ASM Sci. J.Special Issue 2018(1) AiMS2018, 105-113

Removal of Methyl Orange Dye by Manganese/Aluminium- Layered Double Hydroxide

M. Mamat[1,2*], M.A.A. Abdullah[1,2], A.M. Jaafar[3], S.K.C. Soh[4] and C.E. Lee[4]

[1]*Advanced Nano Materials (ANoMa) Research Group,*
School of Fundamental Science, Universiti Malaysia Terengganu,
21030 Kuala Nerus, Terengganu, Malaysia.

[2]*School of Fundamental Science, Universiti Malaysia Terengganu,*
21030 Kuala Nerus, Terengganu, Malaysia.

[3]*Chemistry Department, Faculty of Science,*
Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

[4]*School of Marine and Environmental Sciences,*
Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

As textile production flourishes nowadays, the amount of dyed wastewater entering the water body has also increased. Dyes could have serious negative impacts to the environment and also the human health, hence, they need to be removed from the water body. In this study, layered double hydroxide (LDH) of manganese/aluminium (MnAl) was synthesised to be used as a potential adsorbent to remove methyl orange (MO) dye due to its unique lamellar structure which provides LDH with high anion adsorption and exchange ability. MnAl was synthesized by using co-precipitation method and characterized by powder X-ray diffraction (PXRD), Fourier-Transform Infrared Spectroscopy (FTIR), Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Carbon, Hydrogen, Nitrogen, Sulphur (CHNS) elemental analysers, and Accelerated Surface Area and Porosity Analyzer (ASAP). Adsorption studies were conducted at different contact times and dosages of MnAl to evaluate the performance of MnAl in removing MO from water. Kinetic and isotherm models were tested using pseudo-first order, pseudo-second order, Langmuir isotherm and Freundlich isotherm. MnAl LDH was found to be perfectly fitted into pseudo-second order and Langmuir isotherm.

Keywords: Layered double hydroxide, methyl orange dye, adsorption, pseudo-second order, Langmuir isotherm

I. INTRODUCTION

Various industrial developments such as textiles, printings, leathers, papers and plastics have burdened the environment with many contaminants. The discharged wastewater from the industries contains large amount of dyes, suspended solids, salts and dissolve organic substances causing pollution to freshwater and wa-

*Corresponding author:mazidahmamat@umt.edu.my

ter coloration [1]. This may cause adverse effects to the environment and human health, as dyes may breakdown to toxic products when exposed to sunlight after some time [2]. Thus, researchers attention are drawn to look for alternative solutions and materials to remove dyes from wastewater.

One of the materials that attracts researchers′ attention is layered double hydroxide (LDH) or so-called anionic clay which belongs to two dimensional (2D) ionic lamellar compounds [3]. LDH has stacks of metal hydroxide layers with water molecules and anions occupying the interlayer of the structure to compensate the excess positive charges contributed by the layers of metallic cations [4]. LDHs have been widely reported to be able to adsorb a wide range of anions from water such as bromate [5] and azo dye [6]. LDHs have high anion exchange and adsorption ability [7] which allows them to be an alternative adsorbent or anion-exchanger. The intercalation of heteropoly blue into Zn-Al LDH could induce the adsorption of cationic dye of methylene blue (MB) from aqueous solutions via adsorption process [8].

In this study, methyl orange (MO) (Figure 1) was chosen as a model for anionic dye to evaluate the ability of manganese/aluminium-LDH (MnAl) as a potential adsorbent for the removal of dye from aqueous solution. MO dye may be release to the environment through the discharge of wastewater due to its wide range of applications such as pH indicators, textile dyestuffs, paper printings, cosmetic dyes and so on [9]. It has moderate mobility in soil due to its ionic nature with helps it to cling on clay particle in soil by ion exchange processes which may lead to adsorption on sediment surfaces [10]. This dye is also found to be non-volatile in water due to its ionic nature and aerobic non-biodegradable thus it will persist in water for a long period and leads to bioaccumulation [9]. The oxygenation capacity of the water bodies will be interfered hence, preventing the sunlight from penetrating to the bottom of the water which then limits the photosynthesis of aquatic plants and algae, thus causing stress to the aquatic living organisms [11].

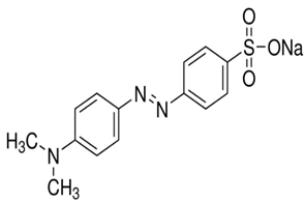

Figure 1. Molecular structure of methyl orange dye

II. MATERIALS AND METHODS

A. Synthesis of Mn/Al-layered double hydroxide

All the chemicals were used as purchased and the solutions were prepared using distilled water. The chemicals used were manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2.4H_2O$, Merck), aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$,

Merck), sodium hydroxide (NaOH, Merck), and methyl orange dye ($C_{14}H_{14}O_3N_3SNa$, Sigma Aldrich).

