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Phenol Removal from Waste Water by Using a Commercial, Microporous Activated Carbon Granules (ACG)

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Abstract

A commercial microporous activated carbon granulate (ACG) was characterized and tested for phenol adsorption from water. The microstructure and surface chemistry of the ACG were characterized using N_2 adsorption, wide angle X-ray diffraction (WAXD), Raman, FTIR, TEM, SEM, and energy dispersive X-ray (SEM – EDX). The influences of ACG dosage, contact time, initial adsorbate concentration and salt concentration on phenol adsorption were studied in the batch mode. Experimental results revealed that: 1) The Freundlich equation and 2nd order kinetics are better models to describe the adsorption equilibrium and kinetics, respectively; 2) ACG presents a phenol capacity of ~ 90 mg/g at the dosage of 5g/L; 3) Phenol uptake on ACG involves both physical as well as chemical adsorption; 4) The adsorption capacity is sensitive to the presence of salts, particularly the divalent salt.

Key words: *Adsorption, activated carbon, mechanism, phenol, water treatment.*

Introduction

Industrial waste water containing phenolic compounds presents serious environmental/health hazards [1, 2],[3] and should be treated adequately before discharge to the environment. The adsorption process is a major technology while the activated carbon (AC) and activated carbon granules (ACG) are the most popular adsorbents in this type of wastewater treatment [4]. The ACG has a number of advantages such as: low-cost, availability, stability, durability, recyclability etc. [5]. The adsorption performance of AC/ACG largely depends on two of their properties: 1) porous structure (pore size and/or surface area), and 2) surface chemistry (functional groups). Such properties can be manipulated to some extent via the selection of carbon precursors, preparation processes, and the post treatments [6],[7-11]. For example, Srivastava et al. tested phenol adsorption on an AC derived from the sugarcane bagasse fly ash, and reported a adsorption capacity of 23.8 mg-phenol/g-AC at a phenol concentration of 55mg/L and a dosage of 10g/L [7]. An AC prepared from biomass (rattan sawdust) showed an capacity of 149 mg/g[8]. Removal of phenol from the petroleum industry's refinery wastewater by activated carbon revealed a high capacity of 262 mg/g[9]. This capacity as high as 303 mg/g[10]to 500 mg/g were also reported from some specifically prepared adsorbents[11]. In addition to the source of carbon, activation process also plays an important role. Activation of carbonaceous material derived from Kraft lignin with NaOH and KOH reveled adsorption capacity of 238 and 213 mg/g, respectively [5]. Phenol uptake by activated carbon from the aqueous solution not only depends on its microstructure but also on the functional groups on the surface. For example, Fierro et al. reported a capacity of 238 mg/g on the NaOH-activated carbonaceous material, probably due to the existence of more functional groups [5]. This is expected as the phenol is a polar molecule, which can present strong electrostatic interaction with the functional groups on carbon surface, in addition to the physical adsorption in the porous networks.

Methods and Materials

Materials*:* The ACG sample was obtained from BPL, Calgon Corporation. Phenol was obtained from the Merck. All other chemicals are of analytical grade. Deionized water was used for all experimental purposes.

Characterizations*:* Fourier transform infrared (FTIR) spectra were obtained using an ATR-FTIR spectrometer (Vertex 70, Bruker) by averaging 128 scans in the 4000 – 400 cm^{-1} spectral ranges at 4 cm^{-1} resolution. Powder X-ray diffraction (XRD) spectrum of ACG was analyzed using an Analytical X'Pert PRO powder Diffractometer. Raman analysis was carried out using a Jobin Yvon Horiba LabRAM spectrometer with back-scattered confocal configuration. N_2 isotherm (at 77K) was measured on the sample using a pore and surface analyzer (Quantachrome

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Auotosorp-1, USA). Prior to the experiment, the sample was degassed at 120 °C and 10^{-5}Torr for 6 hours. The pore size distributions and cumulative pore volume were obtained from the Barrett-Joyner-Halenda(BJH) method [12]. Scanning electron microscope (SEM, JSM) was employed to observe the surface morphology of native and phenol-loaded ACGs. The samples were observed at various magnifications, with simultaneously elementary analysis by the Energy Dispersive X-ray Spectroscopy (EDAX). Transmission electron microscopy (TEM) studies were performed in a FEI Tecnai 20 ST electron microscope (1.1 Å point resolution), equipped with an EDAX microanalysis system for X-ray energy dispersive spectroscopy (EDS) and a GIF for electron energy loss spectroscopy (EELS) experiments.

