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Equilibrium and Kinetic Adsorption Studies of Reactive Orange onto Resorcinol-Formaldehyde Carbon Gel

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Adsorbents in granular form with small particle size are not suitable for continuous adsorption process. Resorcinol-formaldehyde carbon gel is a synthetic polymeric adsorbent that can be moulded to desired size and shape of high surface area and porosity, and controllable porous structures. This work aims to evaluate the feasibility of carbon gel as the adsorbent in dye wastewater treatment. The carbon gels were prepared by mixing resorcinol and formaldehyde in a presence of sodium carbonate catalyst at resorcinol/catalyst (R/C) ratios of 100, 200, 1,000 and 2,000. The carbonisation of carbon gels was fixed at 600 °C for 3 h, whereby part of the carbonised carbon gels was oxidised with nitric acid (HNO_3). The performance of carbon gels was investigated by the adsorption of reactive orange 16 (RO16). Carbon gel with R/C ratio of 1,000 displays a specific surface area of 638.9 m^2/g and RO16 maximum capacity of 6.8 mg/g. The oxidised carbon gels exhibit poorer adsorption performance when compared to the non-oxidised ones. The equilibrium data of RO16 by the non-oxidised carbon gels fitted well with Langmuir model, suggesting a monolayer adsorption process. The kinetics data indicates that physisorption plays a dominating role in the adsorption of RO16.

1. Introduction

The effluent of textile dyes has contributed to dye wastewater and has become one of the major sources of severe pollution problem. Dyes in water are highly stable to light, temperature, detergents, chemicals, soap and other parameter such as bleach and perspiration. Due to these properties, dyes resist biodegradation and remain in environment for an extended period of time (See et al., 2015). Adsorption is the most effective removal method due to the flexibility and simplicity of design, ease of operation and insensitivity of toxic pollutants (Lee and Zaini, 2015). The commercial adsorbents produced nowadays are in granular form with small particles size that are unsuitable for continuous process due to large hydraulic resistance (Masuda et al., 2013).

Materials which can be obtained through the sol-gel method such as carbon gel, can be moulded to the desired size and shape in order to overcome the resistance to flow (Masuda et al., 2013). Carbon gel was first synthesised by Pekala (1989) through the hydrolysis and condensation of resorcinol and formaldehyde.

Carbon gel is formed eventually by an aggregate of nanoparticles. The voids formed between the nanoparticles are in the mesopore size range, while micropores exist within the nanoparticles (Yamamoto et al., 2003). The hierarchical pore system of macropores and mesopores is influenced by the synthesis and drying process, while the development of the micropores takes place during the subsequent carbonisation and activation steps (Lufrano et al., 2011). Carbon gels usually have surfaces of around 600 - 700 m^2/g, while that of activated carbon surfaces can exceed 2,000 m^2/g. Due to these important properties — high porosity, surface area and pore volume, controllable pore structure and pore size distribution, carbon gel can be fitted in specific application and seem to be a promising adsorbent for continuous mode of adsorption (Moreno et al., 2013).

The aim of this study is to evaluate the feasibility of carbon gel as the adsorbent in dye wastewater treatment. The batch mode was used as the first step to establish an insight into the application of continuous mode.

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2. Materials and methods

2.1 Preparation of resorcinol-formaldehyde carbon gel

Formaldehyde, HCHO (37 wt% in water), resorcinol, $C_6H_6O_2$ (99 %), sodium carbonate, Na_2CO_3 (99.5 %), tert-butyl alcohol, $(CH_3)_3COH$ (99 %) were obtained from Wako Pure Chemical Industries Ltd, and nitric acid, HNO_3 (65 %) from R&M Marketing, Essex, U.K. These chemicals were used in the preparation and surface modification of resorcinol-formaldehyde carbon gels. Reactive orange 16 (RO16) with C.I. No. 17757, MW = 617.54 g/mol and λ_{max} = 523 nm was purchased from Sigma-Aldrich, India. It was used as the model dye (adsorbate) to evaluate the removal performance of carbon gels. All chemicals used are of analytical-grade reagents.

