PAPER • OPEN ACCESS

Adsorption Study of Methylene Blue and Eriochrome Black T Dyes on Activated Carbon and Magnetic Carbon Composite

To cite this article: F I Fajarwati *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **599** 012025

View the article online for updates and enhancements.

Adsorption Study of Methylene Blue and Eriochrome Black T Dyes on Activated Carbon and Magnetic Carbon Composite

***F I Fajarwati, M Anugrahwati, I Yanti, R A Safitri, Yeni, E Yuanita**

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia

*Email: febi.indah@uii.ac.id

Abstract. Dye is one of the dangerous contaminants because it can interfere with the health of living things and the environment. This research aims to study the comparison of adsorption capacity between activated carbon and its magnetic composite on methylene blue and eriochrome black T, as azo dyes, an organic compound contains a functional group of –N=N-, that are hardly to be degraded in the environment. The activated carbon used in this study was obtained commercially while the composite material was synthesized using activated carbon which was carried by iron species from a solution of Fe^{2+} and Fe^{3+} salts. The variables studied in this research were contact periodic time and dye concentration. The adsorption process was evaluated using a kinetics and isotherm model. Furthermore, the characterization of the two adsorbents was conducted using Fourier-transform Infrared (FTIR) spectrometer. The results of FTIR characterization show a functional group that indicates of the proper of magnetic carbon composite preparation as indicated at wave number from the vibration of Fe-O bonds. Adsorption result from activated carbon and magnetic carbon composite on both dyes followed the kinetics model pseudo-second order. Meanwhile, the isotherm adsorption model of the adsorbents against methylene blue follows the Langmuir and Freundlich equations for eriochrome black T.

Keyword: adsorption, activated carbon, magnetic composite carbon, pseudo-second order, Langmuir

1. Introduction

Nowadays, contamination of dyes becomes one of focuses to be concerned in liquid waste treatment activities. Source of dyestuff waste originates from various industrial processes such as in the textile, paints, polymers and many other industries. The textile industry plays a role as the largest sources of the presence of dyestuffs in the environment, in which most of the dyes have toxic, mutagenic and carcinogenic properties [1].

Methylene blue (MB) and Eriochrome black T (EBT) are included in azo dye compounds which represents more than half of the global dye production. These reactive azo dyes contain one or more azo bonds (–N=N–) that act as chromophore in the molecular structure. These dyes have been identified as the most problematic dyes in effluents due to its resistance to be degraded by the exposure of light, water and chemicals as it has a complex chemical structure [1].

Several methods in processing dyestuff waste continue to be developed in order to minimize the adverse effects prior its disposal in the environment. Adsorption is one method that is widely used in wastewater treatment processes because it is affordable, effective and easy to be operated [2]. Some materials that potentially applied as adsorbents are activated carbon, fly ash, resin, metal oxides, clay materials, and composite magnetic particles [3,4]. Activated carbon is the most commonly adsorbent applied for the adsorption of organic pollutants because of its large availability, low cost and effectiveness. After adsorption process, separation between activated carbon and the treated solution is usually done by filtration or centrifugation which considerably time consuming, therefore, previous research fabricates it with the magnetic properties in order to be more efficient in practical [13, 14]. However, the fabrication brings consequences such as in its physical properties and adsorption ability to certain organic pollutants [15].

In order to access the adsorption ability, it is important to evaluate how much adsorbate can be adsorbed by the adsorbent which can be analyzed using Langmuir and Freundlich isotherm. The Langmuir model is based on the assumption that monolayer adsorption occurs on a homogeneous surface with a finite number of adsorption sites and negligible mutual interactions between the adsorbed molecules [10, 11]. The linear form of Langmuir equation is given as:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad (1)$$

Where : C_e (mg/L) and q_e (mg/g) are equilibrium concentration and adsorption capacity, respectively, q_m (mg/g) and K_L (L/mg) are the maximum adsorption capacity and rate of adsorption (Langmuir constants), respectively.

