Feasibility Study on the Regeneration of Spent Activated Carbon from Oleochemical Industry with Microwave

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***Abstract*—Regeneration of spent activated carbon through microwave regeneration offers some advantages over conventional treatment methods. The regeneration of spent activated carbon from oleochemical industry through microwave irradiation under different operating conditions has been investigated. The surface porosity and functional group for virgin, spent and regenerated activated carbons samples were characterized in the study. The adsorption uptake of the virgin and regenerated activated carbon was identified through batch adsorption experiment with methylene blue solution. Surface area of the activated carbon exhibit larger mesopore surface area than micropore surface area. Microprore surface did not appear when the spent activated carbon regenerated at power level below 1000 W and heating time below 9 min. Longer heating period are required to preserve the porosity and adsorption performance of the activated carbon in order to high regeneration efficiency.**

***Keywords*— Activated carbon, BET surface area FTIR spectra, Regeneration, Microwave**

I. INTRODUCTION

Carbonaceous material known as activated carbon contains high specific surface area, large pore volume and small pore diameter. For industrial application the activated carbon comes in a form of powdered activated carbon (PAC), granulated activated carbon (GAC), spherical activated carbon, impregnated activated carbon, and polymer coated carbon [1]. Due to its high porosity, activated carbon has been used as adsorbent in food processing, chemical and pharmaceutical industries, wastewater treatment and as well as bleaching agent in improving odor and color of glycerin in oleo chemical process industries [2].

Removal of organic and inorganic pollutants from aqueous media through adsorption by using activated carbon had been proven as an effective process [3]. Activated carbon has great capacity for colour or dye removal from wastewater or industrial effluent. Removal of a wide variety of dyes from wastewater or industrial effluent by adsorption on activated carbon is preferred rather than other expensive treatment [4]. Other than that, activated carbon also widely used in removing heavy metals contaminants [5].

High usage of activated has great impact economically and environmentally. Its limited utilization over time has made it economically in favorable for the fact that it becomes saturated when undergo adsorption process. The saturated or exhausted activated carbon is not able to adsorb further when it reaches saturation limit, hence being discarded as schedule waste in a landfill, hence this solution is not an economically favourable. The regeneration of the spent activated carbon is preferred in minimizing operational expenditures and to reduce waste production [6].

Major techniques of regenerating spent activated carbon are thermal, chemical and bio-regeneration. Thermal regeneration runs in rotary kilns or vertical furnace under inert or oxidizing atmosphere [7]. The process of renewal of the adsorptive capacity of activated carbon by the action of microorganisms commonly being used and known as bio-regeneration of activated carbon. It also defined as phenomenon that happened during the course of processes based on combined biological and activated carbon-adsorption treatments [8] . Desorption or decomposition of adsorbate using specific chemical reagents is performed under chemical regeneration of spent activated carbon. The desorption of the adsorbate from the activated carbon usually being done by solvent or a solution containing any other species that modifies the adsorption equilibrium [9].

Regenerating spent activated carbons through thermal, chemical, and bio-regeneration seem to be efficient. However, those methods have a lot of disadvantages. Thermal regeneration demands high energy, loss or carbon due to attrition, burn-off and washout is high. Chemical regeneration requires further purification of the solvents and the process is expensive. Bio-regeneration is a slow process and the adsorbate that can be decomposed or degraded must be biodegradable [10]. Because of all these, another alternative activated carbons regeneration methods are subject of current investigation. Among them, microwave regeneration can be highlighted. Regenerate spent activated carbon through microwave regeneration offer some advantages over other conventional treatment. Microwave regeneration have greater energy saving and efficiency, rapid and precise temperature control and only require small space to undergo the process [6].

The purpose of the current study is to investigate the regeneration of spent activated carbon from oleochemical industry through microwave irradiation under different operating conditions. The surface porosity and functional group of virgin, spent, and regenerated activated carbons were characterized in the study. The adsorption uptake of the virgin and regenerated spent activated carbon were identified through batch adsorption experiment with methylene blue solution. The results obtained were expected to provide some useful for the regeneration of spent activated carbon from oleochemical industry with microwave irradiation.

II. METHODOLOGY

A. *Materials*

The spent activated carbon used in this study was collected from Emery Oleochemical Sdn. Bhd. The activated carbon was used for bleaching process in the production of glycerin. The activated carbon is coal-based activated carbon and in powder form. The activated carbon was manufactured by OSAKA GAS CHEMICAL COMPANY.