Carbon gel was synthesised using resorcinol (R), formaldehyde (F), sodium carbonate (C) and water (W). Firstly, initial solution recipe was obtained based on fixed R/W ratio, R/F ratio and volume of solution, while R/C ratio was varied from 100 to 2,000. R, F and C were mixed in W and poured into a mould, and allowed at 35 °C for 2 d for gelation of sol solution. Reactions happens between R and F, where C is as catalyst and W acts as a reaction medium. The mould was heated at 60 °C for 3 d for gel aging to increase the crosslinking density by promoting the progress of condensation reaction. Tert-butyl alcohol (TBA) was used for solvent exchange at 50 °C for 3 d to remove excess water. TBA was replaced with the fresh one twice a day. The resultant RF gels were dried at 110 °C in oven for 2 d to remove solvent (Al-Muhtaseb and Ritter, 2003).

The RF gels were ground and sieved to a size of 1 mm, then carbonised at 600 °C for 3 h in furnace to produce RF carbon gels. Part of the carbon gels was mixed with nitric acid for oxidation at room temperature for 3 h and 60 °C for 5 h. The oxidation procedure was carried out to increase the attachment of oxide functional groups to the surface of the carbon gel (Al-Muhtaseb and Ritter, 2003). The oxidised carbon gel was washed with distilled water until pH = 4. The carbon gel was dried prior to ready to characterisation of specific surface area using Pulse Chemi Sorb 2705 at liquid N_2 at 77 K and RO16 adsorption.

The carbon gel yield percentage was calculated as Eq(1),

$$\text{yield}\ (\%) = \frac{m}{m_0} \times 100\ \% \tag{1}$$

where m is the mass (g) of RF carbon gel and m_0 is the mass (g) of RF gel.

2.2 Adsorption analysis

For equilibrium study, about 0.03 g of RF carbon gel was brought into intimate contact with 20 mL of RO16 solution of carrying concentration (2 – 50 ppm). The mixture was allowed to equilibrate on at 30 °C for 120 h. The residual concentration was measured by visible spectrophotometer (HALO VIS-10) at the wavelength of 523 nm. The adsorption capacity was calculated as Eq(2),

$$Q_e = \frac{(C_0 - C_e)}{m} V \tag{2}$$

where Q_e (mg/g) is the equilibrium dye concentration on the carbon gel, C_0 (mg/L) is the initial concentration of dye solution, C_e (mg/L) is the equilibrium concentration of dye solution, m (g) is the mass of carbon gel and V (L) is the volume of dye solution.

Two isotherm models were used to analyse the adsorption data. The Langmuir isotherm describes monolayer adsorption onto a surface containing a limited number of identical sites (Dada et al., 2012), and is expressed as Eq(3),

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \tag{3}$$

where Q_m (mg/g) is the monolayer (maximum) capacity of adsorbent, and b (L/g) is the Langmuir adsorption constant. The separation factor, R_L is the essential features of the Langmuir isotherm (Eq(4)) (Dada et al., 2012).

$$R_L = \frac{1}{1 + b C_0} \tag{4}$$

where C_0 (mg/L) is the maximum initial concentration. R_L value indicates the adsorption nature either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm is commonly applied to non-ideal adsorption on heterogeneous surface and multilayer adsorption (Ho et al., 2002). The Freundlich equation is given as Eq(5),

$$Q_e = KC_e^{1/n} \tag{5}$$

where K ((mg/g)(L/mg)$^{1/n}$) and n are the Freundlich constants.

For kinetic study, 0.03 g of carbon gel was brought into intimate contact with 20 mL of RO16 solution at initial concentrations of 5 and 10 ppm. The mixture was equilibrated at 30 °C. Small volume was withdrawn from the mixture at varying time intervals for concentration measurement. The adsorption capacity at time, t, was computed as Eq(6),

$$Q_t = \frac{(C_0 - C_t)}{m} V \tag{6}$$

where Q_t (mg/g) the amount of dye adsorbed at time t and C_t (mg/L) is the dye concentration at time t.

