

Preparation of Controlled Porosity Resorcinol Formaldehyde Xerogels for Adsorption Applications

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The synthesis of resorcinol formaldehyde xerogels was investigated by controlling its porosity for potential use as adsorbents for heavy metals removal from industrial wastewater. Resorcinol formaldehyde carbon xerogels were synthesised by sol-gel polymerization of resorcinol (R) with formaldehyde (F) in the presence of sodium carbonate (C) and then vacuum dried. Resorcinol formaldehyde (RF) gels were synthesised at same temperature conditions with varying resorcinol / catalyst (R/C) and resorcinol / water (R/W) ratios. The influence of R/C and R/W ratios on the pore structure of the xerogels was investigated. Surface area and porosity of the resorcinol formaldehyde gels were analysed by physical adsorption (physiosorption) of nitrogen (N₂) at 77 K. The result(s) showed an increase in mesoporosity and pore size as R/C ratio increases. At resorcinol / catalyst (R/C) of 200, the pore size and pore volume increased with increase in R/W ratio. From the result, it can be concluded that the resorcinol / catalyst (R/C) and resorcinol / water (R/W) ratios are two contributing factors to determining the pore structure of the xerogels.

1. Introduction

The removal of heavy metals from industrial and municipal waste water has received considerable attention in recent years (Walker and Wetherley, 1997). Many of these heavy metals are known to be toxic, non-biodegradable and bio-accumulative and they have also been known to bio-accumulate in food chain, posing a threat to public health and wildlife. They are toxic and have negative effects on human and the environment (Albadarin et al. 2011a). Sources of this industrial waste water include effluents from metal plating industries, metal processing, battery manufacturing, leather tanning, iron and steel industries. These metals include chromium, cadmium, copper and zinc.

It is clear that as the impact of anthropogenic activities on the environment increases, there must be mitigation processes in place to eradicate heavy metals that arise from industrial processes. This is to ensure that the concentration of heavy metals in wastewater is controlled to an acceptable level. Various methods have been used for heavy metal removal from industrial effluent. These include chemical precipitation, coagulation-flocculation, ion exchange, and membrane filtration. In recent times, adsorption has been shown to be the best economically feasible alternative method of removing trace metals from wastewater. This is based on its simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions (Foo and Hameed 2009).

The adsorption capacity depends on a number of factors such as the type of the adsorbate, the conditions of the solution (pH, ionic strength and concentration of the adsorbate) and the characteristics of the adsorbent (Walker and Weatherley, 2001). Typical adsorbents for heavy metals are activated carbon,

synthetic polymeric and silica-based adsorbents. In recent years, industrial, agricultural and biomass by-products (Albadarin et al. 2011b). Synthetic polymeric adsorbents are highly cross linked polymers. They also have highly porous structure as parts of the polymer matrix. Such polymers include Resorcinol Formaldehyde gels. The increase in the use of these aerogels is as a result of their controllable porous structures (Horikawa et al., 2004). Resorcinol Formaldehyde xerogels have high specific area and porosity which can be varied based on different synthesis parameters (Al-Muhtaseb and Ritter 2003).

2. Experimental

2.1 Synthesis of RF xerogels

RF xerogels were synthesised from the polycondensation of resorcinol, $C_6H_4(OH)_2$ (R) with formaldehyde (HCHO) (F) according to the method proposed by Pekala et al (Mirzaeian, Hall 2009a, Pekala, Schaefer 1993), RF solutions were prepared by mixing resorcinol (R), formaldehyde (F), sodium carbonate (Na_2CO_3) (C) and distilled water. The solution was mixed vigorously for 45 min. The resorcinol/formaldehyde ratio R/F was fixed at 0.5 with the molar ratio of R/C and ratio of R/W (g/cm^3) was varied. The homogenous clear sol was then poured into sealed glass vials to avoid water evaporating during the gelation process. The sealed vials were then placed in an oven set at 25 °C for 24 hours. Oven temperature was then increased to 60 °C for 48 h, and then finally the oven was then increased to 80 °C for an additional 24 h to complete the curing process. The wet gels are then removed from the oven and allowed to cool to room temperature. In order, to remove water from the pores of the gels, the gels were immersed in acetone for solvent exchange at room temperature for three days. After the third day, the acetone was poured out and the gels were placed in a vacuum oven for drying. The gels were dried in a vacuum oven at 64 °C for 3 d.