The Freundlich model assumes that molecules are adsorbed on the heterogeneous surface of adsorbent based on different sites with different adsorption energies [12]. This model takes into account the mutual interaction between adsorbed molecules. The application of the Freundlich equation also suggests that adsorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent. The linear form of Freundlich equation is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (2)$$

Where: $1/n$ and K_F (mg/g).(L/mg) are Freundlich constants related to the favorability of adsorption process and the adsorption capacity of the adsorbent, respectively. The heterogeneity factor, $1/n$ express adsorption intensity of adsorbent; the adsorption bond is stronger with decreasing $1/n$ value.

From the previous research, adsorption study of EBT using activated carbon (AC) has been conducted [17] however, its study using magnetite carbon composite (MCC) has not been done. Therefore, in this research, determination of adsorption capacity of EBT as well as MB (as the model compound) on the MC was studied in comparison with the adsorption on the AC to observe the adsorption abilities of both adsorbents; the characteristic of the adsorbents, effect of the contact time variation and effect of dye concentration on the adsorption processes. Analysis of adsorption kinetics data from the contact time variations was tested by pseudo first-order and pseudo second-order equations. Furthermore, the equilibrium data was also analyzed based on the Langmuir and Freundlich equations.

2. Experimental

2.1. Materials

Materials used in this research for the preparation of adsorbent were activated carbon, $FeCl_3$, $FeSO_4$, NaOH and ethanol 96%. Meanwhile, for the kinetics study the materials used were filter paper methylene blue, eriochrome black T, pH paper. All of these materials were acquired in pro analysis (p.a.) quality from Merck.

2.2. Equipments
Laboratory equipments used in this study were magnetic stirrer, analytical balance, oven, vacuum filter, mortar and pestle. Moreover, analytical instruments which were used i.e. Fourier Transform Infrared (HITACHI), spectrophotometer UV-Vis (U-2010 Spectrophotometer), shaker (SCILOGEX), glassware and plastic apparatuses. All of these equipments are provided by the research laboratory of Department of Chemistry and the Integrated Laboratory of Universitas Islam Indonesia.

2.3. Adsorbents preparation
Activated carbon (AC) used in this research was obtained commercially that could be used directly after being dried at 105 °C in the oven for 1 h. Meanwhile, the preparation of the composite (MCC) was performed based on the procedure of Mohan et al. [5]. The activated carbon that has been obtained was taken as much as 5 g then being soaked in 50 mL of distilled water. The ferric chloride solution was prepared by adding 1.8 g of $FeCl_3$ to 130 mL of distilled water. At the same time, a ferrous sulphate solution was prepared by adding 2 g of $FeSO_4$ into 150 mL of distilled water. The two solutions were then mixed and stirred at 60-70 °C. The suspension formed was then added into the activated carbon suspension at room temperature while stirring slowly for 30 minutes.

After mixing, 10 M of NaOH solution was added drop wise into the mixture suspension until the pH reached 10-11. During the addition of NaOH, the suspension colour became black at pH 10. After stirring for 60 minutes, the suspension was left at room temperature for 24 hours and repeatedly washed with distilled water, followed by ethanol. Then, the formed composite was filtered with a vacuum filter and dried overnight at 50 °C in the oven. Eventually, both of the adsorbents were characterized by FTIR in order to observe the difference emerged.

2.4. Adsorption study

2.4.1 Effect of the contact time on the adsorption process
The kinetic study was carried out using of initial dye concentration of 1000 mg/L and the adsorbent mass of 0.04 g. Each sample of 10 mL dye solution was agitated in a shaker at 260 rpm at room temperature during the adsorption process. Then, the treated samples were collected at pre-determined time interval from 5 to 75 min. After separated from the adsorbents, the final dye concentration was analyzed using UV-Vis spectrophotometer and the adsorption capacity (q_e) was calculated. Here, the kinetic equation of each dye was determined.

