

Congo Red Removal by HNO₃-Modified Resorcinol-Formaldehyde Carbon Gels

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Resorcinol-formaldehyde (RF) carbon gel has gained much attention in various commercial applications including electro-catalysis, ion exchange resin and hydrogen and electrical energy storage owing to its highly sensitive nanostructure. In this work, the resorcinol-formaldehyde carbon gels were synthesised via a sol-gel method from polymerisation of resorcinol and formaldehyde with sodium carbonate (Na₂CO₃) as a catalyst. Different resorcinol to catalyst (R/C) ratios (mol/mol) of 1,000 (RC3) and 2,000 (RC4) were used, and the effect of nitric acid (HNO₃) modification was investigated. The oxidised RC3 and RC4 were denoted as RC7 and RC8. It was found that a further increase in R/C ratio above 1,000 caused a decline in surface area, pore volume and pore size. RC7 gave the highest surface area of 711.49 m²/g with pore size of 7.68 nm. The HNO₃ modification step increased the surface area of RC7, but slightly decreased the surface area of RC8 probably due to crystallisation of the gel to graphite. Adsorptive study was carried out using congo red (CR) as an adsorbate. The carbon gels with higher surface area, pore volume and pore size exhibit a better CR adsorption performance. The HNO₃-modified resorcinol-formaldehyde carbon gels gave a better performance for the removal of congo red. The kinetics data of congo red adsorption could be explained by the pseudo-second-order kinetic model. The maximum adsorption of congo red on resorcinol-formaldehyde carbon gel is comparable to other adsorbents and activated carbons.

1. Introduction

The surge in water pollution due to dye wastewater is a serious cause for concern in the current times. A rich diversity of dyes is widely used in various industries including textiles and apparel, paper, food and pharmaceutical to impart the desired hue. The most common textile industrial dyes are basic, acid and reactive dyes (Salleh et al., 2011). The effusion of dye wastewater into downstream can bring about adverse effect to living organisms in aquatic ecosystem (Tang and Zaini, 2015a). Thus, wastewater treatment prior to release is necessary to ensure that the water quality complies with the regulation standards.

Adsorption using porous material is one of the most extensively employed dye removal technique owing to its simple, economical and efficient operation, and no sludge is generated. Different adsorbents have been studied over the years, like agricultural waste and sewage sludge (Chan et al., 2016). These adsorbents are mainly in granular or powder form, and their mesopores or micropores density can hardly be manipulated to match specific applications. Small particles are prone to rapid pressure drop (hydraulic resistance) during large scale continuous column adsorption. This can lead to deteriorating column performance and exorbitant operating cost.

Carbon gel is a promising porous carbon substitute with a highly flexible shape, pore texture and nanostructure. It can be moulded into a particular shape to elicit the desired type of column packing, so that the surface contact between solute and sorbent can be maximised, and the hydraulic pressure inside the column can be averted. Synthesis of carbon gel comprises of three main stages - (i) preparation of sol-gel mixture (gelation, aging and solvent exchange), (ii) drying and (iii) carbonisation or activation (Al-Muhtaseb and Ritter, 2003). In the first stage, condensation-polymerisation (gelation) of resorcinol and formaldehyde takes place in the presence of an alkaline catalyst (Na₂CO₃) and a solvent (water or acetone). Aging step is

carried out in order to enhance the crosslinking density by boosting the condensation reaction of the hydroxymethyl groups, whereas solvent exchange involves the removal of old solvent which acts as a reaction medium during gelation. The hydrogel or lyogel is then dried via subcritical drying, supercritical drying or freeze drying, which subsequently produces xerogel, aerogel and cryogels. The organic gels are converted into resorcinol-formaldehyde (RF) carbon gels after pyrolysis or activation in the final phase. The density of mesopores and micropores of carbon gel can be tailored independently by adjusting the process condition to control the voids formed during aggregation of nanoparticles (Mukai, 2012).

In this work, resorcinol-formaldehyde (RF) carbon gels were synthesised via sol-gel method and then modified by oxidation using nitric acid. An anionic azo dye, congo red (CR) was selected as a model dye pollutant to evaluate the feasibility of oxidised and unoxidised carbon gel as adsorbents for the CR removal. The RF carbon gels were characterised and the batch adsorption outcomes were analysed.

