Decontamination of benzene from aqueous solution by green functionalization of activated carbon

Hirra Anjum[1]**, Nirmala Gnanasundaram**[2]**, Khairiraihanna Johari**[1]**, Thanabalan Murugesan**[1*]

[1]Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia.
[2]Department of Chemical Engineering, VIT University, Vellore, 632014 Tamil Nadu, India.

[*]murugesan@utp.edu.my

Abstract. Environmental pollution caused by industrial wastewater is at its alarming rate. Benzene falls under the category of those contaminants that most commonly found in produced water from chemical industries. To get rid of this carcinogenic compound, the present study proposed an environmentally benign method to modify the commercially activated carbon by means of 1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide. This green functionalization attempts to simultaneously maximize the removal efficiency of adsorbent by elevating the surface area and pore volume of the modified adsorbent and reduce the overall cost of the process. The activated carbon in pristine and functionalized forms was characterized by using, N_2 adsorption/desorption, FTIR, Thermogravimetric analysis, Raman spectroscopy, XRD analysis and Scanning Electron Microscopy. Batch adsorption experiments were performed and modified activated carbon exhibited higher adsorption capacity compared to that of pristine AC. The Pseudo second order model and Langmuir isotherm model best fitted the data of the adsorption of benzene. Thus, modified activated carbon managed to enhance the benzene removal efficiency up to 87%.

1. Introduction

Aromatic compounds are most commonly used in chemical industries. They are often used as raw materials and solvents in manufacturing processes. Benzene is found to be the most dangerous among them. Because of its carcinogenic and mutagenic nature, it imparts severe health impacts on the environment. Thus, its removal is critical to ensure the safe water supply. A considerable effort has been made by the researchers to develop the most efficient method for the obliteration of benzene but the most widely used is the process of adsorption that can eradicate the unwanted volatile organic compounds even at very low concentrations [1].

There are several economically viable adsorbents namely, activated carbon, clay minerals, zeolites and polymeric resins that have been studied extensively. But activated carbon is found to be the most vital mesoporous adsorbent with high specific surface area and surface to volume ratio, complex surface characteristics. This surface chemistry is the one factor that ultimately defines the sorption capacity of the adsorbent. However, this surface chemistry is directly related to the surface groups. These surface groups can be easily modified by thermal, acidic and basic treatments [2, 3].

Furthermore, ionic liquids gained much attention as an alternative of acidic or alkaline modification due to their unique tuneable properties and diverse characteristics (extremely low vapor pressure, high thermal and chemical stabilities, non-flammability and high solvent capacity) and environmentally friendly nature. In order to ensure the covalent bonding, they act as a binder between the activated carbon and the other component [4]. We selected 1-Hexyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl)imide. The use of bulky group in the conventional position enhances the dispersion ability of surfactant. However, methyl group avoids the deprotonation in the compound. Moreover, most commonly used ILs are imidazolium-based ionic liquids because of easy dispersion and longer chain length with high integrity and stability depending upon the anion used. On the other hand, hydrophobic groups increase the solubility of the surfactant in aqueous media, as perfluorinated sulfonyl imide forms hydrolytically stable hydrophobic ionic liquids with low viscosity and high electrical conductivity [5].

In this paper, the commercial activated carbon was chosen as an adsorbent for the sorption of benzene in aqueous solution. The modification of activated carbon was carried out via ionic liquid treatment in order to introduce oxygen bearing functional groups over the surface of graphitic structure and demonstrate the comparison with the help of detailed characterization, kinetics and isotherm studies revealed that activated carbon functionalized with ionic liquids exhibited a superior sorption capacity compared to the pristine AC.

2. Materials and Methods

Activated carbon (12.01g/mol, < 0.1 mmHg, -100 mesh particle size, Sigma Aldrich), 1-Hexyl-3-methylimadazolium bis(trifluoromethylsulfonyl)imide (447.42g/mol, Merck), ethanol (95.2%, 46.07g/mol) and acetonitrile (99.9%, 46.07g/mol).

Five grams of pretreated AC was dissolved in 500ml of ethanol and 5ml of 1-Hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. Afterwards, 0.02g of Cetyltrimethylammonium (CTAB) was added in solution mixture as a surfactant with continuous stirring in an oil bath at 65°C for 3h. The oxidized AC (O-AC) was filtered and dried overnight at 60°C.

The surface area and pore volume was analyzed by BET surface area analyzer (Micromeritics ASAP 2020), the surface functional groups were evaluated by FTIR (SHIMADZU, 8400S), thermal stability was examined by Thermogravimetric analysis ((Perkin-Elmer TGA, Pyris I), the structural defects were probed by Raman spectroscopy (Horiba Jobin Yvon HR800), crystallographic structure was determined by XRD analysis ((Bruker, D8) and surface morphology was investigated by FESEM (Zeiss Supra 55 VP).