2.2 TGA analysis of xerogels

In order to determine the carbonization conditions for the dried xerogels, the gels were analysed by thermogravimetric analysis (TGA). Thermogravimetric analysis was carried out with Thermogravimetric Analyser, Mettler Toledo TGA. The RF xerogel samples with different R/C ratios were used for the analysis. The weight loss was monitored in the temperature range of 25–1025 °C. About 5–10 mg of gel was used for the analysis for each run. This corresponds to 100% weight percent of the gel sample. The sample was purged with nitrogen flowing at 50 mL/min for 30 min at 25 °C, and then heated to 1,050 °C at 10 °C/min.

2.3 Characterisation of RF xerogels

The characterization of resorcinol formaldehyde (RF) xerogel carried out include porosity, pore size distribution, surface area (BET), scanning electron microscopy (SEM) and X-Ray diffraction (XRD). The surface morphology (SEM) of xerogels was analysed with the aid of JEOL JSM-6500F. The XRD analysis of the adsorbents was performed with a PANalytical X'Pert Pro MPD Diffractometer. The porosity and surface area of the RF xerogels were determined by the analysis of nitrogen adsorption-desorption isotherms measured by Nitrogen Sorption analyser, Nova 4200e, Quantachrome Instruments. The surface area was measured using the BET method, t-plot method was used for micropore analysis, BJH method from desorption branch of the isotherm was used to obtain pore size distribution. The total pore volume was determined from the adsorbed volume of nitrogen at saturation pressure ($P/P_0 = 0.99$) (Mirzaeian, Hall 2009b).

3. Results

3.1 Effect of Resorcinol/Catalyst (R/C) Ratio on Porous Structure

Figure 1a shows the nitrogen adsorption-desorption isotherms at 77 K for RF xerogels synthesised at different R/C ratios. The isotherms are of type IV due to the presence of hysteresis which is indicative of the presence of mesopores. This is as a result of pore condensation whereby gas condenses to a liquid-like phase in pores at a pressure less than the saturation pressure P_0 of the bulk fluid (Lowell et al. 2004). The nature of the adsorption process is monolayer-multilayer adsorption. At low pressure monolayer is formed while the low slope region in the middle of the isotherm indicates the formation of the first few multilayers. The isotherms show lower adsorption capacity at low pressure which then increases with increasing relative pressure. This shows that the RF xerogels have less microporosity and a wider distribution of mesopores. From the plot, it can be seen that for samples R/C = 100 and 200, there was an

initial sharper rise at low P/P₀. This indicates that more micropores are present as well as mesopores in the xerogels. The lower part of the hysteresis loops is indicative of the filling of the mesopores while the upper part indicates the emptying of the mesopores. (Mirzaeian, Hall 2009a) The shift of the isotherms at higher relative pressure with increase in R/C ratio shows the development of mesoporosity and larger mesopores are formed with increasing R/C ratio.

3.2 Pore Size Distribution

The entire porous structure is formed by a wide range of pore sizes. The pore size distribution of the RF gels is shown in figure 1b. There is a shift to the right in the pore size distribution at increasing R/C ratio. This indicates an increase in mesoporosity in the RF gels with increasing R/C ratio. It can be seen that RF gel with R/C = 100 has the narrowest pore size distribution with the maxima occurring at pores of 2 nm. The RF gels with R/C = 200 has a wider pore size distribution with the maxima occurring at pores of 4 nm radius. The width of the pore size distributions increases with increases in R/C ratio. For R/C = 500 and 600 the maxima pore size occur at 20 nm and 40 nm. The maximum pore size for R/C = 700 and 800 was 45 nm. This was due to the fact that the hysteresis was located within the same p/p₀ range (Job et al. 2006). It can be seen from Table 1, the average pore size radius increases with increase in R/C ratio. This can act as a molecular sieve allowing adsorbate molecules of the adsorbent pore size or less to pass through to the exclusion larger molecules. This therefore determines the size of the adsorbates that can enter a pore for adsorption.