Results and Discussion

***Characterization of ACG**:* FTIR spectra (Figure 1) show that the broad and weak peak at around 3400 - 3900 cm^{-1} is due to the O – H vibration of hydroxyl groups. The weak and broad peak in the region of 1700 cm^{-1} could be assigned to the C=O stretching of carboxylic functionalities [13]. Phenolic type C – H peak appeared at ~ 2920 cm^{-1}[14]. Peak at ~2340 cm-1 is due to the asymmetric stretch of CO_2 existed in the activated carbon sample. Figure 2 shows the X-ray diffraction pattern of ACG. Broad asymmetric peaks were spotted at 23.5-26.7º (2θ) and at 43.7º (2θ), which are typical for amorphous carbons with graphite units and could be assigned to the disordered graphitic {002}and {100} planes, respectively [15-17]. In addition, a weak {004} peak was spotted at ~35°.

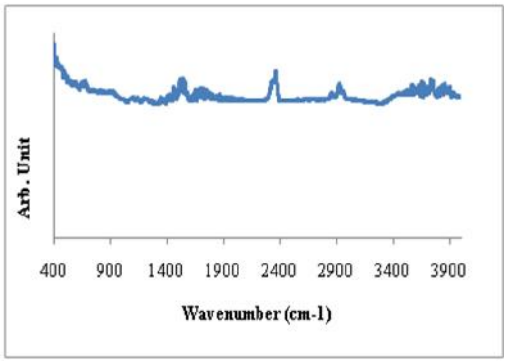


Figure 1: FTIR of the original ACG

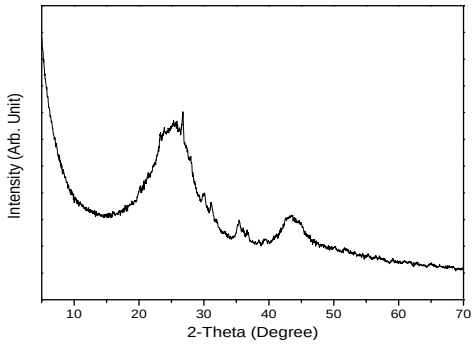


Figure 2: XRD Pattern of Original Activated Carbon Granules

Two sharp Raman peaks (Figure 3), the G (graphite)-band and the D (disorder)-band, appeared at approximately 1580 and 1320 cm^{-1}, respectively. The G- band is associated with the vibration of sp^2 carbon atoms and corresponds to the high degree of symmetry and order of carbon materials. The D-band corresponds to the vibration of sp^3 carbon atoms of defects and disorder in the curved graphite sheet[18]. The intensity ratio of D to G peak (ID/IG) is ~1.103, which shows that the ACG is largely amorphous.