Methylene blue (MB) was chosen as adsorbate. Dye stock of methylene blue solution was prepared by dissolving the dye in distilled water to a concentration of 1000 mg/l. Experimental solutions were obtained by diluting the dye stock of methylene blue solution.

B. *Regeneration experimental setup*

The sample of spent activated carbons are regenerated through Panasonic domestic microwave oven with of a maximum output power 1000 W at frequency 245 MHz. The microwave connected with nitrogen tank gas. A quartz column reactor with diameter of 8 cm was installed into the microwave oven. The spent activated carbon was placed into the column and treated by microwave heating under different conditions. The regeneration were carried with different power and radiation time. Nitrogen gas at a flow rate 250 ml/min was purged in the quartz reactor before the start of microwave heating to produce inert atmosphere inside the microwave. The heating power were 300 W, 600 W and 1000 W while the heating times are 3, 6 and 9 min. Based on previous study, heating time to regenerate activated carbon favourable below 10 minutes to preserve the porous structure of the activated carbon [6].

Fig. 1. Microwave apparatus for activated carbon regeneration

C. *Characterization of virgin and regenerated activated carbons*

The physical characterization was focusing on the surface and pore structure of the virgin and regenerated activated carbon after microwave treatment with different power level and time of heating. The pore structure was analyzed by nitrogen adsorption at 77 K using an automatic Micromeritics 3Flex surface characterization. Prior to gas adsorption measurement, samples of the carbon were degassed for 6 hours at temperature 140 ℃ before being analyzed by the gas adsorption measurement. The specific surface area (S_{BET}) was calculated by the BET equation while the micropore and mesopore surface area were deduced using the *t*-plot method.

The surface of virgin and regenerated activated carbon were characterized using FT-IR (Model: Perkin Elmer/ Spectrum One) to determine the functional groups in the sample. FT-IR spectra were recorded in the 500-4000 cm^{-1} range and minimum of 32 scans with spectral resolution of 4 cm^{-1}.

D. *Adsorption study*

Batch adsorption experiment were carried out in a 250-mL Erlenmeyer flask containing 0.20 g virgin and regenerated spent activated carbons and 200 mL of methylene blue solution with concentration of 30 ppm. The flask was agitated in the mechanical shaker at room condition and shaking speed at 120 rpm for an hour. Methylene blue concentration in the supernatant solution after the batch adsorption were measured using a UV-Vis spectrophotometer. 2, 5, 10, 30, and 50 ppm of methylene blue solution were prepared to perform the calibration for the UV-Vis spectrophotometer. Methylene blue uptake at given time, q_t (mg/g) were determined by:

$$q_t = \frac{(C_o - C_t)V}{W}$$

C_o and C_t (mg/l) are the liquid-phase concentrations of methylene blue at initial and certain time, respectively. V (L) is the solution and W (g) is the mass of adsorbent used. All samples were filtered through filtered through filter papers prior to analysis to minimize interference of carbon fines.

III. RESULTS AND DISCUSSION

A. *Characterization of virgin and spent activated carbon from oleochemical industry*

The activated carbon that being used by the oleochemical industry is characterized based on the porous structure and surface functional group. These two parameters are important factors that’s influencing the adsorption capacity of the activated carbon. The surface area obtain from the BET equation is 1029.4160 m^2/g. The micropore and mesopore surface area obtain from t-lot method area 489.5843 m^2/g and 539.8317 m^2/g, respectively. It shows the surface area of the activated carbon exhibit larger mesopore surface area than micropore surface area. Mesopore is the pore in the activated carbon that having diameter between 2 and 50 nm while micropore is a pores structure that having diameter less than 2nm. The adsorption energy of the micropre is much larger compared to larger mesopores or to the nonporous surface because of the overlapping of adsorption forces from the opposite walls of the micropores. However that the molecular dimensions of the adsorbate are not too large to enter the micropores pores. The surface area of the coal based activated carbon had been stated in previous study that show coal-based activated carbon have surface area between 900-1200 m^2/g [11]. However, most study found the pore friction of micropore is higher than mesopore in the coal-based activated carbon [12]. Micropore surface area constitutes about 95% of the total surface area of the active carbon [13]. The spent activated carbon from oeleochemical industry completely saturated. The BET surface area reduce to 2.9651 m^2/g with no contribution of micropore surface area.