Kinetic models were applied to study the adsorption rate and mechanism. The pseudo-first-order and pseudo-second order models are expressed in Eq(7) and Eq(8).

$$Q_e = Q_e(1 - \exp^{-k_1 t}) \tag{7}$$

$$Q_e = \frac{k_2 {Q_e}^2 t}{1 + k_2 Q_e t} \tag{8}$$

where k_1 (h^{-1}) and k_2 (g/mg.h) are the rate constants of pseudo-first-order adsorption and pseudo-second-order adsorption, respectively.

3. Results and discussion

3.1 Characterisation of RF carbon gel

The yield and textural properties of RF carbon gels are shown in Table 1. The yield after carbonisation is nearly 50 %. The BET surface area and mesoporosity increased with increasing R/C ratio, and somewhat decreased upon oxidation. The specific surface area of carbon gels commonly decreases with the increase in R/C ratio. The interconnection of larger particles formed at higher R/C ratio could result in mesoporous network structure, so the specific surface area of unit mass decreases. However, the shrinkage occurs during drying decreased with increasing the R/C ratio, consequently increasing the surface area (Feng et al., 2011). The R/C ratio of 1,000 gives largest pore size and highest BET surface area among all carbon gels studied.

Table 1: Textural properties, yield of carbon gels and maximum adsorption capacity (Q_m)

Carbon gels	oxidation	R/C ratio	BET surface area (m^2/g)	Mesoporosity (%)	Average pore diameter (nm)	Q_m (mg/g)	Yield (%)
RC1	Non-oxidised	100	476.0	23.74	1.86	0.00	42.8
RC2		200	608.2	46.34	2.38	2.73	49.6
RC3		1,000	638.9	69.80	6.89	6.80	42.6
RC4		2,000	630.5	59.19	3.56	6.46	53.7
RC5	oxidised	100	301.2	0.00	1.33	0.00	42.8
RC6		200	566.7	44.89	2.33	0.00	49.6
RC7		1,000	711.5	75.10	7.68	6.52	42.6
RC8		2,000	586.2	59.34	3.57	5.84	53.7

3.2 Adsorption of reactive orange 16

Figure 1 shows the equilibrium adsorption of Reactive orange 16 (RO16) by RF carbon gels. Clearly, RC2, RC3, RC4, RC7 and RC8 demonstrated a clearly increasing trend in equilibrium adsorption capacity and achieved a saturation point known as maximum capacity at increasing equilibrium concentration.

RC1, RC2, RC5 and RC6 showed ineffective in RO16 adsorption. The average pore diameter of adsorbent should be 2 to 3 times that of the adsorbate for smooth diffusion to happen. Most of the dyes molecular size is around 1 nm, thus micropores are not favourable to capture RO16 molecules (Mohammadi et al., 2010). The average pore diameter of RC1, RC2, RC5 and RC6 are close to 2 nm, which definitely result in poor adsorption performance of RO16.

From Figure 2, it is believed that higher BET surface area and mesoporosity would enhance the adsorption of RO16 onto carbon gel. Both RC3 and RC 7 demonstrated the best adsorption performance (6.8 and 6.5 mg/g) due to high BET surface area (638.9 and 711.9 m^2/g) and rich mesoporosity (69.8 and 75.1 %). RC7 showed slightly lower adsorption capacity when compared to RC3 due to the adsorption of anionic dye is less favourable on surface with more oxide functional groups.