Manganese/aluminium-layered double hydroxide (MnAl) was prepared by co-precipitating mixed metal solutions of manganese nitrate and aluminium nitrate at Mn/Al molar ratio of 2. NaOH (2M) solution was added under vigorous stirring to pH 8.00 ± 0.05. The resulting slurry was then aged at 70°C for 18 hours, then filtered, and washed with excess distilled water and dried in an oven. The obtained MnAl was grounded to fine powder and characterized using powder X-ray diffraction (PXRD) (Rigaku, Miniflex II) and Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer Precisely, Spectrum 100 FT-IR Spectrophotometer). Elemental compositions of the MnAl were determined by ICP-AES, using a VISTA-PRO CCD Simultaneous ICP-AES under the standard conditions and a CHNS analyzer model CHNS-O (FLASH EA 1112 Series). The surface area and average pore diameter of MnAl was determined using Accelerated Surface Area and Porosity Analyzer (ASAP) of Micromeritics ASAP2020.

B. Adsorption studies

Batch adsorption studies were performed to evaluate the ability of MnAl in the removal of methyl orange dye. The different dosages of MnAl (0.01, 0.025, 0.05, 0.1, 0.2 and 0.5 g) were put in contact with 100 mL of 40 ppm MO solution and was shaken with a Thermolyne Big Bill shaker at 100 rpm for 180 minutes. The remaining dye concentrations were determined at pre-set time interval by using a UV-Vis spectrophotometer (Shimadzu Model: UV-1601 PC UV Visible Spectrophotometer) at λ_{max} of 464 nm.

III. RESULTS AND DISCUSSIONS

A. Characterisation of MnAl

The XRD (003) reflection plane appears at 2θ of 9.92° (Figure 2(a)) with the basal spacing of 0.89 nm, is in a good agreement with the study of Narita *et al.* in 2000 for the Mn/Al system containing nitrate ions in the interlayer [12]. MnAl has typical diffraction pattern for LDH in which its exhibits sharp and symmetrical peaks suggesting that the structure of the compound is well-crystallized and well-ordered [13].

Broad band observed in IR spectrum (Figure 2(b)) at around 3435 cm^{-1} is attributed to the OH stretching mode of inter-hydrogen bonding of hydroxyl groups of the layers and the interlayer water molecules [14]. The bending mode of water molecules was observed at 1625 cm^{-1} as the result from the deformation of water molecule vibration in the interlayer [15]. While nitrate anions located in the interlayer region is shown by the NO_3^- vibration peak at 1384 cm^{-1}. The peaks appearing below 1000 cm^{-1}

can be attributed to the vibrations of metal-oxygen bonding (M-O, M-O-M, O-M-O) in the layers [16].

The elemental analysis of the obtained MnAl together with the BET and BJH data is shown in Table Figure 1. The molar ratio of MnAl is 1.8, nearly similar to the prepared mother liquor initial ratio of 2. The weight percentage of C, H and N revealed that there was no C content in MnAl (as expected) showing that the prepared MnAl is free from contamination of CO_3^{2-} from atmosphere in agreement with the FTIR spectrum. The H content in MnAl attributed to the hydroxides and water molecules while N content comes from nitrate group in the interlayer gallery.

The MnAl has the BET adsorption-desorption isotherm (not shown) shapes of the typical Type IV adsorption isotherms, which indicate that the adsorbents are of mesopores structure [17]. The characteristic feature of Type IV isotherms is the hysteresis loop of the materials. MnAl has Type H3 hysteresis loop which has the steep region of the desorption branch leading to a lower closure points occurs at a relative pressure which is almost depending mainly on the nature of the adsorption. This indicates that the materials having aggregates of plate-like particles giving rise to slit-shaped pores [18]. Surface area for MnAl is 28.01 m^2g^{-1} while average pore diameter value is 16.01 nm lies in mesoporous property, as the pore size distribution is spread over the mesopore region (2-50 nm).

B. Adsorption studies

Two parameters which are contact times and MnAl dosages were tested in order to evaluate the performance of MnAl towards the removal of MO dye from aqueous solution. The contact times varied from 0 to 180 minutes (3 hours) while the dosages of MnAl used in the experiment varied from 0.01 to 0.5 g. The graph plots of MO removal percentage versus time (Figure 3) shows the similar trend for all dosages but with different removal percentage. The removal percentage increases rapidly for the first 20 minutes. This is probably because there are a lot of binding sites on MnAl surfaces which are available for the MO dye at the early stage of contact. As the contact time is prolonged the removal percentage plateau until equilibrium is reached. The removal percentage of MO shows no significant change beyond 60 minutes indicating that the adsorption of MO onto MnAl had reached saturation.

