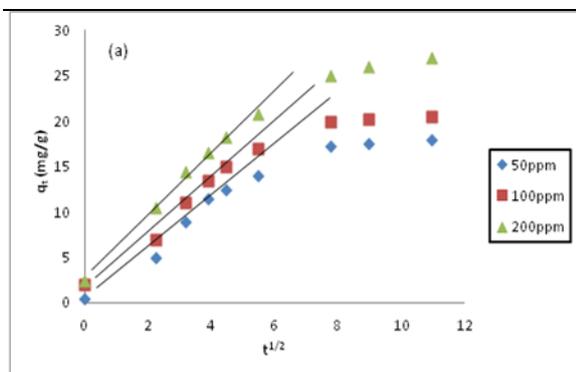
The pseudo-first and the pseudo-second order parameters of both BV and RY on H2 and their correlation coefficient R^2 are listed in Table (2).

Table (2) reveals that the values of R^2 obtained from the pseudo-second order model are greater than that of the 1st order. So, the adsorption of BV and BY by H2 follows pseudo-second order kinetics.

Fig. 6 shows the relation between q_t versus $t^{1/2}$ for the sorption of BV and BY on H2 at 30°C. As can be shown from Fig. 6, the plots of q_t against $t^{1/2}$ consist of initial curved portions which referred to boundary layer effects and linear portions referred to intraparticle effects. Additionally, the linear portion does not cross the origin, indicating the contribution of different mechanisms other than intraparticle diffusion in controlling dye sorption. The Intraparticle diffusion parameters are listed in Table (2). Adsorption of BV dye resulted in a considerable increase in k_{id} than and of BY.

Table (2): The pseudo-first, pseudo-second order and the intraparticle diffusion parameters of BV and (b) BY on H2

Pseudo-first order			Concentration	Dye
			(ppm)	
R²	k₁	q_o (mg/g)		
0.777	0.028	10.54	50	
0.707	0.031	10.68	100	BV
0.913	0.028	16.43	200	
0.78	0.028	10.54	50	
0.71	0.031	10.68	100	BY
0.91	0.028	16.43	200	
Pseudo- second order				
R²	k₂	q_s		
0.99	0.0053	19.61	50	
0.99	0.0059	22.22	100	BV
0.99	0.0042	28.57	200	
0.90	0.002	25.34	50	
0.894	0.020	14.78	100	BY
0.894	0.001	12.231	200	
Intraparticle diffusion parameters				
R²	C	k_{ia}		
0.970	0.013	2.809	50	
0.976	1.545	2.946	100	BV
0.997	2.488	3.672	200	
0.663	6.719	0.159	50	
0.714	9.306	0.156	100	BY
0.855	10.550	0.229	200	



R² values indicate the appropriateness of the application of this model on BV adsorption only.

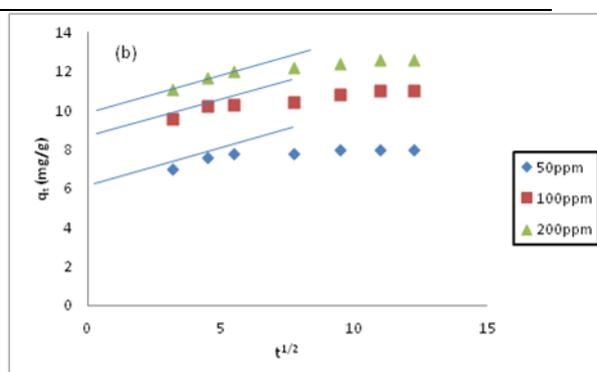


Fig.(6): Intraparticle diffusion isotherms of adsorption of (a) BV and (b) BY dye onto H2.

3.3. The effect of initial concentration on the removal of BV dyes:

The influence of initial BV dye concentration on the sorption equilibrium capacity of all adsorbents (RRH, H1, H2 and H3) is shown in Fig. 7a. Fig. 7a shows that the amount of BV dye adsorbed onto RRH, H1, H2 and H3 increases with increasing the initial dye concentration using a similar fixed amount of adsorbents. This is in accordance with the fact "the higher the dye concentration is, the stronger the driving force of the concentration gradient thus the higher the adsorption capacity". Also, H2 adsorbent gives the highest adsorption capacity. This is attributed to the increase of active sites on sorbent as mentioned in FTIR spectra. Therefore, all experimental are carried out using adsorbent H2.