2. Materials and methods

2.1 Material

Formaldehyde (HCHO, MW = 30.03 g/mol, 37 wt% in water), resorcinol (C₆H₆O₂, MW = 110.11 g/mol, assay 99 %), sodium carbonate (Na₂CO₃, MW = 105.99 g/mol, assay 99.5 %), tert-butyl alcohol ((CH₃)₃COH, MW = 74.12 g/mol, assay 99 %), nitric acid (HNO₃, MW = 63.01, 65 %) and congo red (C₃₂H₂₂N₆Na₂O₆S₂; MW = 696.7 g/mol) were used in the synthesis of RF carbon gels and adsorption studies. The chemicals and CR dye were obtained from Wako Pure Chemical Industries Ltd and R&M Chemicals, and are of analytical reagents grade.

2.2 Synthesis and characterisation of RF carbon gel

The sol mixture was initially prepared using resorcinol, formaldehyde, water (solvent) and sodium carbonate (alkaline catalyst). The resorcinol/catalyst (R/C) ratios of 1,000 and 2,000 mol/mol were selected and denoted as RC3 and RC4. The resorcinol/water (R/W) and resorcinol/formaldehyde (R/F) ratios were fixed at 0.5 g/mL and 0.5 mol/mol. Approximately 25 g of resorcinol, 0.241 g of Na₂CO₃ and 29.7 g of water were mixed in a disposable cup, followed by addition of 36.85 g of formaldehyde. The sol mixture was stirred and poured into a mould to allow gelation of RF sol solution at 35 °C for 2 d (Al-Muhtaseb and Ritter, 2003). Next, the aging step was carried out by heating the cured gel at 60 °C for 3 d. After that, the RF hydrogel was placed into a capped bottle filled with tert-butyl alcohol (TBA) and retained at 50 °C for 3 d to eliminate the surplus water by solvent exchange process. The old TBA was exchanged with a fresh one twice a day. The RF organic gel was then dried at 110 °C for 2 d and crushed to obtain uniform particle size of 1 mm. Lastly, the organic gel was carbonised at 600 °C for 3 h to produce RF carbon gel and was labelled as RC3 (R/C = 1,000 mol/mol) and RC4 (R/C = 2,000 mol/mol). The additional oxidation step was performed by soaking the carbon gel in HNO₃ (65 - 66 %) at room temperature for 3 h, followed by heating at 60 °C for 5 h. The oxidised RC3 and RC4 were labelled as RC7 and RC8. The resultant materials were washed with distilled until a constant pH was elicited. The textural properties of the samples were examined using a surface area analyser (Micrometrics PulseChemiSorb 2705, USA) at liquid nitrogen temperature of 77 K.

2.3 Batch adsorption studies

Congo red (CR) adsorption tests were executed in batch mode by weighing 0.03 g of carbon gel and adding it to 20 mL of CR solution with different initial concentrations (2 - 50 mg/L). The original solution pH was maintained and monitored using pH meter (HANNA HI8424) during the adsorption experiments. After 5 d (120 h), the dye solution was extracted and separated using a centrifuge. The clear supernatant was analysed for CR concentration on a visible spectrometer (Dynamica Halo VIS-10) at a maximum wavelength of 510 nm. The equilibrium adsorption capacity (q_e) was calculated as Eq(1),

$$q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

where q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, C_o (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.

3. Results and discussion

3.1 Physical characteristics of RF carbon gels

The textural properties of RF carbon gels are summarised in Table 1. It is discovered that a higher R/C ratio gives a better yield owing to the greater quantity of resorcinol (reactant) compared to Na₂CO₃ (catalyst).

During carbonisation, almost all hydrogen groups and residual oxides are eliminated, resulting in a highly dense pure carbon nanostructure.

Table 1: Physical properties of RF carbon gels.

	Oxidised		Unoxidised	
	RC3	RC4	RC7	RC8
R/C ratio (mol/mol)	1,000	2,000	1,000	2,000
Yield (%)	42.6	53.5	42.6	53.5
BET surface area (m ² /g)	639	631	711	586
Total pore volume (cm ³ /g)	0.632	0.536	0.817	0.500
Micropore volume (cm ³ /g)	0.191	0.219	0.203	0.203
Mesopore volume (cm ³ /g)	0.441	0.317	0.614	0.297
Mesoporosity (%)	69.8	59.2	75.1	59.3
Average pore diameter (nm)	6.89	3.56	7.68	3.57

The mass reduction of RF carbon gels is around 50 % after pyrolysis at 600 °C and these findings (Table 1) are consistent with the study of Al-Muhtaseb and Ritter (2003). The diminished mass in the gel is closely attributed to the burnout of the organic matters, which gives rise to the formation of new voids or micropores and mesopores, thus increasing the surface area of carbon gel. In this work, the average pore diameter of the synthesised RF carbon gels is in the range of 3.56 to 7.68 nm, suggesting a higher concentration of mesopores (2 - 50 nm) or mesoporosity (59.2 - 75.1 %).