3. Results and Discussions

3.1. Pore Structure Characterization

N_2 adsorption/desorption isotherms of Pristine and modified activated carbon at 77K is illustrated in figure 1a. The initial curvature of the isotherm defines the monolayer coverage and rounded knee is the evidence of the presence of some micropores in the modified activated carbon [6]. The knee of O-AC is broader which indicates larger monolayer coverage as compared to that of raw sample. This large monolayer coverage implies that O-AC have much larger surface area than that of the P-AC.

Since surface area is the function of pore size and the number of pores. So, pore size distribution is presented as the evidence of the effect of chemical treatment on the performance of activated carbon after oxidation as depicted in figure 1b. It is evident that micropore size distribution is quite pronounced in the ionic liquid modified sample as compared to that of the un-functionalized sample which is due to the diffusion of the oxidizing agent through the graphitic structure as a matrix to create porosity in the framework for the removal of BTX [7].
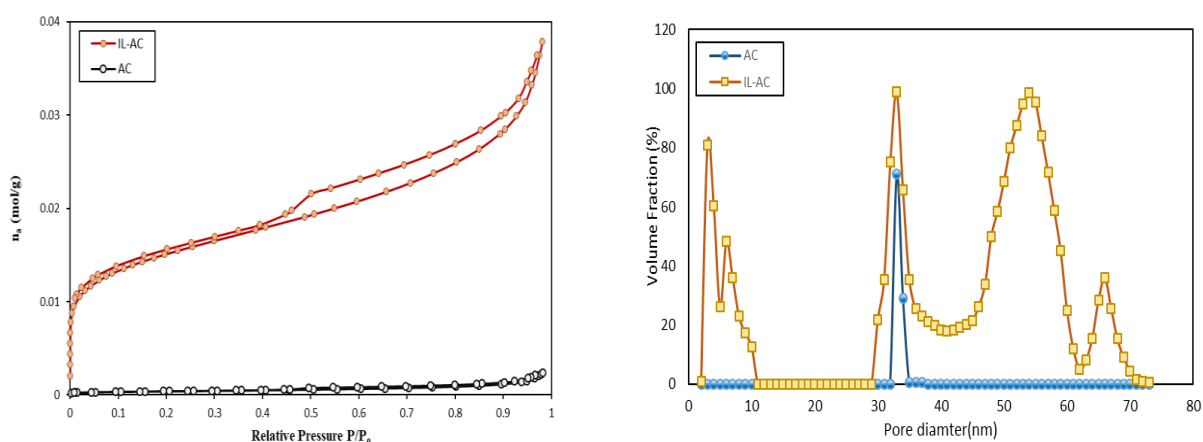
Figure 1. a) Adsorption/desorption isotherms. b) Particle size distribution of P-AC and O-AC.

Hence, the generation of these micropores is observed to be helpful in the enhanced sorption capacity of activated carbon.

3.2. FTIR

The IR spectra of P-AC and O-AC are exhibited in figure 2. It is clear that the peaks are more pronounced after modification with a combination of ionic liquid as compared to that of other modifications. The bands at $3400cm^{-1}$, $3163.3cm^{-1}$, $2961.7cm^{-1}$, $2869.2cm^{-1}$ are related to –OH stretch from carboxylic acid groups, -CH stretch asymmetric and symmetric from CH_3 group respectively. The band $2369cm^{-1}$ is found in all peaks after modification, that is related to strongly hydrogen bonded COOH group [8].
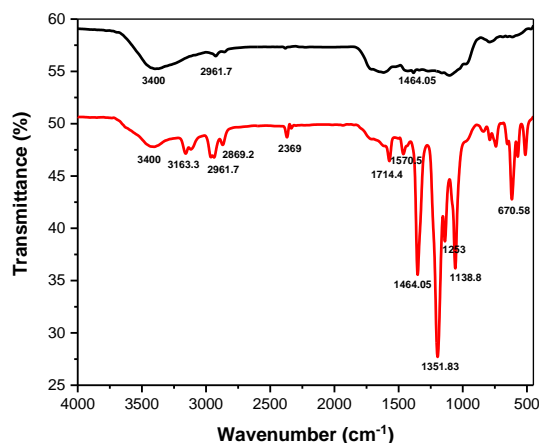

Figure 2. IR spectra of P-AC and O-AC.