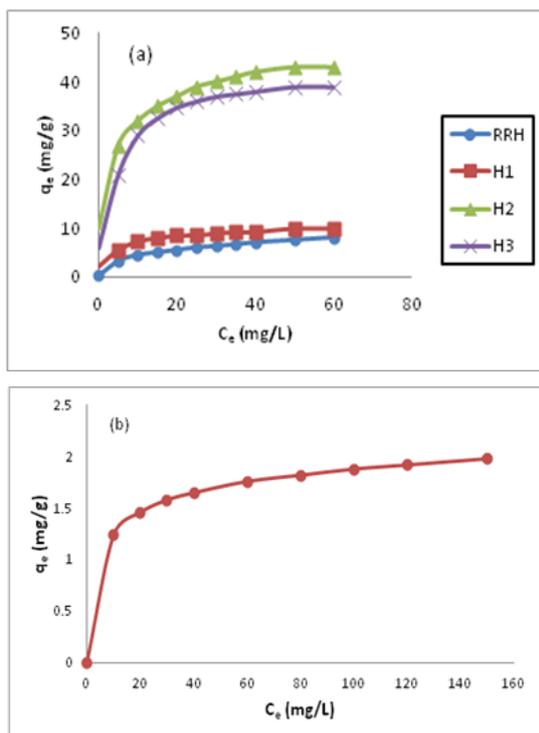


Fig.(7): Equilibrium curve for the sorption of (a) BV dye onto R, H1, H2 and H3 and (b) BY on H2.

Fig. 7b shows the impact of initial BY dye concentration on the equilibrium adsorption capacity on adsorbate (H2).

The Langmuir, Freundlich and D-R parameters with correlation coefficient for BV and BY on H2 are listed in Table (3).

It is apparent that the H2 sorbent adsorbed BV dye especially but showed a very low affinity for BY dye in dye solutions. These can be explained in terms of the dissociation of dyes in their aqueous solutions into charged species. The BV dye molecules dissociate into positively charged components and Cl^- ions. However, BY dissociate into positively charged components and negatively charged moieties containing sulphonate (SO_3^{2-}) groups. The potential of H2 sorbent to sorb charged species positively is attributed to the presence of binding sites such as hydroxyl and carboxyl groups on the surface as mentioned before [43,44]. The low affinity of H2 sorbent for BY dye is due to the coulombic repulsion between the negatively charged surface of H2 sorbent and sulphonate groups of the dye molecules [45,46] as a result the amount adsorption decreases.

Inspection to Table (3), both Langmuir and Freundlich models are fit to dyes adsorption. By comparing the values of calculated q_{mcal} with experimental q_{mexp} obtained from these models, experimental q_{mexp} values are well-correlated with those calculated from Langmuir model. This indicates that Langmuir model fits better with the experimental data.

Fig. 8 shows the effect of temperatures on the adsorption of BV and BY onto H2 where the amount adsorbed decreases by the increase of temperature from 303K to 323K, i.e. the adsorption of dyes on H2 is an exothermic process.

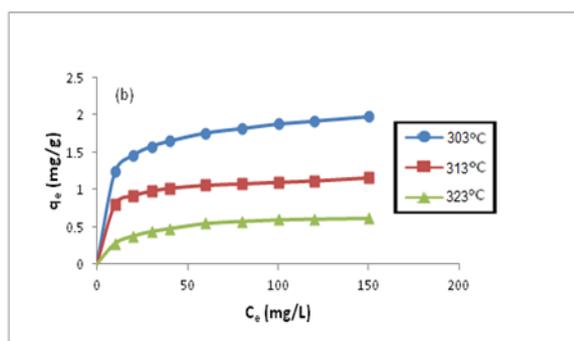
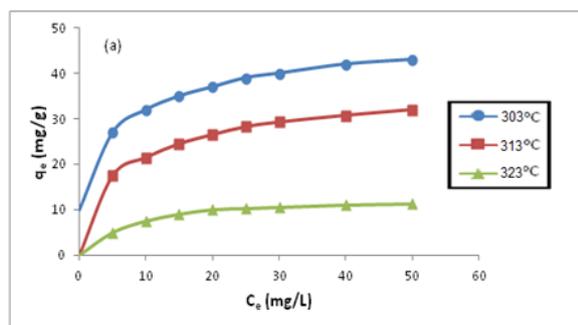


Fig.(8): Thermodynamic isotherms of adsorption of (a) BV and (b) BY dyes onto H2 at different temperatures.