Table 1 shows that there is no notable change in the yield and textural properties of carbon gel after oxidation. The surface area, pore volume and mesoporosity and average pore diameter of RC7 increased slightly, while that of RC8 decreased slightly except for mesoporosity and average pore diameter which remained almost the same. Al-Muhtaseb and Ritter (2003) also reported similar outcomes.

3.2 Adsorption isotherm

Adsorption isotherm is indispensable in understanding the interaction between the adsorbed dye on carbon gel and the remaining dye in the bulk solution. In the present work, the equilibrium data are fitted into two isotherm models - Langmuir and Freundlich to determine the adsorption behaviour for efficient design of adsorption process. Adsorption equilibrium is attained when the dye adsorption rate is equivalent to the desorption rate (Tang and Zaini, 2015b). The Langmuir equation is given as Eq(2),

$$q_e = \frac{q_m b C_e}{(1 + b C_e)} \quad (2)$$

where b (L/mg) is the Langmuir isotherm constant and q_m (mg/g) is the maximum monolayer coverage.

Table 2 revealed that the Langmuir isotherm is a better fit for the equilibrium data and this indicates that the CR adsorption is a monolayer adsorption onto homogeneous surface of RF carbon gel. The maximum adsorption capacity (q_m) was found to be in the range of 2.25 to 10.58 mg/g. The oxidised carbon gels have a higher q_m than the unoxidised carbon gels owing to greater mesoporosity and average pore diameter. The separation factor (R_L) is a dimensionless constant of Langmuir isotherm and is expressed as $R_L = 1/(1 + b C_0)$. The affinity between adsorbate and adsorbent can be determined through R_L : unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$) (Chan et al., 2016). As shown in Figure 1(b), the R_L values are in the range of 0 to 1 and decreased with increasing C_0 , indicating a favourable adsorption process. The Freundlich isotherm is used to describe multilayer adsorption over a heterogeneous surface of adsorbents. The Freundlich equation is given as,

$$q_e = K_F (C_e)^{1/n} \quad (3)$$

where K_F ((mg/g)(L/mg)^{1/n}) and n are the Freundlich isotherm constants. The values of n and K_F are listed in Table 2. The lower R^2 values showed that the Freundlich isotherm is a poor fit. The adsorption of CR molecules onto carbon gel is unlikely a multilayer. Higher K_F values demonstrate greater adsorption capacity or affinity towards CR anions. The constant n is the heterogeneous factor: linear adsorption ($n = 1$), cooperative adsorption ($n < 1$) and ideal Langmuir isotherm ($n > 1$) (Prahas et al., 2008). All the $1/n$ values are below 1, denoting an ideal Langmuir adsorption, and this further confirms the good applicability of Langmuir isotherm.

Figure 1 illustrates the CR equilibrium adsorption onto carbon gels. The equilibrium removal increases with increasing CR concentration until a maximum adsorption capacity is achieved (horizontal plane). When there

is a contrast between the amount of adsorbate in bulk solution and surface of adsorbent, a concentration gradient is created and it acts as a driving force in adsorption process. The saturation point is achieved at the horizontal level, whereby almost all the active sites of RF carbon gels are occupied by dye molecules.

Table 2: Langmuir and Freundlich isotherm constants of CR adsorption onto carbon gels.

Carbon gels	Langmuir			Freundlich		
	q_m (mg/g)	b (L/mg)	R^2	N	$K_F ((\text{mg/g})(\text{L/mg})^{1/n})$	R^2
RC3	2.25	25.6	0.995	10.0	1.78	0.751
RC4	2.51	6.34	0.975	8.09	2.41	0.177
RC7	10.6	0.72	0.914	1.37	2.48	0.863
RC8	4.36	1.00	0.651	1.53	2.30	0.523