The peaks at $1714.4cm^{-1}$ and $1570.5cm^{-1}$ signify the –C=O and OC=O stretch. However, the bands at $1351.83cm^{-1}$, $1196.07cm^{-1}$, $1138.8cm^{-1}$, and $1058cm^{-1}$ are introduced in ionic liquid modified only and are an indication of the presence of (carboxylate anion) CH3COO-, (alcoholic) -OC, COH, and phenolic -OH groups respectively.

3.3. Thermogravimetric Analysis

Thermo-gravimetric analysis of the activated carbon before and after modification enabled ascertaining their thermal stability to state the optimum conditions for calculation. The plot (figure 3) exhibits that

in the first region that is related to moisture evaporation, the thermal stability of pristine and ionic liquid treated activated carbon is 71.03% and 99.97% respectively. Even after degradation of hydroxyl groups the thermal stability of ionic liquid treated activated carbon is the higher than that of P-AC.
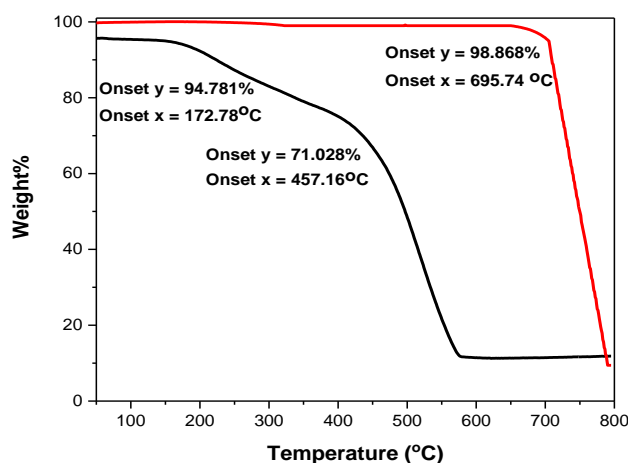

Figure 3. TGA curves of P-AC and O-AC.

The difference in the weight loss between pristine and oxidized AC can be assigned to the change in the hydrophilic nature due to the replacement of carboxylic groups on AC. In the second stage where rapid weight loss occurs due to decomposition of carbon, the thermal stability of pristine and ionic liquid treated activated carbon is 11.32% and 98.86%. The third weight loss is associated with decomposition of the chemical structure at around 795°C in which of pristine and ionic liquid treated activated carbon show 11.85%, and 9.44% stability. The remaining material in pristine activated carbon is most probably the catalyst that was removed in other oxidation treatments and improved the overall purity of the surface modified activated carbon. In conclusion, O-AC samples exhibit much higher thermal decomposition temperature which is the indication of a thermally stable combination of adsorbent. This increase in thermal stability might be due to increased intermolecular interactions and coordinating nature of 1-hexyl-3-methylimidazolium triflorosulfonylimide.

3.4. Raman Spectroscopy

The structural fingerprints are identified by the vibrational spectroscopic approach called as Raman spectroscopy (figure 4). The spectrum is enunciated in a form of the intensity of scattered light versus Raman shift (inverse of wavelength). The degree of functionalization (I_D/I_G ratio) can be determined by Lorentzian fitting areas of D and G band [9]. The degree of functionalization (I_D/I_G ratio) was found to be 1.00, 1.55 for pristine and ionic liquid treated activated carbon, respectively.

This finding reveals that attachment of the oxygen-bearing groups over the carbon lattice leads to an addition of more sp^3 hybridized carbon atoms, stipulating that higher quality functionalized activated carbon are formed. Consequently, the overall profile of modified sample suggests that even after chemical treatment the inherent hexagonal structure of activated carbon remains unmutilated.
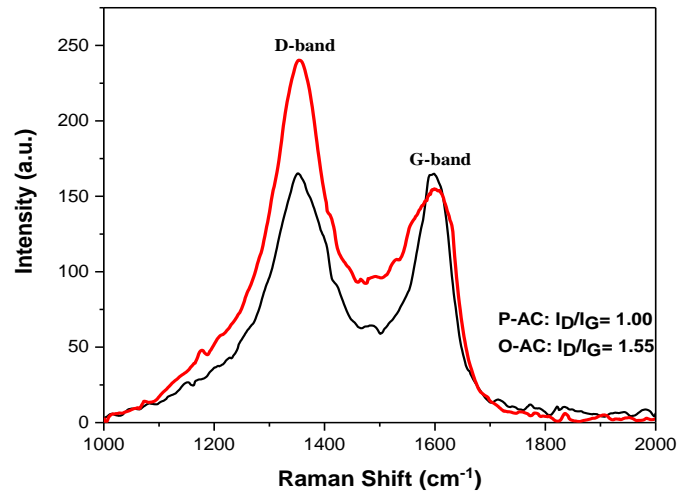
Figure 4. Raman spectra of P-AC and O-AC.

