

Preparation of Carbonaceous Adsorbent from Plant of *Calotropis Gigantea* by Thermo-Chemical Activation Process and its Adsorption Behavior for Removal of Methylene Blue

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Abstract: The plant of *Calotropis Gigantea* was used as source material for preparation of carbonaceous adsorbent using K_2CO_3 and $KHCO_3$ as activation agents in thermo-chemical process. The effects of carbonization time (30-120 min), temperature (400-700°C) and impregnation ratio (0.5-1.5) of chemical agents on the adsorption capacity and yield of products were investigated. The effect of initial pH on adsorption of methylene blue on carbonaceous adsorbent showed the optimum pH was natural pH. The adsorption isotherms of Langmuir and Freundlich for adsorption of methylene blue on carbonaceous adsorbent were studied. The results indicated that the Langmuir isotherm model fits better than the Freundlich isotherm model.

Key words: Carbonaceous adsorbent • Chemical activation • Methylene blue adsorption • K_2CO_3 and $KHCO_3$

INTRODUCTION

The plant of Carbonaceous adsorbent are well known as very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry and high degree of surface reactivity [1,2]. The ability of carbonaceous adsorbent and specially activated carbons for removal of organic and inorganic pollutants from gaseous and liquid phases makes them very versatile materials for purification and treatment of chemicals [3].

Any carbonaceous material high in carbon content with low ash, natural or synthetic, can be used as precursor for the preparation of carbonaceous adsorbent. Accordingly a large number of feed stocks of botanical origin and agricultural wastes have been extensively used for preparation of carbonaceous adsorbent and activated carbon reported in reviews [4-7]. The process for preparation of activation carbons involves physical or chemical activation. Physical activation is normally made by carbonization followed by activation using steam or CO_2 ; during carbonization, the material is pyrolyzed to remove non-carbon elements, then

activation occurs, at temperatures ranging from 700 to 1100°C, using gases that open and develop the porosity of the carbonized material [8,9]. Chemical activation is a one-step method used for the preparation of Activated carbons; different chemical activating agents like $ZnCl_2$ [10,11], H_3PO_4 [12-14], KOH [15-17], $NaOH$ [18], K_2CO_3 [19-21] and H_2SO_4 [22,23] might be used. These chemical agents help to develop the activated porosity, by means of dehydration and degradation; the mixture of the chemical and the carbon is then heated at a maximum of around 800°C.

Important advantages of the chemical activation compared to the physical activation are lower treatment temperatures and shorter treatment time. In addition carbonaceous adsorbent, obtained by chemical activation possess large surface area and well-developed micro porosity, which can be controlled and maintained in narrow ranges. Among the chemical activation agents, K_2CO_3 has great advantages in comparison to other activation agents, especially consumption of water for recovery, production of low environmental pollutants and relatively low activation temperature and largely used for preparation of activated carbon.

In the present investigation, carbonaceous adsorbents were prepared from *Calotropis Gigantea* by impregnation with K_2CO_3 and $KHCO_3$ followed by thermal treatment at $600^\circ C$. Testing of the adsorption capacity from solution was carried out by determining the adsorption isotherms of methylene blue.

MATERIALS AND METHODS

Material and Chemical Reagent: *Calotropis Gigantea* (Giant Stabragh) was used as a source of carbonaceous adsorbent, belongs to the family Asclepiadaceae. *Calotropis Gigantea* is a native to west and east of Africa, the Arabian Peninsula, south Asia, Indochina, south of Iran and central South America. It was collected from Minab at the south of Iran.

Potassium carbonate (K_2CO_3) and potassium hydrogen carbonate ($KHCO_3$) (Merck chemical company, Germany) were dissolved in distilled water to prepare 20% w/v solutions. 0.2500 g analytical grade methylene blue (Merck chemical company, Germany) was dissolved in 500 ml distilled water to prepare a stock solution of 500 mg/l.

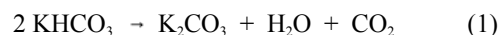
Preparation of Carbonaceous Adsorbent: The stems of *Calotropis Gigantea* (Giant Stabragh) was harvested at March of 2007 and dried at room temperature and cut to small sizes. Production of primary carbon has involved by the carbonization of *Calotropis Gigantea* (Giant Stabragh) in a negligibly ventilated atmosphere to drive out volatiles, leaving a porous carbon structure with low surface area. For activation of produced carbonaceous material, the raw carbon was crushed and sieved to particle less than 120 mesh size. Then solution of 20% w/v potassium carbonate or potassium hydrogen carbonate as activating agents was added at various impregnated ratio (0.5, 1.0, 1.5) and after 24 h, dried at $50^\circ C$ for 4 h and then placed in a furnace and heated at various temperature programs according to Table 2. After cooling, the produced material was repeatedly washed with hot deionized distilled water and after centrifugation, dried at $105^\circ C$. The produced carbonaceous adsorbent used for characterization and adsorption experiments.