The thermodynamic parameters of the adsorption processes were determined by applying equations (14 and 15) [47].

$$\Delta G^{\circ} = -RT \ln K \quad (14)$$

Where ΔG° is the change in free energy (g/mol), R is the universal gas constant (8.314 J/mol), T is the absolute temperature (K) and K is the adsorption equilibrium constant obtained from Langmuir isotherms at 303, 313 and 323K in Table (3).

The effect of temperature on the equilibrium constant is determined as follows:

$$\ln K = \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (15)$$

Where (ΔH°) in this equation is the change in enthalpy in (J/mol) and ΔS° is the change in the entropy (J/mol). ΔH° and ΔS° were calculated from the slope and intercept of the van't Hoff plots of $\ln K$ against $1/T$ respectively, as shown in Fig. (9). All data are listed in Table (4) with coefficient constant.

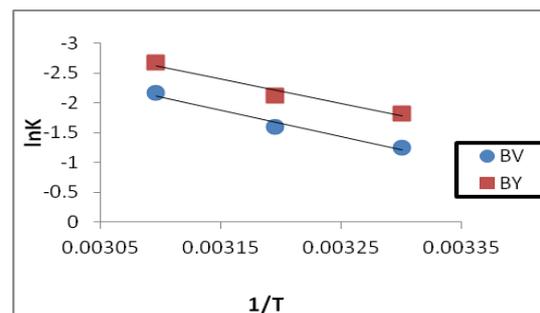


Fig. (9): Plot of $\ln k_2$ vs $1/T$.

Table (3): Langmuir, Freundlich and R-D parameters with correlation coefficient for BV and BY adsorption on H2:

Langmuir parameters				Dye
R ²	b	q _m	Temp. (K)	
0.973	0.285	45.455	303	BV
0.975	0.203	34.483	313	
0.994	0.115	13.889	323	
0.969	0.161	1.968	303	BY
0.978	0.219	1.150	313	
0.993	0.069	0.0672	323	
Freundlich parameters				
R ²	n	k _f		
0.976	5.208	20.450		BV
0.982	7.576	1.180		BY
D-R parameters				
R ²	k _{dr}	q _m		
0.816	0.001	37.599		BV
0.787	115.7	1.886		BY

The negative values of ΔG° show that the dye adsorption onto H2 is a spontaneous and an endothermic process. The negative value of ΔS° connotes that both enthalpy and entropy are responsible for making ΔG° negative, so that the adsorption is a spontaneous process, though the enthalpy contribution is much greater than that of the entropy.

The negative value of ΔG° denotes that the randomness decreases at the solid-solution interface during the dye adsorption onto the modified RH.

Table (4): Thermodynamic parameters of adsorption of BV and BY on H2:

R^2	ΔH° (J/mol)	ΔS° (J/mol)	ΔG° (g/mol)	Temp. (K)	Sample
0.973	131.5275	-36806.08	-3162.19	303	BV
			-4149.47	313	
			-5808.09	323	
			-4600.84	303	
0.967	128.2019	-34353.45	-3952.04	313	BY
			-7179.88	323	

Conclusion

This study shows that H_2SO_4 -modified rice husk can be used as an effective and low-cost adsorbent for the removal of BV and BY dyes from aqueous solutions. The operational parameters such as initial dye concentration, contact time and temperature affect the adsorption efficiency of modified rice husk. The adsorption kinetics followed pseudo-second order model indicating chemisorption. The intraparticle diffusion model was the rate controlling step in the adsorption of BV dye only. BV and BY adsorption onto modified rice husk followed Langmuir isotherm model. The thermodynamic parameters demonstrated that the adsorption is a spontaneous process and exothermic in nature. Both FT-IR and SEM analyses have shown a good agreement with each other and conform to the surface and dye-adsorption obtained results. From all the above- obtained results, it can be concluded that H_2SO_4 -modified rice husk should be a promising low-cost, and effective adsorbent for the removal of dyes from water.