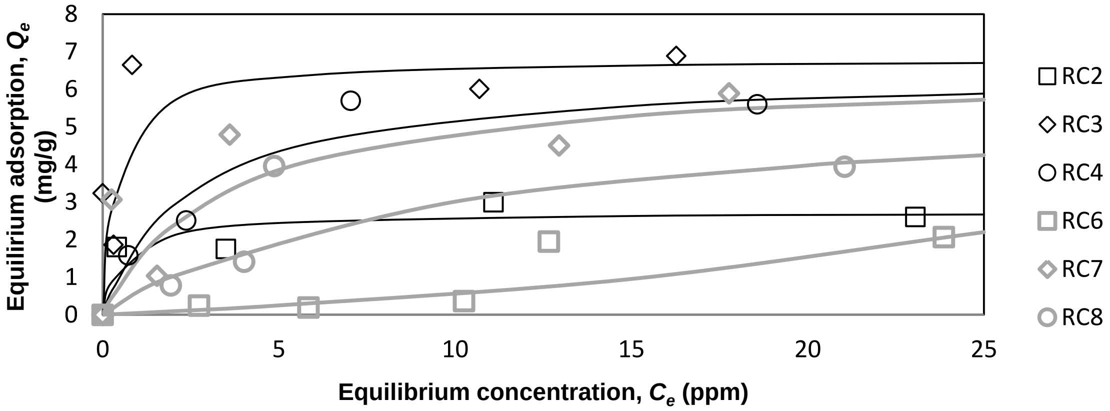

Figure 1: Effect of initial concentration on the RO16 adsorption by carbon gels

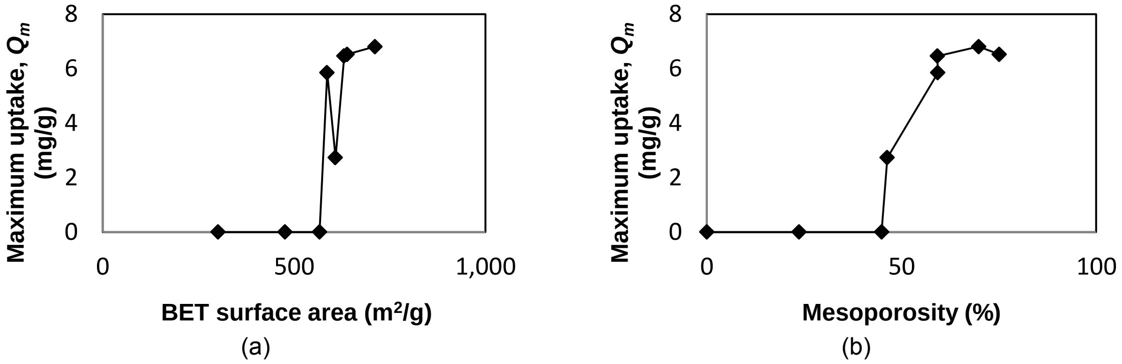

Figure 2: Possible influenced properties on adsorption of RO16: (a) BET surface area and (b) mesoporosity

Table 2 summarised the constants of isotherm models for RO16 adsorption by carbon gels. The correlation of determination (R^2) values of Langmuir model for these four carbon gels are closer to 1. This indicates the applicability of Langmuir isotherm in adsorption of RO16. The adsorption process can be described as homogeneous nature of carbon gel surface via the formation of monolayer coverage of RO16.

Table 2: Langmuir and Freundlich isotherm constants

Carbon gel	Langmuir				Freundlich		
	Q_m (mg/g)	b (L/mg)	R_L	R^2	n	K ((mg/g)(L/mg)$^{1/n}$)	R^2
RC3	6.803	2.521	0.015	0.992	6.550	4.493	0.445
RC4	6.460	0.408	0.083	0.979	2.851	2.211	0.822
RC7	6.523	0.285	0.117	0.840	4.185	2.727	0.513
RC8	5.845	0.106	0.259	0.766	2.455	1.209	0.530

Table 3 shows the recent studies of Adsorption type and mechanisms could influence the RO16 adsorption efficiency. Effective RO16 adsorption through multilayer and heterogeneous mechanisms was reported by Obaid et al. (2016) and Masitah et al. (2011), while monolayer and homogeneous adsorption in this study result in low RO16 adsorption capacity.