FTIR spectrum analysis was used to investigate variations in the functional groups of the virgin and spent activated carbon from the oleochemical industry. The FTIR spectra of the virgin coal based activated carbon presented a characteristic band at 1698 cm^{-1}.These bands could be assigned to the ketone C=O stretch. C=O and C–O stretching in between 1640 - 1750 cm^{-1} attributed to phenolic ester, carboxylic acid and conjugated ketonic structures [14]. The peak 1541cm^{-1} corresponding to the aromatic C=C stretching. The broad peak at 3747 cm^{-1} is assigned to phenolic group (O–H stretch) [15]. The peak was less affected when the activated carbons used for the bleaching process. Peak of 3297cm^{-1}

(phenol O=H stretch) 1524cm^{-1} and 1555cm^{-1} (aromatic C=C bending), 1456 cm^{-1} (alkyl C–H stretch) and 1039cm^{-1} (CO–C stretch) appear on the surface of the activated carbon after the bleaching process.

Additionally, surface functional groups are one of the most important factors influencing its adsorption properties. Surface functional group determine the acidic and basic character of the activated carbon. The acidic character of activated carbon surfaces is related to the surface oxygen concentration. Oxygen-containing functional groups, such as carboxyl, phenolic, lactone, lactol and quinone groups are primarily located at the edges of graphene layers that contribute to the building blocks of activated carbons [16]. The basic character of activated carbon is not well known and normally they are Lewis type basic sites associated with the carbon structure itself [17]. Carbon-oxygen surface groups are by far the most important surface groups that influence the surface characteristics such as the wettability, polarity, and acidity, and the physico-chemical properties such as catalytic, electrical, and chemical reactivity of these materials [18].

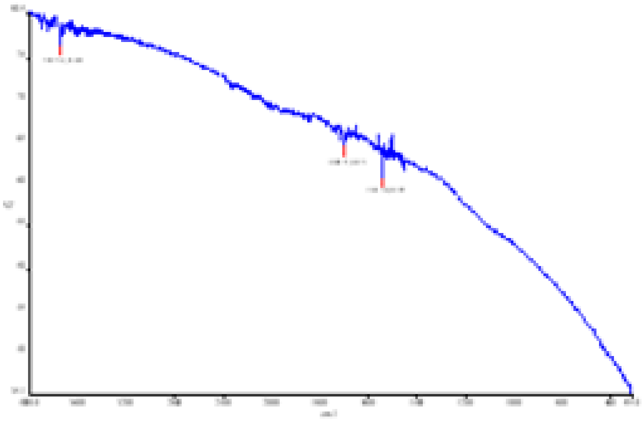

Fig. 2. FTIR spectra of the virgin activated carbon

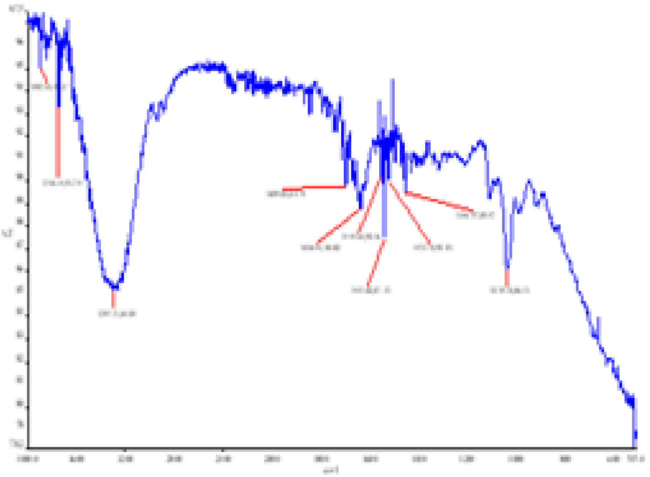

Fig. 3. FTIR spectra of the spent activated carbon

Table 2
Functional group on virgin activated carbon

Spectral feature	Position	Group/Structure
Peak	1698 cm^{-1}	ketone C=O stretch
Peak	1541cm^{-1}	aromatic C=C stretch

Table 3
Functional group on spent activated carbon

Spectral feature	Position	Group/Structure
Peak	1698 cm^{-1}	ketone C=O stretch
Peak	1541cm^{-1}	aromatic C=C stretch
Peak	3297cm^{-1}	alcohol O=H stretch
Peak	1524cm^{-1}	aromatic C=C bending
Peak	1555cm^{-1}	aromatic C=C bending
Peak	1039cm^{-1}	C–O–C stretch
Peak	1456 cm^{-1}	alkyl C–H stretch

B. Effect of power level and heating time on the porous structure of the spent activated carbon

The microwave power was regarded as the most important factor in this experiment since the temperature that the activated carbon could reach was directly related to the power level. The investigated power levels were 300, 600 and 1000 W and the heating time was remained constant at 3, 6 and 9 min.