References

- 1- Alzaydien AS. Adsorption of methylene blue from aqueous solution onto a low-cost Natural Sordania Tripoli. Am. J. of Environ. Sci. 2009; 5:197-208.
- 2- Zheng T, Holford TR, Mayne ST, Owens PH, Boyle P, Zhang B, Zhang YW, Zahm SH. Use of their colouring products and breast cancer risk: a case-control study in Connecticut. Eur J. Cancer 2002; 38: 1647-52.
- 3- Salleh MAM, Mahmoud DK, Karim WAWA, Idris A. Cationic and anionic dye adsorption by agricultural solid wastes. A comprehensive review. Desalination 2011; 280: 1-13.
- 4- Arivoli S, Thankuzhali M. Adsorption of Rhodamine B by acid activated carbon. Kinetic, thermodynamic and equilibrium. Orbital 2009; 2:138-155.
- 5- Kumer KV, Porkodi K. Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel, Dyes and pigments 2007; 74(3):590-4.
- 6- Abdel-Nasser A. El-Hendawy, S. E. Samra and B. S. Girgis "Adsorption characteristics of activated carbons obtained from corncobs", Colloids and Surfaces A, 180 (2001) 209-221.
- 7- Abdel-Nasser A. El-Hendawy "Influence of HNO_3 oxidation on the structure and adsorptive properties of corncob-based activated carbon" Carbon 41 (2003) 713-722.
- 8- Sumanjit, Prased N. Adsorption of dyes on rice husk ash. Indian Journal of Chemistry. Section A. 2001; 40(4): 388-91.

- 9- Sohair A. Sayed Ahmed, Laila B. Khalil, Thoria El-Nabarawy. Removal of Reactive Blue 19 dye from Aqueous solution using natural and modified orange peel. carbon letters 2012;13(4), 212-20.
- 10- Sohair A. Sayed Ahmed, Laila B. Khalil, El-Nabarawy Th., Modified Activated Carbons from Tea Waste for the Removal of Cu(II) and Pb(II) Ions. Egypt. J. Chem. 2015; 58(2): 183 – 202 .
- 11- Sohair A. Sayed Ahmed, Amina A. Attia, Laila B. Khalil. Liquid-Phase Adsorption of Phenol using Modified Rice Husks: Kinetics, Isotherms and Thermodynamics Studies. Asian Journal of Applied Sciences (ISSN: 2321 – 0893) 2015; 3(4): 589-606.
- 12- Belala Z, Jeguirium M, Belhachemi M, Addoun F, Trouve G. Biosorption of copper from aqueous solutions by date stones and palm-trees waste. Environ. Chem. Lett. 2011; 9(1): 65-9.
- 13- Ong ST, Lee CK, Zainal Z. Removal of basic and reactive dyes using ethylenediamine modified rice hull. Bioresource Technology 2007; 98: 2792-9.
- 14- Nigam P. Physical removal of textile dyes form effluents and solid state fermentation of dye-adsorbed agricultural residues. Biores. Technol. 2000; 72: 219-26.
- 15- Gomez V, Larrechi MS, Callao MP. Kinetic and adsorption study of acid dye removal using activated carbon. Chemosphe 2007; 69(7): 1151-8.
- 16- Sleiman M, Vildoza D, Ferronato C, Chovelon JM, Photocatalytic degradation of azo dye Metanil yellow: optimization and kinetic modeling using a chemometric approach. Appl. Catal. B: Environ, 2007; 77(1-2): 1-11.
- 17- Khadhraoui M, Trabelsi H, Ksibi M, Bouguerra S, Elleuch B. Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse. J. Hazard Mater. 2009; 161: 974-81.
- 18- Isik M, Sponza DT. Anaerobic/aerobic treatment of a simulated textile wastewater. Sep. Purif Technol. 2008; 60(1): 64-72.
- 19- Tahir Amin M, Ali Alazba A, Muhammad Shafiq. Adsorptive Removal of Reactive Black 5 from Wastewater Using Bentonite Clay: Isotherms, Kinetics and Thermodynamics. Sustainability 2015; 7(11): 15302-18.
- 20- Cleiton A. Nunese, Mário C. Guerreiro. Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers, Quim. Nova 2011; 34(3): 472-6.
- 21- Ocampo-Perez, R, Leyva-Ramos, R, Mendoza-Barron, J, Guerrero-Coronado, RM. Adsorption rate of phenol from aqueous solution onto organobentonite: surface diffusion and kinetic models. J. Collid Interface Sci. 2011; 364(1): 195-204.
- 22- Lagergren S. Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Vetenskapsakademiens. Handlinger. 1898; 24(4): 1-39.
- 23- Ho YS. Adsorption of heavy metals from waste streams by peat. University of Birmingham, Birmingham, UK, Ph. D. Thesis, 1995
- 24- Weber WJ, Morris JC. Kinetic of adsorption carbon solution. J. Saint. Eng. Div. Am. Soc. Civ. Eng. 1963; 89: 31-59.
- 25- Hall KR, Eagleton LC, Andreas Acrivos, Theodore Vermeulen. Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions. Ind. Eng. Chem. 1966; 5:212–23.
- 26- Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 1918; 40: 1362-1403.