2.4.2 Effect of concentration on the adsorption process
For the isotherm study, the experiment was performed using 10 mL dye solution and adsorbent mass of 0.04 g. Concentration variation of methylene blue was in the range of 200 to 1000 mg/L and eriochrome black T was 50 to 250 mg/L. The dye solutions were agitated in a shaker at 260 rpm at the optimum time of adsorption process that was 15 min. After separation from the adsorbents, the final dye concentration was analyzed using UV-Vis spectrophotometer and the adsorption capacity (q_e) was calculated. Finally, the equations of Freundlich and Langmuir were determined.

3. Results and discussion

3.1 Material characterization
In this study, the preparation of the composite was performed using the same activated carbon obtained commercially and then both characteristics were compared. In the process of preparing MCC, mixtures of Fe^{2+} and Fe^{3+} cations were used to form iron oxides on the carbon surface as a result of the adsorption, hydrolysis and precipitation processes. In this preparation, when NaOH was added to the mixture, the colour of the solution changes with increasing pH, from light brown, dark brown and finally to black at pH of 10 which indicates the formation of magnetite (Fe_3O_4), material which is a mixture of iron oxide from Fe^{2+} and Fe^{3+} [6]. As an adsorbent, AC is commonly separated via filtration from the treated water sample,

meanwhile, MCC can be separated from the sample using magnetic field as it has a magnetic property resulting more efficient separation process after adsorption process.

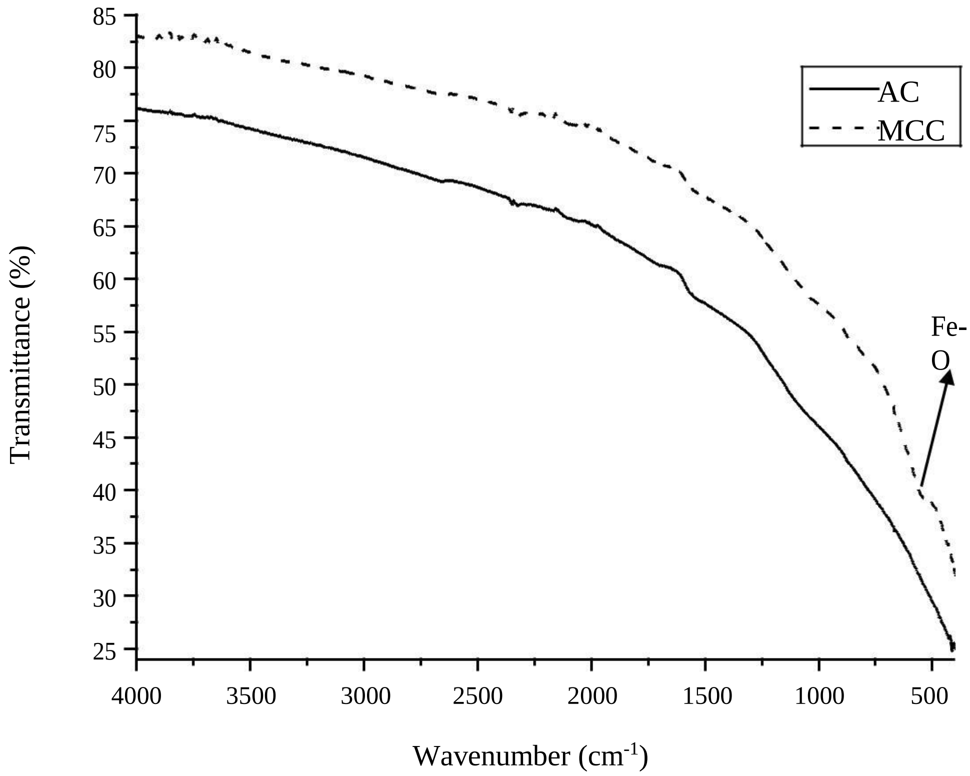
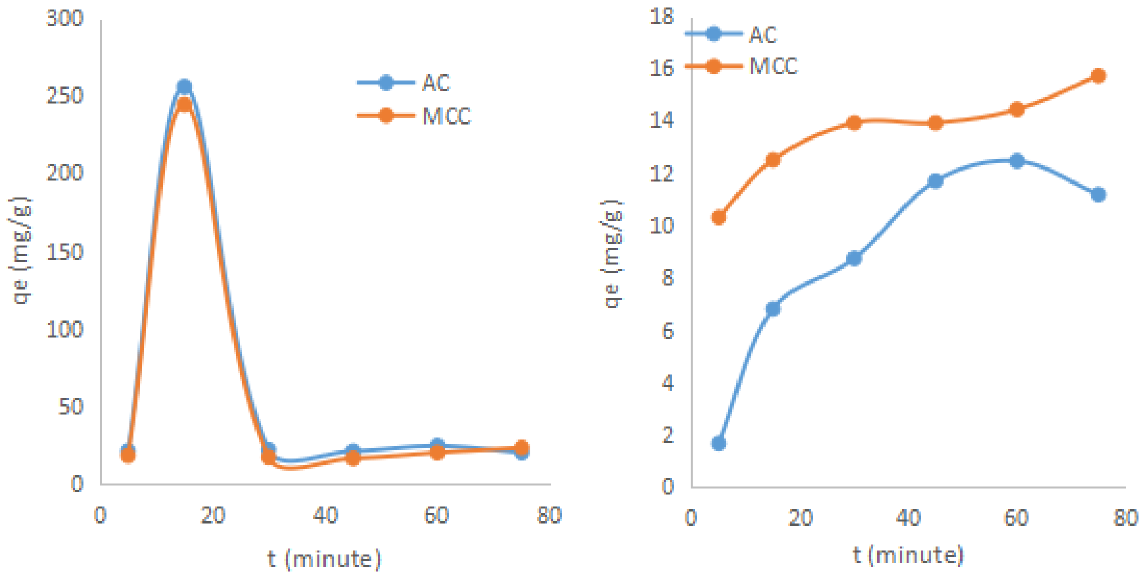