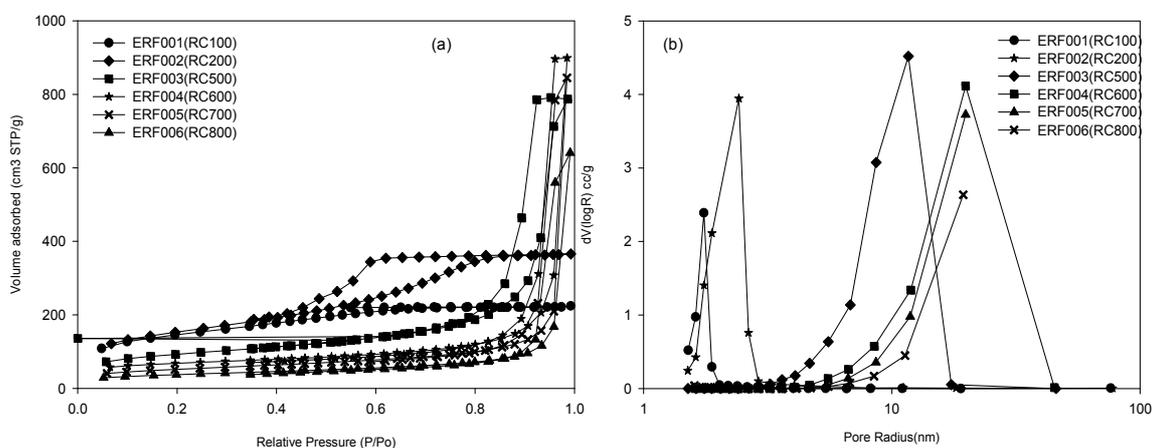


Figure 1: (a) N₂ adsorption-desorption isotherms of RF xerogels at 77K (b) Pore size distributions of RF xerogels with different R/C ratios

Table 1: Porous characteristics of RF xerogels with different R/C ratios

Samples RF	R/C	R/W (g/mL)	S _{BET} (m ² /g)	V _{total} (cc/g)	V _{micro} (cc/g)	V _{meso} (cc/g)	%V _{micro}	%V _{meso}	R _{avg} (nm)	
ERF001	0.5	100	0.1	489.23	0.347	0.07	0.227	20.17	79.83	1.41851
ERF002	0.5	200	0.1	522.31	0.566	0.034	0.532	6.01	93.99	2.15745
ERF003	0.5	500	0.1	309.83	1.218	0.042	1.176	3.45	96.55	7.85972
ERF004	0.5	600	0.1	217.47	1.391	0.051	1.34	3.67	96.33	12.7919
ERF005	0.5	700	0.1	174.99	1.307	0.022	1.285	1.68	98.32	14.9412
ERF006	0.5	800	0.1	126.57	0.991	0.016	0.975	1.61	98.39	15.6606

The surface area (Table 1) of RF xerogels increased from 489.23 m²/g for R/C =100 to 522.31 m²/g for R/C = 200 and then decreased continuously with further increase in the R/C ratio. The R/C ratio controls the surface area of the RF xerogels. This determines the availability of accessible adsorption sites for the adsorbates. Hence, the adsorptive capacity of the xerogels is proportional to the specific surface area.

3.3 Effect of Resorcinol/Water (R/W) Ratio on Porous Structure

The effect of R/W ratio on the porous structure of the R/C ratio of 200 xerogels was studied (Figure 2a and 2b). The RF = 200 was chosen for this study based on this having the largest surface area. The isotherms

show lower adsorption at low pressure and increases in adsorption with increasing relative pressure. This indicates that the RF xerogels have less microporosity and a wider distribution of mesopores. The plateau regions of the isotherms reflect the situation where the pore is completely filled with liquid and separated from the bulk gas phase by a hemispherical meniscus (Lowell et al. 2004). The shift of the isotherms at higher relative pressure with increase in R/W ratio indicates the development of mesoporosity with larger mesopores formed at increased R/W ratios.

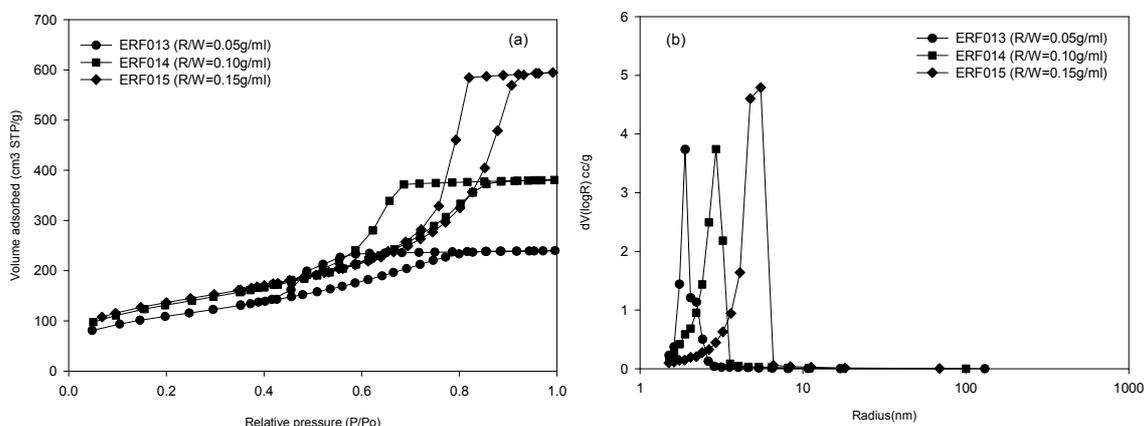


Figure 2: (a) N_2 adsorption-desorption isotherms of RF xerogels with $R/C = 200$ at 77K (b) Pore size distributions of RF gels with $R/C=200$ and different R/W ratios