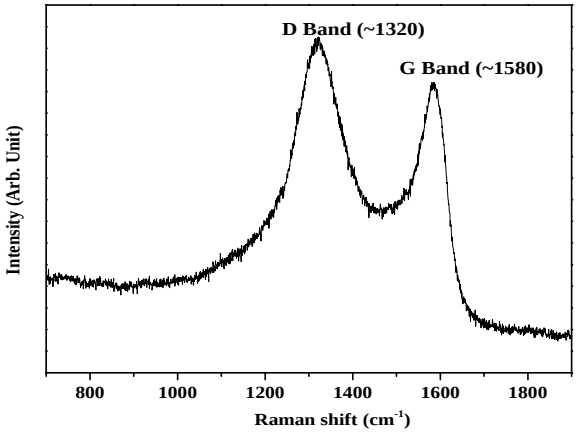


Figure 3: Raman Spectroscopy of the ACG

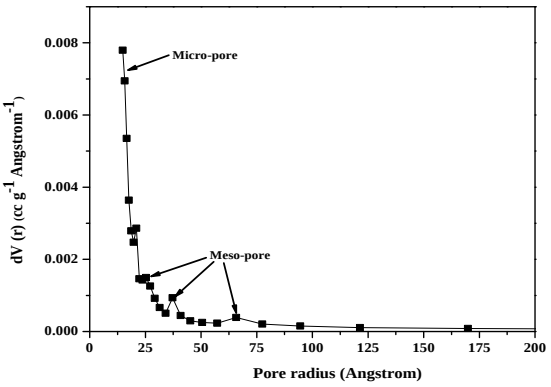
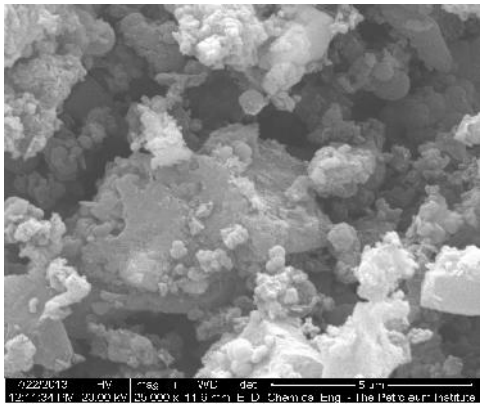
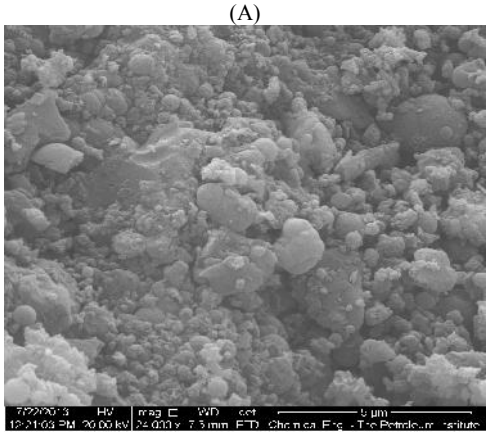


Figure 4: Pore Size Distribution of the ACG

Figure 4 and Table 1 present the structural characteristics of the ACG. It is seen that the ACG is essentially microporous (with the major peak of pore size <2 nm). Small mesopore peaks were also spotted around 3 and 6 nm. Such mesopores generally exist between graphite units and play important role for interparticle diffusion [19].



(A)



(B)

Figure 5: SEM Micrographs of ACG (A) before Phenol Adsorption and (B) after Phenol Adsorption

Figures 5 show the SEM surface morphology of the ACG before and after phenol adsorption respectively. It is seen that ACG had a significant open structure before adsorption (5a), which became densely packed after adsorption (5b). This observation suggests that adsorbed phenol molecules collapsed/blocked some of the porous structure[17]. EDX results (Table 1) revealed that native sample

Table 1 The Characteristics of ACG Sample

BET Analysis (Native ACG samples)		EDX Analysis	
Characteristics	Values	Elements	Concentration (% w/w)
BET surface area (m^2/g)	1,024	Original ACG C	93.4
		O	6.7
Total pore volume (cm^3/g) at P/Po = 0.99	0.59	Phenol loaded ACG C	94.3
Average pore diameter (Å)	~12	O	5.7

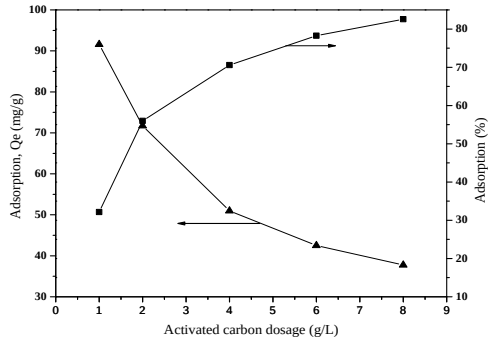


Figure 6: Effect of ACG dosage on adsorption of phenol [C0= 150 mg.L-1, ACG dosage 1-8 g.L-1, adsorption time: 24 h, ■ Adsorption, Qe; ▲ Adsorption (%)]