Adsorption Experiments: The adsorption of methylene blue from aqueous solution on carbonaceous adsorbent was performed using batch experiments conducted in this study. The aqueous solution of methylene blue was prepared by dissolving dyestuff in deionised distilled water to produce a stock solution of 500 mg l^{-1} . Solutions of the required concentrations were prepared by

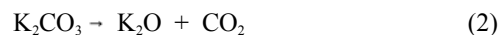
successive dilution of the stock solution. The effect of initial pH on dye adsorption was studied by performing the adsorption experiments at four different pH levels; 3.0, 5.0, 7.0 and 9.0. The pH of the solution (50 mg l^{-1}) was adjusted with 1 M solution of HCl or NaOH by using a pH meter (Orion 420A, USA). After 60 min contact time, the residual concentration of methylene blue in solutions was determined using a calibration curve prepared at the corresponding optimum wavelength (λ_{max}) of 665 nm using a Uv-Vis spectrophotometer (Jasco, Japan). After optimization of pH, all further studies for evaluation of adsorbent were carried out at pH of 7.0. The experiments for evaluation of adsorption studies were carried out at different dye concentrations (50, 75, 100 and 125 mg l^{-1}) to investigate the adsorptive capacity of *Calotropis Gigantea* (Giant Stabragh) activated carbons as adsorbent. The experiments were carried out at fixed adsorbent dose (20 mg/50 ml) in the aqueous solutions at room temperature. The flasks were agitated at room temperature at 150 rpm for 60 min. The dye solution was separated from the adsorbent by centrifugation (Sigma, Germany) at 2000 rpm for 10 min. The residual concentration of the dye was determined and employed for plotting of Langmuir and Freundlich isotherms to determine the adsorption capacity of the adsorbents.

RESULTS AND DISCUSSION

Comparison of K_2CO_3 and $KHCO_3$ for Preparation of Carbonaceous Adsorbent: Some physical properties of potassium carbonate and potassium hydrogen carbonate have been summarized in Table 1. These compounds have similar properties, but K_2CO_3 is thermally more stable than $KHCO_3$. Above $60^\circ C$, $KHCO_3$ gradually decomposes into potassium carbonate, water and carbon dioxide as showed in following reaction. The conversion is fast at $200^\circ C$:



Further heating converts the carbonate into the oxide as:



Based on the above reactions in comparison with potassium carbonate, potassium hydrogen carbonate was selected for preparation of carbonaceous adsorbent from Giant Stabraq. Table 2, shows the temperature programming for preparation of carbonaceous adsorbent from raw materials. The results showed the yield of thermo-chemical process decreased as the activation

Table 1: Physical properties of potassium carbonate and potassium hydrogen carbonate

Chemical formula	CAS number	Molecular weight (g/mol)	pH of 1% solution at 22°C	Solubility in water at 20°C (g/mol)
K ₂ CO ₃	[584-08-7]	138.20	11.50	112.0
KHCO ₃	[298-14-6]	100.11	8.20	32.2

Table 2: The results of preparation of carbonaceous adsorbent from plant of Giant Stabragh by K₂CO₃ and KHCO₃ at various temperatures and times

No	Temperature (°C)			Time (min)			K ₂ CO ₃		KHCO ₃	
	T ₁	T ₂	T ₃	t ₁	t ₂	t ₃	%yield	q _e MB	%yield	q _e MB
1	200	400	600	30	60	30	71	131	76	140
2	200	500	600	30	60	30	64	137	65	156
3	200	400	700	30	60	30	57	146	56	159
4	200	500	700	30	60	30	46	158	47	161
5	200	400	600	-	90	30	52	167	55	176
6	200	500	700	-	90	30	37	174	39	178

Table 3: The results of using various impregnation ratios of K₂CO₃ and KHCO₃ for preparation of carbonaceous adsorbent

Impregnation Ratio	K ₂ CO ₃		KHCO ₃	
	%yield	q _e MB	%yield	q _e MB
0.5	58	134	62	132
1.0	65	141	67	144
1.5	61	140	66	142

temperature increased, but the adsorption of methylene blue from solution increased. These results supported when chemical activation with K₂CO₃ and KHCO₃ impregnation was used; increasing the carbonization temperature, decreased the yield progressively due to the release of volatile products. But these dehydration and elimination reactions increased the porosity and surface area of activated carbon. Based on these results the conditions no 5 (Temperatures 400 and 600°C and times of 90 and 30 min respectively) was selected for preparation of carbonaceous adsorbent. The comparison of K₂CO₃ and KHCO₃ showed that KHCO₃ was more effective than K₂CO₃ for preparation of carbonaceous adsorbent from Calotropis Gigantea (Giant Stabragh) due to higher yield and adsorption of methylene blue from dye solution.