3.5. X-ray Diffraction

The phase analysis by x-ray diffraction of P-AC, and O-AC is exhibited in figure 5. In both samples, the broad peak at 26.8^{o} and 25.4^{o} is observed for P-AC and O-AC respectively. It is due to the reflections from planes can be noticed which is clear indication of the presence of graphitic ordering (amorphous carbon) in molecular planes[10]. The peak has become clearly broad in O-AC which is the validation of the presence of amorphous carbon in the structure. Other sharp peaks signify the presence of impurities in the samples. These peaks tend to attenuate in the O-AC plot and remain in micro range. From this (002) broad peak, interplaner distance (dhkl) was determined by utilizing Braggs law and average crystal size with the help of Deby- Scherrer equation [11, 12].
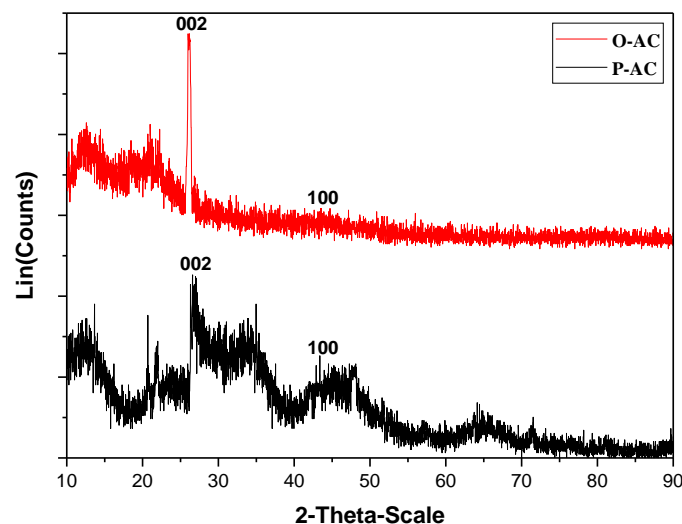

Figure 5. XRD peaks for P-AC and O-AC.

The crystalline dimensions of activated carbon before and after surface modification has been summarized in table 1. It reveals that with the increase in peak intensity at (002), O-AC exhibits the highest crystalline dimension as compared to that of other samples.
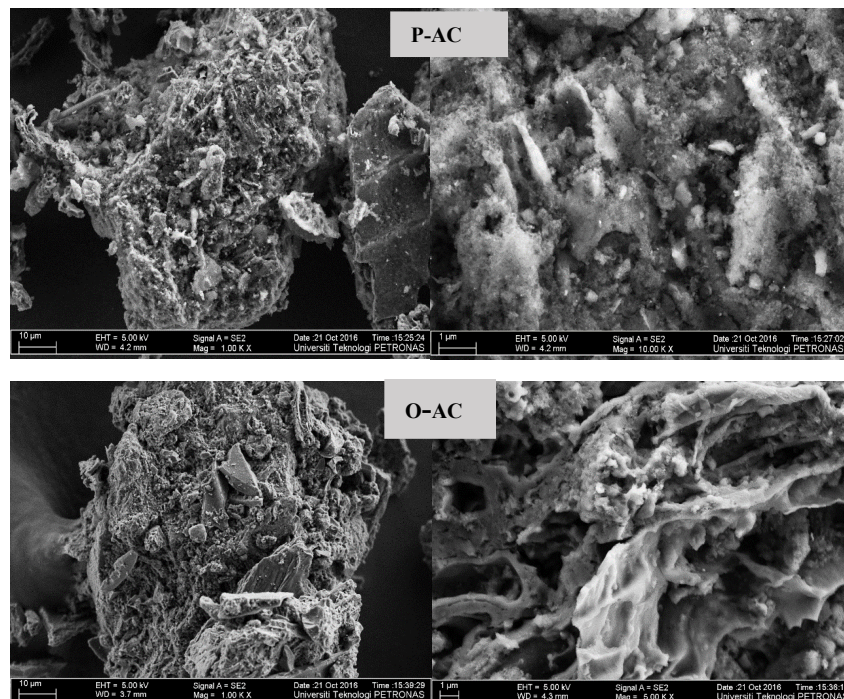
Table 1. Crystalline dimensions of pristine and oxidized activated carbon.