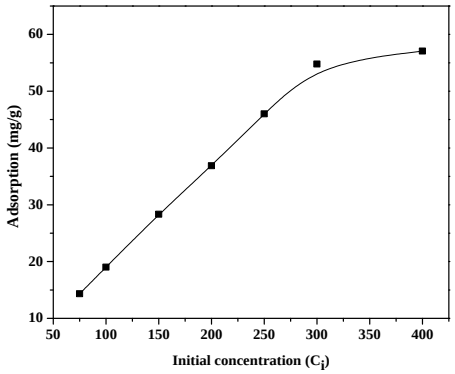


Figure 7 Influence of Initial Phenol Concentration C_0 on ACG [C0 = (75 – 300) mg.L-1, ACG Loading: 5 g.L-1, Adsorption Time: 16 h];

has some oxygen groups on its surface. Oxygen functional groups (e.g. C=O, – COOH etc.) are very important characteristics of the activated carbons because they play an important role in the surface chemistry and thereby affect phenol adsorption.

Influence of adsorbent dosage*:* Figure 6 show that the adsorption efficiency (%) increases with the increase of adsorbent dosage (g-ACG/L) till a plateau is reached, while the adsorption capacity decreases gradually. This is in line with the expectation that higher dosage corresponds to more adsorption sites [14]. The residual concentration of phenol is high at low dosage due to the saturation of adsorbent [20]. The initial experimental result revealed that a dosage of 5 g/L is enough for the quantitative removal of phenol with the ACG sample, and therefore, was fixed forthe rest of the experiments.

Adsorption Isotherms*:* Figure 7A plots the phenol adsorption vs the initial phenol concentration. It is seen that, when the initial concentration increases, the adsorption (Q_e) increases linearly while adsorption efficiency (%) decreases slightly (95.39% adsorption at C_i 75 ppm and 91.28% adsorption at C_i of 300 ppm). With the higher initial phenol concentration, the mass transfer driving force hence the rate at which phenol molecules diffuse from thebulk solution to the activated carbon surface increases [21]. Meanwhile, at higher adsorbate concentration, the capacity of the adsorbent approaches saturation, resulting in decrease in

overall removal [2].Adsorption isotherm is important to describe how adsorbate molecules interact with the adsorbent, and is critical in optimizing the system design. Two popular isotherm models, i.e. Langmuir and Freundlich are fitted to the experimental data. The Langmuir model is applicable to a homogeneous surface with monolayer adsorption [1, 8], while the Freundlich isotherm model is more applicable for adsorption on a heterogeneous surface. The fitting results are listed in Table 2.

Table 2 Isotherms and Kinetics Parameters for Phenol Adsorption on ACG

Isotherm	Isotherm parameters	Kinetic constants
Langmuir $C_\mu = \frac{Q_0 bC}{1+bC}$	Q_0 = 90.1 mg/g b = 0.047 L/mg R^2 = 0.95	***Pseudo-first-order constants*** k_1 = 0.2341 (h^{-1}) R^2 = 0.95
Freundlich $C_\mu = K_F C^{1/n}$	n = 1.57 K_F=6.8 (mg/g)(L/mg)$^{1/n}$ R^2 = 0.99	***Pseudo-second-order constan***ts k_2= 0.091 g.mg^{-1}.h^{-1}, R^2 = 1

We see in Table 2 that the Freundlich equation gives a better fit (R^2 = 0.99) vs Langmuir (R^2 = 0.95) equation. This may suggest that surface of ACG presents a certain degree of heterogeneity, largely due to the existence of functional groups, as revealed by the previous characterization results[22].