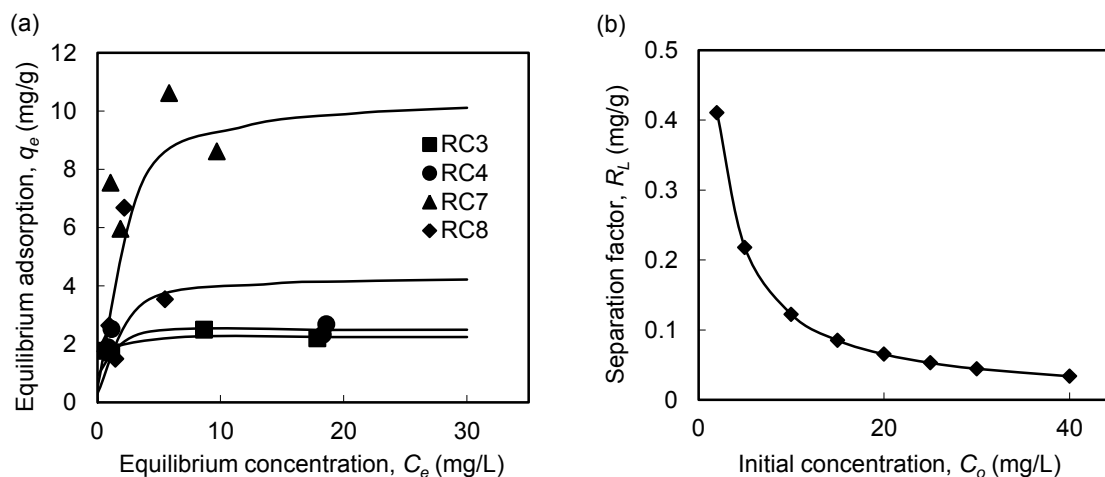


Figure 1: (a) Equilibrium adsorption of CR predicted by Langmuir model (b) Relationship between R_L and C_o (adsorbent dosage = 0.03 g, solution volume = 20 mL, CR initial concentration = 2 to 50 mg/L, contact time = 120 h)

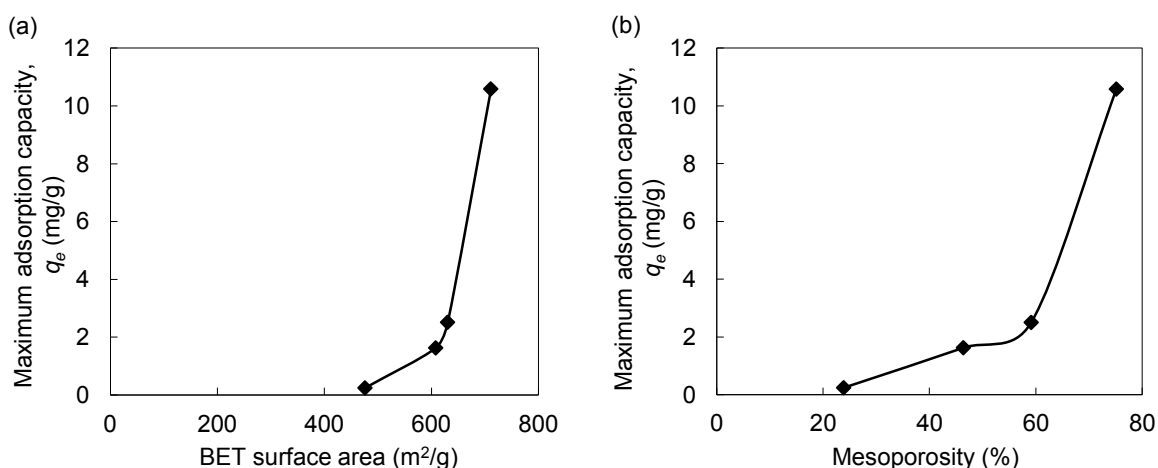


Figure 2: Relationships between maximum capacity with (a) BET surface area; (b) mesoporosity

The textural properties of carbon gel play a significant role in the dye removal performance. Figure 2 shows the relationships between the maximum adsorption capacity, and BET surface area and mesoporosity. The adsorption performance increased significantly with an increase in mesoporosity and BET surface area. Higher surface area and mesoporosity provide more number of active sites available for adsorption of CR anions. The carbon gels with greater mesoporosity or mesopore (2 - 50 nm) volume are more favourable to

accommodate CR molecules with a single dimension of 2.62 nm (width), 0.74 nm (depth) and 0.43 nm (thickness) (Cotoruelo et al., 2010). An obstruction in CR adsorption process may occur for microporous adsorbents because the width of CR molecule is greater than 2 nm.

3.3 Adsorption kinetics

To further comprehend the sorption mechanism of CR onto carbon gels, the kinetics data were simulated with the pseudo-second-order kinetic model, which can be expressed as,

$$q_e = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where t (h) is the period of adsorption, q_t (mg/g) is the amount of dye adsorbed at time t and k_2 (g/mg.h) is the rate constant for pseudo-second-order sorption. The calculated q_e and k_2 values are tabulated in Table 3. Higher k_2 values corresponds to greater affinity of carbon gels towards CR at certain concentration. RC7 has the highest k_2 value at C_o of 10 mg/L. Table 3 also shows that the experimental q_e are close to the theoretical q_e (high R^2), indicating that chemisorption may govern the adsorption process whereby valence forces through exchange or sharing of electron between adsorbent and adsorbate predominates (Prahas et al., 2008). The effect of contact time on the uptake of CR by carbon gels was studied for 120 hat concentrations of 5 and 10 mg/L. From Figure 3, it can be observed that the kinetics behaviour of RC7 and RC8 consists of three phases - a rapid initial adsorption over 10 h, followed by a significantly slower adsorption (40 h) and finally a gradual equilibrium contact time.