Table 3: Maximum adsorption capacity (Q_m) of reactive orange 16 by various adsorbents

Adsorbent	BET surface area (m^2/g)	Q_m (mg/g)	Reference
Modified kenaf core fibers	-	416.86	Obaid et al. (2016)
Cross-linked Chitosan/oil palm ash composite beads	-	303.00	Masitah et al. (2011)
Polyaniline/extracellular polymeric substances composite	-	293.20	Janaki et al. (2012)
$MgAlNO_3$ layered double hydroxides	-	111.0	Sumari et al. (2010)
Gracilaria verrucosa (marine algae)	-	86.03	Amarnath and Padmesh (2009)
Resorcinol-formaldehyde carbon gel	638.9	6.80	This study
Zeolite synthesised from coat fly ash	53.4	1.14	Carvalho et al. (2010)
Zeolite synthesised from fly ash	-	0.58	Fungaro et al. (2008)
Waste brewery yeast	13.2	0.02	Kim et al. (2008)

The kinetic constants are tabulated in Table 4. The values of R^2 for pseudo-first-order are closer to 1.0 than that of the pseudo-second-order, indicating that the applicability of the pseudo-first-order model to describe the rate of adsorption, which relies on the assumption that physisorption may be the rate-limiting step. The interaction between dye molecules and surface of carbon gel could be due to the van der Waals force (Huang and Zhang, 2015). RO16 adsorbed by various adsorbents.

Table 4: Kinetics constants of Pseudo-first-order and Pseudo-second-order models

Carbon gel	C_o (ppm)	Q_e, exp (mg/g)	pseudo-first-order			Pseudo-second-order		
			k_1 (h^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg.h)	Q_e (mg/g)	R^2
RC3	5	3.820	0.02	3.693	0.968	0.006	4.522	0.901
	10	5.912	0.03	5.572	0.978	0.004	6.884	0.953
RC4	5	3.869	0.01	4.898	0.987	0.001	7.222	0.663
	10	6.131	0.02	6.169	0.992	0.003	7.797	0.970
RC7	5	2.044	0.02	2.043	0.987	0.008	2.640	0.432
	10	3.650	0.04	3.347	0.983	0.008	2.640	0.920
RC8	5	2.482	0.04	2.363	0.976	0.017	2.734	0.893
	10	3.309	0.05	3.029	0.969	0.021	3.391	0.948

4. Conclusion

The performance of resorcinol-formaldehyde carbon gels was investigated based on the adsorption of reactive orange 16. Carbon gel prepared with R/C ratio of 1,000 had a specific surface area of 638.9 m^2/g and showed the highest maximum adsorption capacity of 6.8 mg/g. The adsorption capacity is directly related to specific surface area and mesoporosity of carbon gel. The equilibrium and kinetics data were best fitted to the Langmuir and pseudo-first-order models, respectively, indicating that the adsorption is a monolayer and a physical process. Higher specific surface area, larger pore size and higher mesopore volume of carbon gel are favourable characteristics to capture dye molecules. However, the adsorption performance of dyes is also affected by other factors like temperature, pH and agitation speed. The desired textural properties of carbon gel can be tailored by manipulating the preparation process to meet the preferred adsorption applications.

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Reference

Al-Muhtaseb S.A., Ritter J.A., 2003, Preparation and properties of resorcinol-formaldehyde organic and carbon gels, Advanced Materials 15 (2), 101-114.

Amarnath D.R., Padmesh T.V.N., 2009, Adsorption of reactive orange 16 onto gracilaria species a marine alga, Asian Journal of Chemistry 21 (5), 4039-4046.

Carvalho T.E.M., Fungaro D.A., Izidoro J.C., 2010, Adsorption of reactive orange 16 from aqueous solutions by synthesized zeolite, Quim, Nova 33 (2), 358-363.

Dada A.O., Olaleka, A.P., Olatunya A.M., Dada O., 2012, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn2+onto phosphoric acid modified rice husk, Journal of Applied Chemistry 3 (1), 38-45.

Feng J., Feng J., Zhang C., 2011, Shrinkage and pore structure in preparation of carbon aerogels, Journal of Sol-gel Science and Technology 59, 371-380.