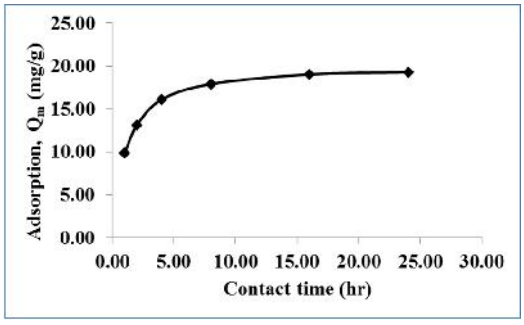


Figure 8A: Effect of Contact Time on Phenol Adsorption by ACG

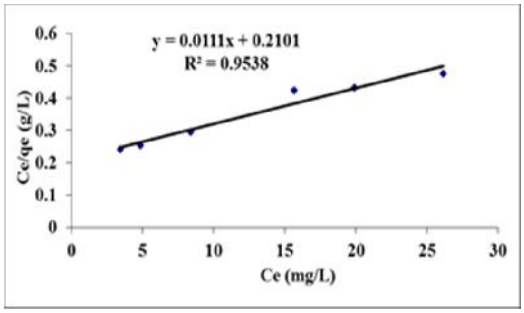


Figure 8B: 1storder Kinetic Model of Phenol Adsorption on ACG

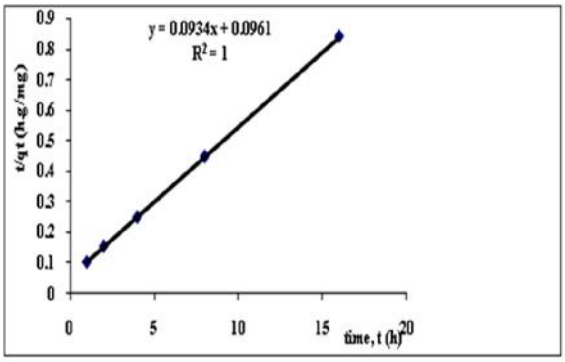


Figure 8C: 2nd Order Kinetic Model of Phenol Adsorption on ACG

Adsorption kinetics*:* Figures 8 shows the rate of phenol adsorption at the initial concentration of 100 ppm. The experimental result suggests that the curves rise sharply in the initial stages, until a plateau is reached (8A)[1,8]. Adsorption kinetics are dictated by the underlining adsorption mechanisms [23] and are generally represented by either pseudo 1st order (8B) or the 2ndorder (8C) kinetic equations. In general, the 2nd order equation is based on the adsorption rate control over the whole long time range. Table 2 revealed that the 2nd order equation fits the experimental data slightly better (R^2~1) than that the 1st order mode[8].

Influence of ion concentration*:* The industrial effluent contains many salts together with organic pollutants. Dissolved salts in the aqueous media often influences adsorption capacity [4]. Therefore, NaCl and Na_2SO_4were used as the model salts to investigate their influence (ionic strength) on the phenol adsorption. It is seen in Figure 9 that NaCl plays a relatively stable role (~ 10% decrease in phenol capacity when its dosage increases from 1 to 8g/L), while sulphate (SO_4^{2-}) plays an significant role (a decrease of ~ 20% at the dosage of 8 g/L). This capacity decrease is caused by the ions which block the microporous structure (physical adsorption) and interact with the functional groups on ACG's surface (chemical adsorption) [12]. Because sulphate possesses a large molecular size and more charges, it exerted a stronger influence on phenol uptake than its counterpart.

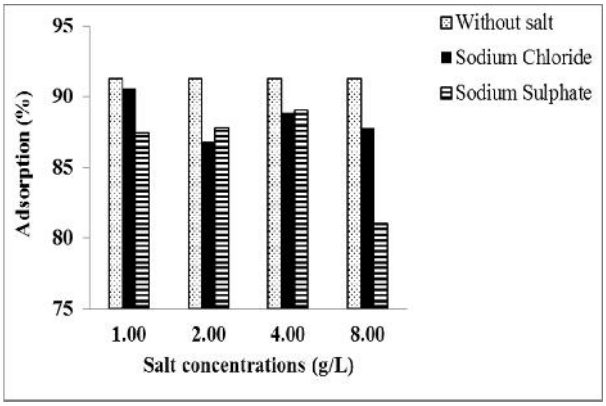
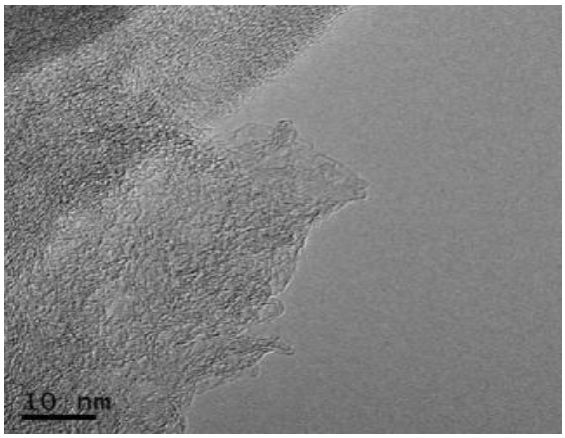