Figure 1. FTIR spectra of AC and MCC.

The material characterization in this study was conducted with FTIR aiming to determine the active groups present in AC and MCC. Through FTIR spectra, it can also be observed the formation of magnetic property from the presence of new absorption peak. Figure 1. shows the FTIR spectra of the two adsorbents used in this study in which each spectrum shows a wave number in the range of 400-4000 cm^{-1}. The two spectra almost depict the same characteristics of the functional group in the activated carbon while the difference that appears in the composite material spectra (MCC) compared with the spectra of AC is the absorption peak at wave number of 533.47 cm^{-1}, that indicates the presence of vibration from Fe-O bond, i.e. characteristic for magnetite [14].

3.2 Adsorption

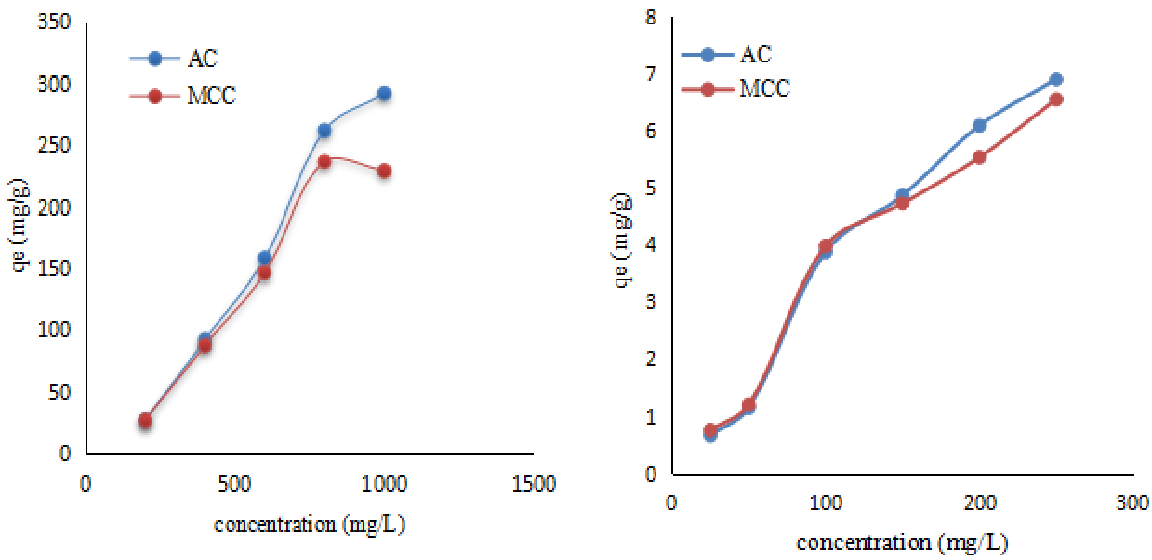
For the adsorption study, the effect of various contact time was observed to study the kinetics of the adsorption process as well as to find out the optimum contact time which then used in the experiment of the effect of the dyes concentration on the adsorption process. In Figure 2., it is known that contact time affects the adsorption of dyes (both MB and EBT) on the AC and MCC. In the Figure 2.a MB adsorption occurs quickly at the beginning of contact time, i.e. 15 minute with the adsorption capacity of 6.81 mg/g for AC and 12.5 mg/g for MCC, this adsorption capacity decreases with the increasing of the contact time until the equilibrium is reached. The same trend also occurs for EBT adsorption (Figure 2.b), the adsorption capacity is rapid at the beginning, i.e. 15 minutes with adsorption capacity of 255.72 mg/g for AC and 244.27 mg/g for MCC. As time increases, the EBT adsorption capacity decreases significantly and the increase is hardly observed.



(a) (b)

Figure 2. Adsorption study of methylene blue (a) and eriochrome black T (b) using activated carbon (AC) and magnetic carbon composite (MCC) in the variation of time.

From Figure 3. it can be seen that the adsorption capacity of MB and EBT is different in which the capacity increases with the addition of the adsorbate concentration. The adsorption of methylene blue (Figure 3.a) by AC and MCC has a maximum adsorption capacity at a concentration of 600 mg/L with q_e of 158.02 mg/g for AC and 146.18 mg/g for MCC. Whereas in the EBT adsorption (Figure 3.b), the maximum capacity was obtained at a concentration of 100 mg/L with q_e of 3.88 mg/g for AC and 3.98 mg/g for MCC.



(a) (b)

Figure 3. Adsorption study of methylene blue (a) and eriochrome black T (b) using activated carbon (AC) and magnetic carbon composite (MCC) in the variation of dye concentration.

Based on the value of R^2 obtained in Table 1. it was observed that MB adsorption by AC and MCC in this study tended to follow pseudo second order kinetics while EBT adsorption by AC and MCC followed pseudo first-order kinetic equations. If the kinetics model follows a pseudo-first order, the adsorption reaction is likely to occur in the form of physisorption whereas if the kinetics model follows a pseudo second order, the adsorption reaction is likely to occur in the form of chemisorption. According to Hamdaoui [7] the pseudo second-order kinetic equation model shows that adsorption runs in a two-stage process; which is fast at the initial and slower at the second stage. The first stage of the adsorption process begins through physical adsorption via van der waals interaction, i.e. the adsorbate approaches the surface of the adsorbent to form an ionic or covalent bond which then results in a chemical adsorption process which causes the adsorbate to adhere strongly to the adsorbent and the adsorbate is not easily being desorbed. In the adsorption process, most dyes adsorption processes follow the chemisorption process which is influenced by the chemical characteristics of the adsorbent material in the form of biomass (organic) to the dye [8]

Table 1. Kinetics data of methylene blue and eriochrome black T adsorption using activated carbon and magnetic carbon composite