Fungaro D.A., Borrely S.I., Carvalho T.E.M., 2008, Adsorption of Reactive Orange 16 onto zeolite synthesized from fly ash: kinetics and equilibrium studies, Proceedings of the Symposium Brazil-Japan in Economy, Science and Technological Innovation, 14-16 June, Brazil, paper 178.

Ho Y.S., Porter J.F., Mckay G., 2002, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water, Air and Soil Pollution 141, 1-33.

Huang H., Zhang G., 2015, Adsorption of rhodamine b onto a yellow-brown soil: kinetics, thermodynamics, and role of soil organic matter, Environment Progress and Sustainable Energy 35 (5), 1936-1403.

Janaki V., Vijayaraghayanb K., Ramasamya A.K., Lee K.J., Ohc B.T., Kamala-Kannanc S., 2012, Competitive adsorption of Reactive Orange 16 and Reactive Brilliant Blue R on polyaniline/bacterial extracellular polysaccharides composite—A novel eco-friendly polymer, Journal of Hazardous Materials 241–242, 110–117.

Kim T.Y., Min B.J., Choi S.Y., Park S.S., Cho S.Y., Kim S.J., 2008, Separation characteristics of reactive orange dye from aqueous solution using biosorbent, Proceedings of the World Congress on Engineering and Computer Science 2008 (WCECS 2008), 22 - 24 October, San Francisco, USA, 89-94.

Lee L.Z., Zaini M.A.A., 2015, Metals-chloride activate castor bean residue for methylene blue removal, Jurnal Teknologi 74 (7), 65-69.

Lufrano F., Staiti P., Calvo E.G., Juarez-Perez E.J., Menendez J.A., Arenillas A., 2011, Carbon xerogel and manganese oxide capacitive materials for advanced supercapacitors, International Journal of Electrochemical Science 6, 596-612.

Masitah H., Bassim H.H., Latif A.A., Zuifakar M., Naimah I., Salwa M.Z.M., 2011, Low cost removal of reactive orange16 dye using cross-linked chitosan/oil palm ash composite beads, Journal of Applied Sciences 11 (13), 2292-2298.

Masuda T., Ogino I., Mukai S.R., 2013, Immobilization of magnesium ammonium phosphate crystals within microchannels for efficient ammonia removal, Water Science and Technology 67 (2), 359-365.

Mohammadi M., Hassani A.J., Mohamed A.R., Najafpour G.D, 2010, Removal of rhodamine b from aqueous solution using palm shell-based activated carbon: adsorption and kinetic studies, Journal of Chemical and Engineering Data 55, 5777-5785.

Morento A.H., Arenillas A., Calvo E.G., Bermudez J.M., Menendez J.A., 2013, Carbonisation of resorcinol-formaldehyde oraganic xerogels: effect of temperature, particle size and heating rate on the porosity of carbon xerogels, Journal of Analytical and Applied Pyrolysis 100, 111-116.

Obaid M.K., Abdullah L.C., Idan I.J., 2016, Removal of reactive orange 16 dye from aqueous solution by using modified Kenaf core fiber, Journal of Chemistry 2016, DOI: 10.1155/2016/4262578

Pekala R.W., 1989, US Patent 4873218, Low density, resorcinol-formaldehyde aerogels, The United States Department of Energy, United States.

See M.T., Quah Z.Y., Lee L.Z., Aw Y.P.Y., Zaini M.A.A., 2015, Dyes in water: characteristics, impacts to the environment and human health, and the removal strategies, Ed. Taylor J.C., Advances in Chemistry Research 23, 143-156.

Sumari S.M., Hamzah Z. and Yasin Y., 2010, Adsorption of reactive orange16 from aqueous solutions by MgAlNO3-LDH: kinetic and equilibrium studies, International conference on science and social research (CSSR 2010), 5-7 December, Kuala Lumpur, Malaysia, 16-20.

Yamamoto T., Mukai S.R., Endo A., Nakaiwa M., Tamon H., 2003, Interpretation of structure formation during the sol-gel transition of a resorcinol-formaldehyde solution by population balance, Journal of Colloid and Interface Science 264 (2), 532-537.