Based on the result, it can be easily seen the surface area of the activated carbon larger at high output power and longer heating time. The larger surface area produced is 343.20 m^2/g when the spent activated carbon was regenerated at 1000 W and 9 min heating time. The regenerated spent activated having 15.90 m^2/g micropore surface area and 327.29 m^2/g mesopore surface area distribution. The difference of surface area between spent activated and sample that were being regenerated at 3 and 6 min heating times is not significant. The result clearly shown that microprore surface did not appear when the spent activated carbon regenerated at power level below 1000 W and heating time below 9 min. The activated carbon regeneration efficiency increases with the increase of heating time and power level.

Based on previous study, this phenomena happened because of temperature evolution [19].The temperature obtained in the microwave irradiation strongly depends on the microwave power applied to the regenerated sample. It can be stated that a larger microwave out power led to stronger temperature evolution. The temperature of the spent activated carbon was not high enough to start desorption of adsorbate from the activated carbon if the temperature was lower than the adsorbate vapor, the adsorbate may be adsorbed again in the pores of the activated carbon. When the exhausted carbons were exposed to the microwaves, the input power used to reach the regeneration temperature 850℃ had to be increased from 300 to 800 W. In most cases, heating the samples in the microwave device was quite fast, less than 6 min being needed to reach 850 ℃ [7].

Sample	Heating time (min)	BET surface area (m^2/g)	Micropore surface area (m^2/g)	Mesopre surface area (m^2/g)	Pore Size (Å)
Regenerated activated carbon at 1000 W	3	23.7411		25.5913	112.6683
	6	164.1630		190.7276	54.6798
	9	343.1971	15.9033	327.2938	40.2464
Regenerated activated carbon at 600 W	3	15.5924		17.4842	70.7689
	6	148.0086		167.7494	50.6439
	9	254.5513		278.4658	46.7290
Regenerated activated carbon at 300 W	3	9.7744		10.3909	118.0328
	6	24.1630		25.9002	118.0518
	9	36.0907		40.6945	84.4841
Virgin activated carbon		1,029.4200	489.5843	539.8317	28.3726
Spent activated carbon		2.9651			189.8704

Table 1
Structural properties of the virgin, spent and regenerated spent activated carbon

C. Adsorption uptake of the regenerated spent activated carbon on methylene blue solution

The adsorption capability of the regenerated spent activated carbons were being tested through batch adsorption experiment with methylene blue solution.

Form the result, it can be clearly seen that the regenerated spent activated capable to adsorb adsorbate which is methylene blue even the surface area of the regenerated spent activated carbon smaller compared to the virgin activated carbon. Sample of spent activated carbon that being regenerated under 1000 W power level at 9 min heating time capable to reduce the concentration of methylene blue solution from 30 ppm to 10.6852 ppm. The adsorption uptake of the sample is 19.3148 mg/g which more than half of value of adsorption uptake of virgin activated which is 27.5962 mg/g respectively even the distribution of surface area for the regenerated sample (343.1971 m^2/g) smaller compared to the virgin activated carbon (1,029.4160 m^2/g). The adsorption uptake on methylene solution is increase as the heating time and power output of the microwave increase and also increase as the BET surface area of the activated carbon increase. The changes in the surface chemistry could favor the adsorption of methylene blue solution onto the surface of activated carbon [6].

Table 4
Adsorption uptake on methylene blue solution of the regenerated spent activated carbon

Sample of regenerated AC	Heating time	Adsorption uptake (mg/g)
1000 W microwave power output	3	9.0349
	6	15.0488
	9	19.3148
600 W microwave power output	3	7.6477
	6	14.2183
	9	17.2183
300 W microwave power output	3	5.8131
	6	9.5545
	9	10.0614
Virgin activated carbon	-	27.5962

D. Changes of surface functional group on the regenerated spent activated carbon surface

Functional group of alcohol (O–H) stretch disappear when the spent activated carbons were regenerated at microwave power output of 600 W and 1000 W. However, functional group of alcohol O–H bend appear at surface of all the regenerated sample. The functional group of alcohol (O–H) stretch did not disappear or decomposed for spent activated carbons regenerated at microwave power output of 300 W.