Dyes	**Kinetic models**	**Parameter**	**Adsorbent**	
			Active carbon(AC)	Magnetic carbon composite (MCC)
Methylene blue	Pseudo-first order	R^2	0.1822	0.1797
		k (1/minute)	0.0818	0.0806
	Pseudo-second order	$_R2$	0.9577	0.8972
		qe (cal)(mol/g)	19.8020	20.7039
		k (g/mol.minute)	-0.0086	-0.0499
Eriochrom black T	Pseudo-first order	R^2	0.7526	0.9135
		k (1/minute)	-0.0792	-0.0509
	Pseudo-second order	R^2	0.8531	0.9939
		qe (cal)(mol/g)	18.2482	15.9744
		k (g/mol.minute)	0.0016	0.0147

From the values of some parameters shown in Table 2., the maximum adsorption ability (q_{max}) value is obtained from the adsorbent that shows the limited capacity of the adsorbent surface to adsorb the adsorbate. The maximum adsorption ability of MB by AC and MCC was 333 mg/g and 250 mg/g, respectively. Whereas the maximum adsorption of EBT by AC and MCC was -16.4474 mg/g and 20 mg/g that are smaller than ones in methylene blue.

Table 2. Parameters of Langmuir and Freundlich isotherm models.

Dyes	**Model Isotherm**	**Parameter**	**Adsorbent**	
			Active carbon	Magnetic composite carbon
Methylene Blue	Langmuir	qmax (mg/g)	333.0000	250.0000
		K (L/g)	0.0571	0.0358
		E (kJ/mol)	7.1389	-8.3045
		R^2	0.9819	0.9817
	Freundlich	K (L/g)	-0.0526	-0.0821
		n	0.6030	0.3990
		R^2	0.9238	0.9665
Eriochrom	Langmuir	qmax (mg/g)	-16.4474	20.7900

black T		K (L/g)	-0.0429	0.0500
		E (kJ/mol)	0	-7.4717
		R^2	0.5716	0.4973
	Freundlich	K (L/g)	0.0123	0.0009
		n	1.2297	0.9278
		R^2	0.9898	0.9485

In addition, apart from the q_{max} value, other parameters used to determine the adsorption ability of an adsorbent is from the energy isotherm. According to Gasser [9] chemical adsorption has adsorption energy of 40-480 kJ/mol while physical adsorption requires a lower range of energy. Therefore, according to the data, the adsorption energy of the dyes by the adsorbents is assumed to be categorized as physical adsorption considering its low adsorption energy value.

4. Conclusion

It can be conclude from the study that alteration of the adsorbent characteristic affects the adsorption activity for the same adsorbate as well as the structure of the adsorbate itself. Adsorption of MB and EBT on both adsorbents in accordance with the kinetics equation of pseudo second order, however, the adsorption capacity of EBT on the AC and MCC is lower than that of MB as it is shown from the adsorption energy value.

5. References

[1] Barka N., Abdennouri M and Makhfouk, M.E., 2010, Removal of Methylene Blue and Eriochrome Black T from aqueous solutions by biosorption on Scolymus hispanicus L.: Kinetics, equilibrium and thermo dynamics, *Journal of the Taiwan Institute of Chemical Engineers*, **42**, 320-326

[2] Zahra N.L., Sugiyana D and Notodarmojo S., 2014, Adsorption of Reactive Red 141 Textile Dye Onto Natural Local Clay, *Arena Tekstil*, **29(2),** 68-72.