Effect of the Impregnation Ratio of K₂CO₃ and KHCO₃ on Preparation of Carbonaceous Adsorbent: The effect of the impregnation ratio of K₂CO₃ and KHCO₃ on the yield and adsorption capacity of the prepared carbonaceous adsorbent has been shown in Table 3. In the selected experimental conditions (Temperatures 200, 400 and 600°C and times of 30, 60 and 30 min respectively), the use of impregnation ratios 0.5, 1 and 1.5, resulted the highest yields and relatively high adsorption capacities at R=1 in

both cases of K₂CO₃ and KHCO₃. When impregnation ratio of 1.5 was used, the yield of products decreased but the adsorption capacity of dye on carbonaceous adsorbent increased. Therefore the impregnation ratio of 1, which is economically and environmentally advantages, was selected for preparation of carbonaceous adsorbent.

Effect of Initial Ph on Adsorption: The initial pH of the aqueous solution plays an important role in the whole adsorption process and particularly on the adsorption capacity of adsorbent. The acidity of solution, influencing not only the surface charge of the adsorbent and the degree of ionization of the material present in the solution, but also the solution chemistry of adsorbent [24]. Therefore it was important to indicate the effect of pH on adsorption capacity of prepared carbonaceous adsorbent.

Fig. 1 shows the effect of initial pH of methylene blue solution on adsorption capacity of carbonaceous adsorbent prepared by impregnation of K₂CO₃ and KHCO₃. Evidently pH significantly affected the extent of adsorption of dye over both adsorbents. It is observed that the methylene blue uptake by both adsorbents is higher at pH=7. At lower pH values (pH=3 and pH=5), the concentration of hydrogen ions is higher and the surfaces of the carbonaceous adsorbent becomes positively charged thus, the repulsion of positive charges inhibits the adsorption of dye cation on surfaces of both adsorbents. A higher adsorption capacity was obtained at pH=7, that is due to the increasing electrostatic attraction between positively charged dye cation and negatively charged adsorption sites and the dispersive interactions between methylene blue molecules and

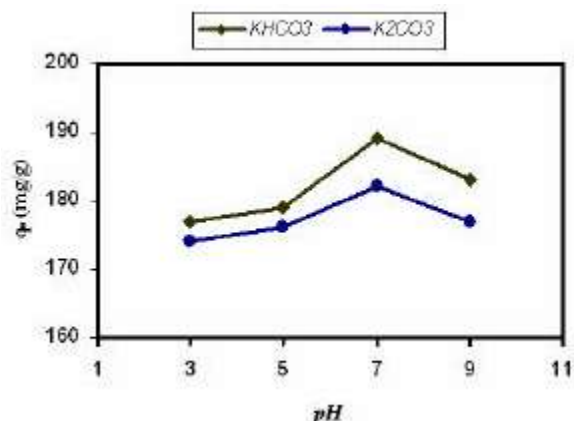


Fig. 1: The effect of initial pH on adsorption of methylene blue on carbonaceous adsorbent by K₂CO₃ and KHCO₃

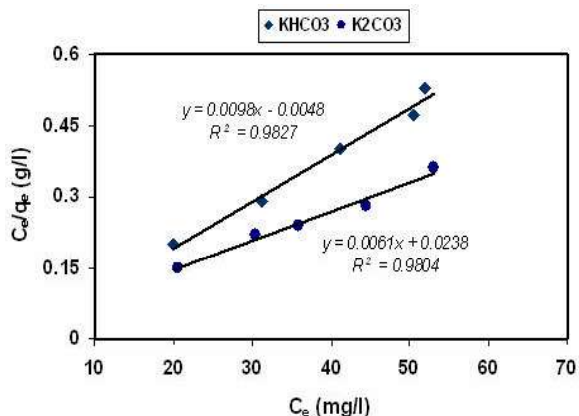


Fig. 2: Langmuir plots for the adsorption of methylene blue on prepared carbonaceous adsorbent by K₂CO₃ and KHCO₃ at 25°C

Table 4: Adsorption isotherm constants for the adsorption of methylene blue on carbonaceous adsorbent

	Langmuir				Freundlich	
	q _{max} (mg g ⁻¹)	K _L (l mg ⁻¹)	r _L ²	n	K _F (l g ⁻¹)	r _F ²
K ₂ CO ₃	163.93	0.26	0.980	9.76	71.94	0.777
KHCO ₃	102.04	2.04	0.983	5.99	81.56	0.797

the layers of carbonaceous adsorbent [25]. At higher pH (pH=9), the surface of the carbonaceous adsorbent becomes more negatively charged, at this condition, the presence of other cations in solution competes with dye cation for adsorption on surfaces of adsorbent, therefore the tendency of adsorbent for adsorption of dye cation decreased as seen in Fig.1. Thus pH=7 was selected as the optimum pH value for all further experiments due to the advantages of neutral pH.