All the aromatic C=C that appear on the surface of virgin and spent activated carbon decomposed even the activated regenerated at low power output and short heating time. The functional group C–O–C stretch in the surface of spent activated carbon did not disappear when the activated carbon being regenerated through microwave irradiation below 1000 w power output and 9 min heating. The regeneration process does not alter the functional group of ketone C=O stretch which are the main oxygen-containing functional groups for the activated carbon that contribute to the acidic character of activated carbon [17] .

All the sample of regenerated activated carbon contain oxygen-containing functional groups and hydrogen bond. It helps for the adsorption process of the activated carbon. The oxygen-containing functional groups strength the binding energy between activated carbon surface and adsorbate. The adsorption forces are mainly from hydrogen bonds between functional groups and adsorbate [20].

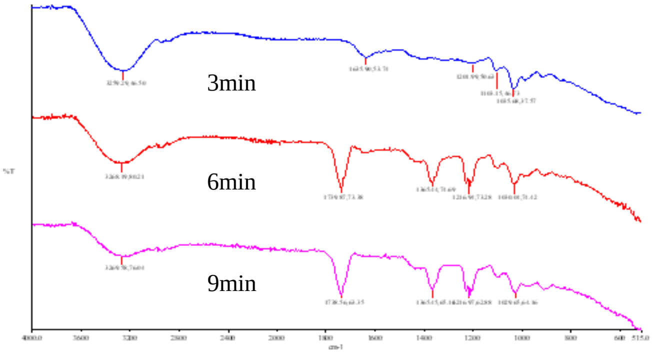

Fig. 4. FTIR spectra of the spent activated carbon regenerated at 300 W power output

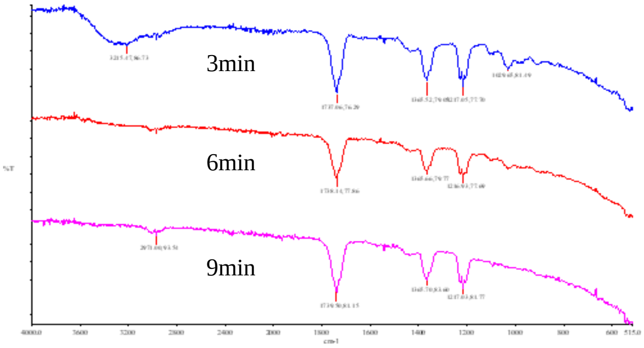

Fig. 5. FTIR spectra of the spent activated carbon regenerated at 600 W power output

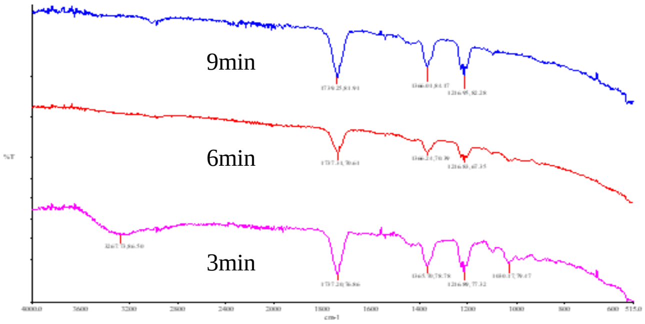

Fig. 6. FTIR spectra of the spent activated carbon regenerated at 1000 W power output

IV. CONCLUSION

This study has demonstrated that spent activated carbon from oleochemical industry can be regenerated with microwave regeneration. The consistency of the mesopore surface areas and alteration in surface functional group allowed the spent activated carbons to be reused. However, longer heating period are required to preserve the porosity and adsorption performance of the activated carbon in order to high regeneration efficiency. From an economic point of view, regenerate spent activated carbon with regeneration open the door to explore the possibility of recovery intermediate compound from the oleochemical industry. Uptake of organic compound by the regenerated activated carbon from aqueous solution can be investigate in the near future.

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References

[1] M. El Gamal, H. A. Mousa, M. H. El-naas, R. Zacharia, and S. Judd, “Bio-regeneration of activated carbon : A comprehensive review,” vol. 197, no. August 2017, pp. 345–359, 2018.