- 27- Hutson ND, Yang RT .Adsorption. *J. Colloid Interf. Sci.* 2000; 189.
- 28- E. Voudrias, F.Fytianos and E.Bozani : Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials, *Global Nest, The Int.J.* 2002 4(1),75-83.
- 29- S. Mohan, and J.Karthikeyan. Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal“, *Environ. Pollut.* 97,(1997) pp.183-187.
- 30- A. Dabrowski, Adsorption—from theory to practice, *Adv. Colloid Interface Sci.* 93 (2001) 135–224.
- 31- M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, *Chem. Rev.* 60 (1960) 235–266.
- 32- J.P. Hobson, Physical adsorption isotherms extending from ultra-high vacuum to vapor pressure, *J. Phys. Chem.* 73 (1969) 2720–2727.
- 33- K.Y. Foo and B.H. Hameed, Insights into the modeling of adsorption isotherm systems, *Review Chemical Engineering Journal* 156 (2010) 2–10.
- 34- Lu, G.Q. and D.D. Lau, 1996. Characterisation of sewage sludge-derived adsorbents for H₂S removal. Part 2: Surface and pore structural evolution in chemical activation. *Gas Separat. Purificat.*, 10: 103-111.
- 35- S.B. Daffalla, H. Mukhtar and M.S. Shaharun Characterization of Adsorbent Developed from Rice Husk: Effect of Surface Functional Group on Phenol Adsorption *Journal of Applied Sciences* Volume 10 (12): 1060-1067, 2010
- 36- Bansal, M., U. Garg, D. Singh and V.K. Garg, 2009. Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *J. Hazard. Mater.*, 162: 312-320.
- 37- Srivastava, V.C., I.D. Mall and I.M. Mishra, 2006. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J. Hazard. Mater.*, 134: 257-267.
- 38- Abdel-Nasser A. El-Hendawy; Surface and adsorptive properties of carbons prepared from biomass; *Applied Surface Science* 252 (2005) 287–295.
- 39- Abdel-Nasser A. El-Hendawy, Andrew J. Alexandar, Robert J. Andrews, Gavin Forrest; Effects of Activation schemes on porous, surface and thermal properties of activated carbons prepared from cotton stalks; *J. Anal. Appl. Pyrolysis* 82 (2008) 272-278.
- 40- Srivastava, VC, Mall ID and Mishra IM, "Equilibrium modeling of single and binary adsorption of cadmium and nickel onto baggas fly ash", *J. Chem Eng.*, Vol. 117, 2006, pp. 79-91.
- 41- A chak M, HapidiA, Ouazzani N, Sayadic S and Mandi I., "Low cosbisorbent banana peel for the removal of phenolic compounds from olive mill wastewater kinetic and equilibrium studies", *J. Hazard. Mate.*, Vol 166, 2009, pp. 117-125.
- 42- Wafaa E. Rashwan, Sahar M. El-Khouly, Hamdy Farag and Abdel-Nasser A. El-Hendawy. Influence of Mechanical Milling on the Surface and Morphological Properties of Nanoparticle Molybdenum Disulfide, *Egypt. J. Chem.* 59, No. 6, (2016) 1029 -1044.

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- 43- Tang, P.L., Lee, C.K., Low, K.S., Zainal, Z., 2003. Sorption of Cr(IV) and Cu(II) in aqueous solution by ethylenediamine modified rice hull. *Environ. Technol.* 24, 1243-1251.
 - 44- Munaf, E., Zein, R. 1997. The use of rice husk for removal of toxic metals from waste water. *Environ. Tehcnol.* 18, 359-362.
 - 45- Lee, C.K., Low, K.S., Gan, P.Y., 1998. Removal of some organic dyes by acid treated spent bleaching earth. *Enviorn. Technol.* 20, 99-104.
 - 46- Low, K.S., Lee, C.K., 1997. Quaternized rice husk as sorbent for reactive dyes. *Biores. Tehcnol.* 61, 121-125.
 - 47- L.Y. Fraiji, D.M. Hayes, T.C. Werner, Static and dynamic fluorescence quenching experiments for the physical chemistry Laboratory, *J. Chem., Edu.* 69 (1992) 424-428.