Crystalline dimensions	P-AC	O-AC
d_{hkl} (nm) $$d_{hkl} = \frac{n\lambda}{2sin\theta_{B(hkl)}}$$	0.332	0.3506
L_c (nm) $$L_c = \frac{k\lambda}{FWHM_{hkl}\,cos\theta_{B(hkl)}}$$	2.254	3.495
L_a (nm) $$L_a = \frac{k\lambda}{FWHM_{hkl}\,cos\theta_{B(hkl)}}$$	4.862	7.495
N_p $$N_p = \frac{L_c}{d_{hkl}}$$	6.789	9.968

Although, the calculated values are believed to be lower than the true crystallite dimensions but can be used as a relative estimate of these quantities [13]. Since, there is no significant difference in diffractogram of all plots, recommending that the surface modification process did not affect the microstructure of carbon material.

3.6. Scanning Electron microscope
The morphological behavior of pristine and modified activated carbon is summarized in figure 6. Two different magnifications (10μm and 1μm) were employed to detect the surface morphology before and after the functionalization. It is clear that the P-AC is comprised of irregular, heterogeneous surface before functionalization.

Figure 6. FESEM of P-AC and O-AC**.**

After the surface modification with the ionic liquid, no apparent damage to the structure is observed. The surface roughness has gradually been improved from ionic liquid treatment which is associated with the introduction of oxygen-containing functional groups. Furthermore, the amorphous nature of

activated carbon has been approved by the introduction of small and larger pores in the structure after functionalization. These microspheres are believed to be responsible for the high specific surface area and total pore volume. O-AC showed a larger number of pores in their structures which implies the fact that other than preparation method, the morphology of activated carbon strongly depends upon the oxidizing agent used [14].

3.7. Adsorption Study

3.7.1. Adsorption kinetic study. Adsorption kinetic models are used to evaluate the rate of sorption mechanism and the efficacy of the sorbents for the removal of hydrophobic contaminants. In this study, the adsorption data of benzene by O-AC were fitted by three well known kinetic models i.e. pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

Table 2. Parameters of kinetic models obtained of this study.

| Sample | Pseudo first order | | | | Pseudo second order | | | Intra particle diffusion | | |
| | q_{exp} | $q_{e(cal)}$ | K_1 | R^2 | $q_{e(cal)}$ | K_2 | R^2 | K_{ID} | C | R^2 |
	mg/g	mg/g	1/hr		mg/g	g/mg.hr		g/mg.hr$^{1/2}$	mg/g	
P-AC	87.5	155.85	0.0294	0.905	88.50	0.0140	0.998	18.76	82.69	0.9865
O-AC	184.00	150.66	0.048	0.9217	181.82	0.0644	0.9954	11.24	132.29	0.8289

It is clear from table 2 that pseudo second order model best suited for the sorption of benzene by O-AC. Moreover, the equilibrium adsorption capacity calculated by using this kinetic model is rationally comparable to sorption capacity attained from the experiments.

3.7.2. Adsorption Isotherm study. In order to design the adsorption system, adsorption isotherms are used. Adsorption equilibrium data of benzene using pure and O-AC was fitted with Langmuir, Freundlich, and D-R isotherm model.

Table 3. Parameters of isotherm models obtained from this study.

| Sample | Langmuir Isotherm | | | Freundlich Isotherm | | | Dubinin–Radushkevich isotherm | | | |
	Q_{max}	K_L	R^2	K_F	1/n	R^2	K_{DR}	q_s	E	R^2
P-AC	89.29	0.0102	0.9929	1.63	1.0731	0.9706	63.05	79.58	0.0890	0.9813
O-AC	188.68	0.0053	0.9941	11.82	4.1427	0.9155	145.83	171.16	0.0586	0.8961

It is evident from the table 3 that Langmuir model best describes the monolayer adsorption with maximum adsorption capacity of 188.68 mg/g while Freundlich model provides information about heterogeneous adsorption on adsorbent surface.

4. Conclusion

Commercial activated carbon is modified with 1-Hexyl-3-methyl imidazolium bis TFSI. As a result of surface modification high surface area and pore volume with a wide distribution of porosity are obtained within micro and mesopore ranges. O-AC exhibited the promising performance under the suggested modification route. Subsequently, this functionalization resulted in the introduction of oxygen-bearing complexes over the surface of graphitic carbon network structure which ultimately resulted in increased sorption capacity of modified AC. The obliteration of benzene was carried out in batch experiments.

Results demonstrated that the higher removal of benzene with O-AC occurs under similar the experimental conditions as with that of O-AC. Kinetic studies revealed that adsorption of benzene obeys a pseudo-second-order model. Adsorption isotherms study indicated that Langmuir isotherm models demonstrate very good fit with experimental data as 89.29mg/g and 188.68 mg/g for P-AC and O-AC respectively.

Acknowledgement

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