Table 3: Parameters of pseudo-second-order kinetic model for CR adsorption.

Carbon gels	q_e (mg/g)	Pseudo-second order		
		Cal. q_e (mg/g)	k_2 (g/mg.h)	R^2
RC3 (5 mg/L)	3.26	2.94	0.0153	0.837
RC4 (5 mg/L)	2.99	2.98	0.0354	0.975
RC7 (5 mg/L)	3.22	3.19	0.180	0.999
RC8 (5 mg/L)	3.37	3.01	0.0670	0.966
RC3 (10 mg/L)	4.04	3.58	0.0102	0.801
RC4 (10 mg/L)	4.57	3.93	0.0142	0.690
RC7 (10 mg/L)	4.98	4.73	0.379	0.993
RC8 (10 mg/L)	4.73	4.73	0.104	0.999

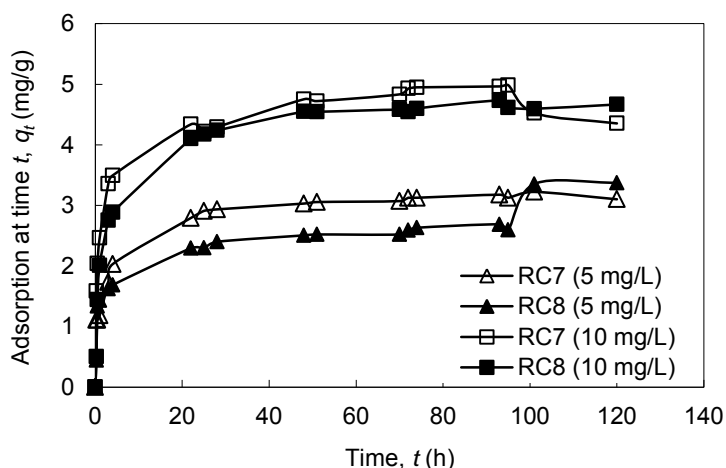


Figure 3: Effect of contact time on CR adsorption ($m = 0.03$ g, $t = 120$ h, $C_o = 5$ and 10 mg/L)

3.4 Comparison of CR removal with various adsorbents

The maximum monolayer adsorption (q_m) of CR in this study was compared with other adsorbents as summarised in Table 4. It can be seen that the oxidised RF carbon gel (RC7) portrayed a better maximum monolayer adsorption of CR (10.58 mg/g) than majority of the previously developed adsorbents. This shows that the oxidised RF carbon gel is a potential adsorbent for the removal of congo red and other anionic dyes.

Table 4: CR removal using various adsorbents

Adsorbent	Surface area (m ² /g)	pH	q _m (mg/g)	Reference
Activated carbon from apricot stone	88.1	-	32.9	Abbas and Trari (2015)
Pineapple plant stem	2.39	-	12.0	Chan et al. (2016)
RF carbon gel	711	5.40	10.6	This study
Acid-activated red mud	-	-	7.08	Salleh et al. (2011)
Benzyltrimethylammonium chloride (BTMA) bentonite	-	-	6.58	Fosso-Kankeu et al. (2016)
Tris(hydroxymethyl)aminomethane (THMA) bentonite	-	-	2.82	Fosso-Kankeu et al. (2016)
Kaolin	10.6	-	5.94	Zenasni et al. (2014)
Eichhorniacrassipes root	-	-	1.58	Wanyonyi et al. (2014)
Gold nanoparticle-coated AC	-	6.50	0.50	Pal and Deb (2014)

4. Conclusion

In the present work, RF carbon gels have been successfully synthesised via a sol-gel method, and oxidised with HNO₃. The oxidised and unoxidised carbon gels were characterised for textural properties, and applied for the removal of CR from aqueous solution. The effects of initial concentration and contact time on CR adsorption were discussed. Langmuir isotherm provided a good fit for the equilibrium data, indicating a monolayer adsorption. RC7 possesses the highest q_m of 10.58 mg/g, in which the oxidised carbon gels perform better than the unoxidised ones. The kinetics data fitted well to the pseudo-second-order kinetic model, suggesting that chemisorption may predominate. The oxidised RF carbon gel is a promising adsorbent for the CR adsorption process.

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