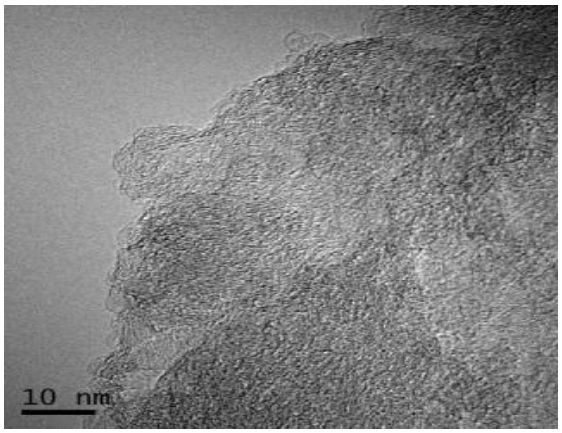
Figure 9: Influence of Two Salts on the Adsorption of Phenol by ACG (Phenol Conc: 300 mg/L, ACG dosage: 5 g/L, Adsorption Time: 16 h)

Mechanism of phenol adsorption on ACG*:* Phenol adsorption on carbon is a complicated process, which depends on the surface area, pore size, pore volume and surface functional groups of the adsorbent. The phenol molecule consists of the aromatic ring and

hydroxyl group (–OH) which is an electron donor. Therefore, the presence of carboxylic group (-COOH) and other oxygen containing groups (as indicated by FTIR spectra) on the activated carbon surface would enhance the interaction/adsorption by the ester bond formation between the two type of functional groups. The physical adsorption occurs mainly due to the dispersive interactions between the benzene ring and the basal graphite plane [6], which is a strong function of the pore size. Other electrostatic attraction may include: H-bonding, dipole-dipole and dipole-induced dipole interactions, etc. [24]. In addition to these, phenol adsorption could also occur due to the diffusion of phenol molecules from the aqueous solution to the porous structure of the activated carbon. Porosity of the activated carbon granules takes a major driving role for the adsorption of phenol from the aqueous solution. The pore adsorption mainly takes place in ultramicropores (d<0.7 nm) and micropores (d<2 nm), which are similar in size as compared with the molecular diameter of phenol (kinetic molecular diameter of phenol is around 0.62 nm) [13]. However, as only few of them are presents on the outer surface. Therefore, both micropores and mesopores are also important for the passage of the phenol molecules to the micropores/ultra-micropores [25].



(A)



(B)

Figure 10: TEM Images of the (A) Native and (B) Phenol Loaded ACG Samples

The TEM images of the native and phenol loaded ACGs are shown in Figures 10. The predominant microporosity of the ACG gives a largely homogeneous morphology view. The bright shapes are considered to be the pores. It is seen in Figure 10A that the native sample has a typical turbostratic, disordered porous microstructure with tightly curled carbon layers. Some wider spaces are found among the hexagonal stacks near the surface, which may reflect the mesopores. After adsorption, it is seen in Figure 10B that surface morphology has significantly changed due to the load of phenol molecules [26]. The local chemical composition for particleobtained using X-ray EDS showed that the native sample has an atomic % C and O % of 97.7 and 2.03, respectively. After adsorption with phenol, the atomic % C content increased to (98.67%) while that of O dropped to 1.32 due to the influence of aromatic phenol molecule (C_6H_5OH) on adsorbents.

Conclusions

The activated carbon granule possesses a microporous structure and complicated surface chemistry. The adsorption equilibrium is better described by the Freundlich isotherm, suggesting a heterogeneous surface towards phenol molecules. The adsorption kinetics was represented by the pseudo-second-order kinetic models. The addition of divalent salt drastically reduces the phenol adsorption both physically and chemically. SEM and TEM results revealed that both physical and chemical adsorption may play important roles on phenol adsorption on the sample.

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