[3] Zohdi N., Mahdavi F., Abdullah L. C and Choong T.S.Y., 2014, Removal of boron from aqueous solution using magnetic carbon nanotube improved with tartaric acid, *Journal of Enviromental Health Sciences and Engineering*, **12(3)**, 1-12

[4] Raveendra R.S., Prashanth P.A and Malini B.R., Nagabhushana B.M., 2015, Adsorption of Eriochrome black-T azo Dye from Aqueous solution on Low cost Activated Carbon prepared from Tridax procumbens, *Res. J. Chem. Sci*., **5(3)**, 9-13

[5] Mohan, D., Sarswat, A., Singh, V.K., Alexandre-Franco, M., Pittman Jr., C.U., 2011 Development of magnetic activated carbon from almond shells for trinitrophenol removal from water, *Chemical Engineering Journal* **172**(2-3) 1111-1125

[6] Ahn, T., Kim, J.H., Yang, H., Lee, J.W., dan Kim, J., 2012, Formation Pathways of Magnetite Nanoparticles by Coprecipitation Method, *Journal of Physical Chemistry C*, **116**, 6069-6076

[7] Hamdaoui O. 2006 Batch Study of Liquid-Phase Adsorption of Methylene Blue Using Cedar Sawdust and Crushed Brick, *J. Hazard Mater* **135** 264-273

[8] Eren, Z. and Acar F.N. 2006 Adsorption of Reactive Black 5 from an Aqueous Solution: Equilibrium and Kinetic Studies, *Desalinat ion* **194**, 1-10

[9] Gasser, R.P., 1987, *An Introductionto Chemisorption and Catalysis by Metals*, Oxford Science Publication, New York

[10] Esfandiar, N., B.N., and T.Ebadi 2014 Removal of Mn (II) from groundwater by sugarcane bagasse and activated carbon (a comperative study): Application of response surfase methodology (RSM) , *Journal of Industrial and Engineering Chemistry* **20** 3726-3736

[11] Asfaram, A., Ghaedi, M., Hajati, S, Rezaeinejad, M., Goudarzi, A., and Purkait, M.K. 2015 Rapid Removal of Auramine-O and Methylene blue by ZnS:Cu Nanoparticles

IOP Conf. Series: Materials Science and Engineering **599** (2019) 012025 doi:10.1088/1757-899X/599/1/012025

Loaded on Activated Carbon: A Response Surface Methodology Approach, *Journal of The Taiwan Institute of Chemical Engineers* **53** 80-91

[12] Han, Y., Li, W., Zhang, J., Meng, H., Xu, Y. and Zhang, X., 2015, Adsorption Behavior of Rhodamine B on Nanoporous Polymer, *RSC Adv*. **2015**(5) 104915-104922

[13] Zhu, X., Liu, Y., Zhou, C., Zhang, S., and Chen, J. 2014 Novel and High-Performance Magnetic Carbon Composite Prepared from Waste Hydrochar for Dye Removal, *ACS Sustainable Chem. Eng*. 2 (**4**) 969-977

[14] Cazetta, A.L., Pezoli, O., Bedin, K.C., Silva, T.L., Junior, A.P., Asefa, T., and Almeida, V.C. 2016 Magnetic Activated Carbon Derived from Biomass Waste by Concurrent Synthesis: Efficient Adsorbent for Toxic Dyes, *ACS Sustainable Chem. Eng*., **4** (3), 1058-1068

[15] Juang, R., Yei, Y., Liao, C., Lin, K., Lu, H., Wang, S., and Sun, A. 2018 Synthesis of Magnetic Fe_3O_4/activated Carbon Nanocomposites with High Surface Area as Recoverable Adsorbents, *Journal of the Taiwan Institute of Chemical Engineers* **90** 51-60

[16] Ahmad AA, Hameed BH.2009 Fixed-bed Adsorption of Reactive Azo Dye Onto Granular Activated Carbon Prepared From Waste, J *Hazard Mater* **175** 298

[17] de Luna, M.D.G., Flores E.D., Genuino, D.A.D., Futalan, C.M., Wan, M. 2013 Adsorption of Eriochrome Black T (EBT) Dye Using Activated Carbon Prepared From Waste Rice Hulls – Optimization, Isotherm and Kinetic Studies, *Journal of the Taiwan Institute of Chemical Engineers* **44** 646-653