[2] F. K. Yuen and B. H. Hameed, “Recent developments in the preparation and regeneration of activated carbons by microwaves,” *Adv. Colloid Interface Sci.*, vol. 149, no. 1–2, pp. 19–27, 2009.

[3] C. Y. Yin, M. K. Aroua, and W. M. A. W. Daud, “Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions,” *Sep. Purif. Technol.*, vol. 52, no. 3, pp. 403–415, 2007.

[4] G. Crini, “Non-conventional low-cost adsorbents for dye removal: A review,” *Bioresour. Technol.*, vol. 97, no. 9, pp. 1061–1085, 2006.

[5] Y. Fu and T. Viraraghavan, “Removal of Congo Red from an aqueous solution by fungus Aspergillus niger,” *Adv. Environ. Res.*, vol. 7, no. 1, pp. 239–247, 2002.

[6] K. Y. Foo and B. H. Hameed, “Microwave-assisted regeneration of activated carbon,” *Bioresour. Technol.*, vol. 119, no. May, pp. 41–47, 2012.

[7] J. J. Pis, C. O. Ania, J. B. Parra, and J. A. Mene, “Effect of microwave and conventional regeneration on the microporous and mesoporous network and on the adsorptive capacity of activated carbons,” vol. 85, pp. 7–15, 2005.

[8] W. Oh, P. Lim, C. Seng, A. Ngilmi, and A. Sujari, “Bioresource Technology Bioregeneration of granular activated carbon in simultaneous adsorption and biodegradation of chlorophenols,” vol. 102, pp. 9497–9502, 2011.

[9] Q. Li, Y. Qi, and C. Gao, “Chemical regeneration of spent powdered activated carbon used in decolorization of sodium salicylate for the pharmaceutical industry,” *J. Clean. Prod.*, vol. 86, pp. 424–431, 2015.

[10] J. Jaramillo and E. M. Rodr, “Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol,” vol. 38, pp. 2155–2165, 2004.

[11] M. Kwiatkowski and E. Broniek, “An analysis of the porous structure of activated carbons obtained from hazelnut shells by various physical and chemical methods of activation,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 529, pp. 443–453, 2017.

[12] E. Yagmur, S. Turkoglu, A. Banford, and Z. Aktas, “The relative performance of microwave regenerated activated carbons on the removal of phenolic pollutants,” *J. Clean. Prod.*, vol. 149, pp. 1109–1117, 2017.

[13] M. (2005). A. C. A. C. P. Bansal, R. C., & Goyal, *Bansal, etal.,2005*. 2005.

[14] a. Nakase, N. Fujita, K. Takashima, and T. Suzuki, “Recurrence after resection in carcinoma of the pancreas, with special reference to its intraductal implantation,” *J. Japan Soc. Cancer Ther.*, vol. 7, no. 3, pp. 233–237, 1972.

[15] A. Barroso-Bogeat, M. Alexandre-Franco, C. Fernández-González, and V. Gómez-Serrano, “FT-ir analysis of pyrone and chromene structures in activated carbon,” *Energy and Fuels*, vol. 28, no. 6, pp. 4096–4103, 2014.

[16] K. Wang, Y. Zhang, R. Qi, M. Yang, and R. Deng, “Effects of activated carbon surface chemistry and pore structure on adsorption of HAAs from water,” *Huagong Xuebao/Journal Chem. Ind. Eng.*, vol. 57, no. 7, pp. 1659–1663, 2006.

[17] S. F. Fang, P. Pendleton, and A. Badalyan, “Effects of surface functional groups of activated carbon on adsorption of triclosan from aqueous solution,” *Int. J. Environ. Technol. Manag.*, vol. 10, no. 1, p. 36, 2008.

[18] T. J. Bandosz and C. O. Ania, “Chapter 4 Surface chemistry of activated carbons and its characterization,” *Interface Sci. Technol.*, vol. 7, no. C, pp. 159–229, 2006.

[19] M. Chen, J. Huang, J. Wang, P. Ning, Y. Jiang, and Y. Xu, “Thermal behaviors and regeneration of activated carbon saturated with toluene induced by microwave irradiation,” *J. Chem. Eng. Japan*, vol. 42, no. 5, pp. 325–329, 2009.

[20] Y. Guo and E. Du, “The Effects of Thermal Regeneration Conditions and Inorganic Compounds on the Characteristics of Activated Carbon Used in Power Plant,” *Energy Procedia*, vol. 17, pp. 444–449, 2012.