Adsorption Isotherms: The equilibrium adsorption isotherm is one of the most important ways for characterizing of produced carbonaceous adsorbent. In this manner, the Langmuir and Freundlich isotherm equations were used to interpret the mechanism of the adsorption.

The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption occurs at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation is

based on the assumption of a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur [26].

The Linear Form of the Langmuir Isotherm Equation [3,27] Is Presented by Following Equation:

$$C_e / q_e = 1 / q_{max}K_L + C_e / q_{max} \quad (3)$$

Where q_e (mg g⁻¹) is the equilibrium dye concentration on the adsorbent, C_e (mg l⁻¹) the equilibrium dye concentration in the solution, q_{max} the monolayer adsorption capacity of the adsorbent (mg g⁻¹) and K_L is the Langmuir adsorption constant (l mg⁻¹) and related to the free energy of adsorption. The plots of C_e/q_e versus C_e for the adsorption give a straight line with slope of 1/q_{max} and intercept of 1/q_{max}K_L. The experimental plots of Langmuir adsorption isotherm of methylene blue on carbonaceous adsorbent has been shown at Fig. 2. Based on the slopes and intercepts of these plots, the q_{max} and K_L for adsorption of methylene blue on prepared carbonaceous adsorbents were calculated and listed in Table 4.

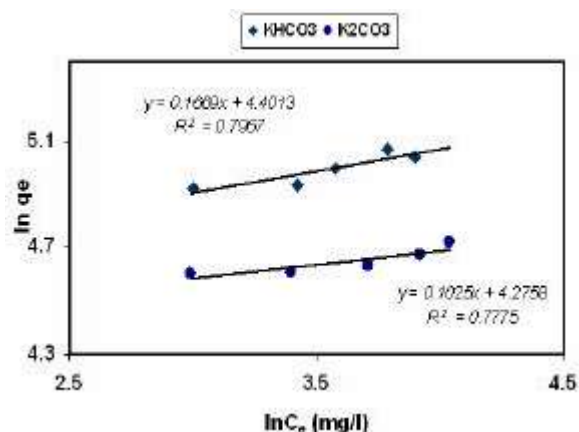


Fig. 3: Freundlich plots for the adsorption of methylene blue on prepared carbonaceous adsorbent by K_2CO_3 and $KHCO_3$ at $25^\circ C$

The Freundlich equation [3,28] is an empirical equation employed to describe heterogeneous systems, characterized by the heterogeneity factor $1/n$, describes reversible adsorption and is not restricted to the formation of the monolayer. A linear form of the Freundlich equation is:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

Where K_F ($l \text{ g}^{-1}$) and n (dimensionless) are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The plots of $\ln q_e$ versus $\ln C_e$ for the adsorption of methylene blue on carbonaceous adsorbent were employed to generate the intercept value of K_F and the slope of $1/n$ (Fig. 3).

The Freundlich isotherm parameters for the adsorption of methylene blue onto carbonaceous adsorbent are listed in Table 4. It is evident from these data that the surface of activated carbon is made up homogeneous adsorption patches. In other words, the Langmuir isotherm model fits better than the Freundlich isotherm model, when the r^2 values of the models are compared in Table 4.

CONCLUSION

A procedure for preparation of carbonaceous adsorbent from the plant of *Calotropis Gigantea* by chemical activation with K_2CO_3 and $KHCO_3$ was purposed. The results showed that $KHCO_3$ was more effective than K_2CO_3 for preparation of carbonaceous

adsorbent due to higher yield and adsorption of methylene blue from dye solution. The impregnation ratio of 1 was selected for preparation of carbonaceous adsorbent. The effect of initial pH on adsorption of methylene blue on prepared carbonaceous adsorbent showed the dependence of adsorption to the existence of two parallel adsorption mechanisms, the electrostatic interactions and the dispersive interactions between methylene blue molecules and the layers of carbonaceous adsorbent. The adsorption isotherms of Langmuir and Freundlich for adsorption of methylene blue on carbonaceous adsorbent were studied. The results indicated that the Langmuir isotherm model fits better than the Freundlich isotherm model.

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