3.4 Pore Size Distribution

Figure 2b shows the pore size distribution of the RF gels with $R/C = 200$ at different R/W ratio. It can be seen that there is a shift to the right in the pore size distribution at increasing R/W ratio. This indicates increase in mesoporosity in the RF gels with increasing R/W ratio. The RF gel with $R/W = 0.5$ has the narrowest pore size distribution with the maxima occurring at pores of 2 nm. The RF gels with $R/W = 0.1$ has a wider pore size distribution with the maxima occurring at pores of 4 nm radius. For $R/W = 0.15$ the maxima pore size occur at 6 nm. Thus, the width of the pore size distributions increased with increase in R/W ratio. Hence, the amount of distilled water (W) used in the synthesis of the Resorcinol Formaldehyde (RF) xerogels determines the pore size distribution. This creates voids in the gel structure (Tamon et al. 1998).

The average pore size radius increased with increase in R/W ratio (Table 2). This again offers a molecular sieve capability. The surface area (Table 2) of RF xerogels with $R/C = 200$ at different R/W ratio increased with increase in R/W ratio. The R/W ratio controls the surface area of the RF xerogels which determines the availability of accessible adsorption sites for the adsorbates. Hence, the adsorptive capacity of the xerogels is proportional to the specific surface area. Therefore, the R/W ratio which is an indication of the concentration of the solids in the sol affects the properties of RF xerogels.

Table 2: Porous characteristics of RF xerogels with $R/C=200$ and different R/W ratios.

Samples	R/F	R/C	R/W (g/ml)	SBET(m ² /g)	Vtotal(cc/g)	Vmicro (cc/g)	Vmeso (cc/g)	%Vmicro	%Vmeso	Ravg(nm)
ERF013	0.5	200	0.05	376.16	0.3708	0.016	0.3548	4.31	95.69	1.97167
ERF014	0.5	200	0.1	453.92	0.5891	0.02	0.5691	3.4	96.6	2.59573
ERF015	0.5	200	0.15	465.01	0.9199	0.04	0.8799	4.35	95.65	3.9566

3.5 Surface Characterisation of Resorcinol Formaldehyde xerogels

Thermogravimetric Analysis (TGA) measured the mass of a RF xerogel sample as it was purged for 30 min at 25 °C, and then heated to 1,050 °C at 10 °C / min with nitrogen flowing at 50 ml/min. Figure 3a shows the weight loss of RF xerogel versus temperature. It can be seen that there was a total weight loss of about 50% during carbonization in N_2 and the mass of the RF xerogel sample was constant at temperature above 800 °C. There are three major weight losses - Figures 3a and 3b, the first at

temperature between 80-200 °C, then at 300-400 °C and finally at 500-600 °C. The derivative thermogravimetric (DTG) curve (Figure 3b) showed that the maximum weight losses occurred at 150 °C, 380 °C and 580 °C. The peaks are as a result of removal of adsorbed moisture, solvent and polymer decomposition during carbonization. The polymer decomposition includes the breakage of C-O bonds and C-H bonds at 350 °C and 580 °C respectively (Lin, and Ritter 1997).

The XRD patterns (Figure 3(c)) showed that RF xerogels with different R/C ratios have similar patterns with narrow peaks at $2\theta = 20^\circ$, 26° and halo peak at $2\theta = 15-20^\circ$. This indicated that RF xerogels had both amorphous and crystalline phases. The crystalline structure of RF xerogels was similar to the structure of graphite.

From the SEM images (Figures 4(a) – (f)), it can be seen that the RF xerogels are made up of large numbers of microclusters in a uniform manner. These microclusters are interconnected which showed a continuous porous network (Awadallah and Al-Muhtaseb 2012). The sizes of the microclusters increased as the R/C ratio of the RF xerogels increased. Thus, the particle size of RF xerogels can be controlled by controlling the R/C ratio.

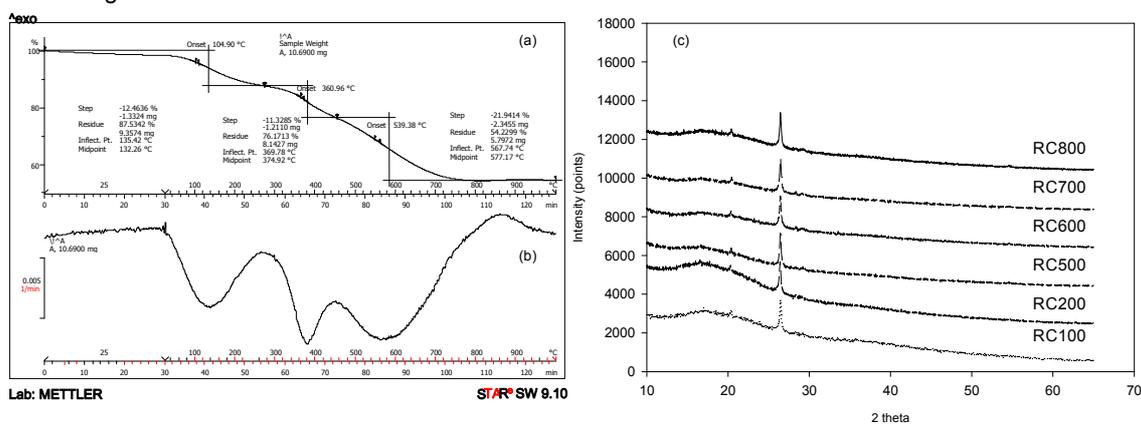


Figure 3: Thermogravimetric analysis (TGA) of RF xerogel (R/C = 200) (a) weight % versus temperature/time and (b) derivative thermogravimetry (DTG) and (c) XRD patterns of RF xerogels at different R/C ratios.

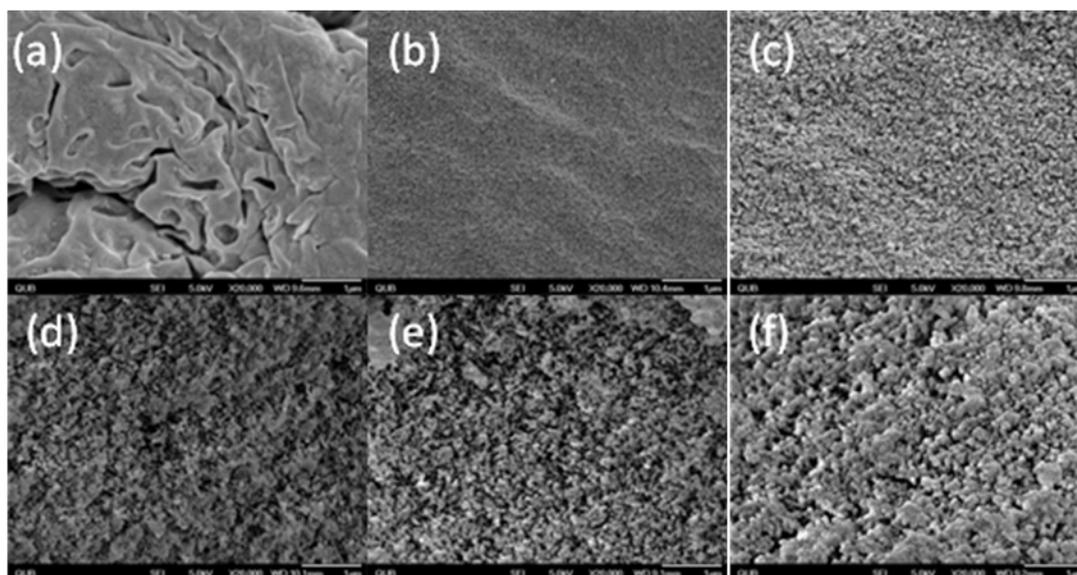


Figure 4: SEM images of RF xerogel (a) RC=100(b) RC=200, (c) RC=500, (d) RC=600, (e) RC=700 and (f) RC=800

4. Conclusions

The high surface area and porosity of RF xerogels are important characteristics of good adsorbents. From the analysis of experimental data, it can be seen that resorcinol catalyst (R/C) ratio controls the surface area and porosity of RF xerogels. The mesoporosity of the RF xerogels increased with increasing resorcinol catalyst (R/C) ratio and resorcinol water (R/W) ratio.

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