The removal percentage of MO depends on the amount of MnAl available in the solution, as shown in the graph plotted, removal percentage at different amount of MnAl (Figure 4). The percentage of MO removal increases drastically as the amount of MnAl increases. This is due to the increase of the number of binding site for MO dye as the amount of MnAl increases, thus more surface area are available as adsorp-

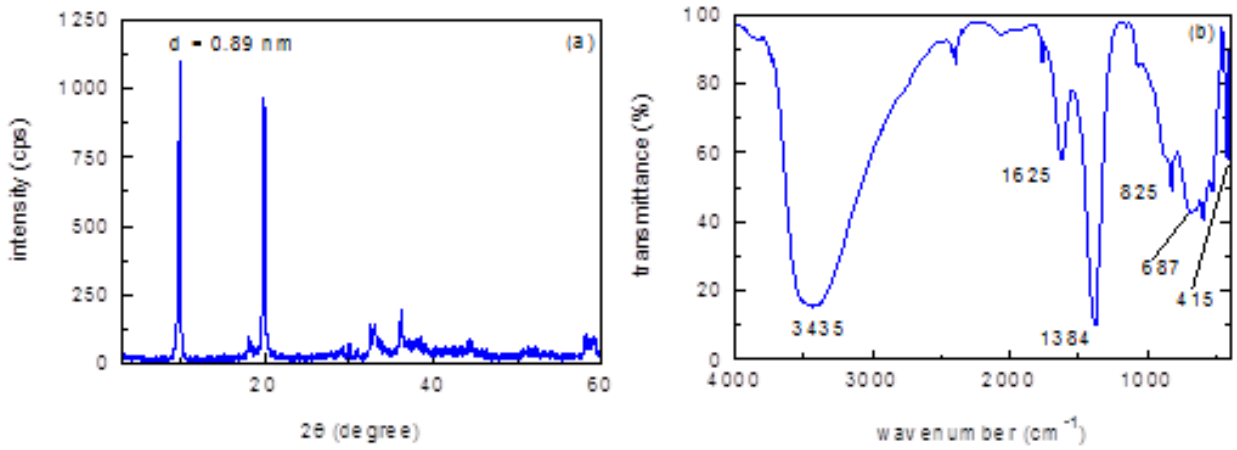

Figure 2. (a) X-ray diffraction pattern and (b) FTIR spectrum of MnAl

Table 1. Elemental analysis, BET and BJH of MnAl

Ratio of	Basal spacing	Weight percentage (%)			BET surface	BJH desorption
Mn/Al	(nm)	C	H	N	area(m^2g^{-1})	average pore (nm)
1.8	0.89	0.00	2.34	2.69	28.01	16.01

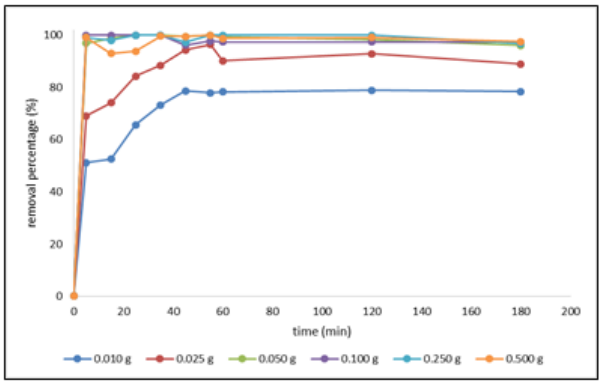

Figure 3. Removal percentage of MO by MnAl at different contact times

tion sites until it reaches the optimum mass of 0.100 g [19]. Further increment of MnAl amount beyond the optimum mass shows no significant changes due to the over-crowding of MnAl in the solution thus the binding sites are overlapped [20].

The experimental kinetic data at optimum mass of 0.100 g was further tested using two kinetic models namely pseudo-first order and pseudo-second order. By using the kinetic analysis approach, the solute uptake rate can be established, the performance and also the mechanisms of the reaction can be determined [21]. The kinetic adsorption was analysed by the pseudo-first order equation as follows:

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)t \quad \text{..... Eq.1}$$

where q_e and q_t are the amount of MO adsorbed on MnAl at equilibrium and time, t, respectively (mg/g), and k_1 is the rate constant of pseudo-first order sorption adsorption (min^{-1}) [22]. The second kinetic model used is

pseudo-second order which can be represented as [21]:

$$t/q_t = 1 \ / \ k_2 q_e^2 + (1 \ / \ q_e)t \ \ldots\ldots \text{Eq.2}$$

where k_2 is the pseudo-second order rate constant of adsorption (g mg^{-1} min^{-1}).

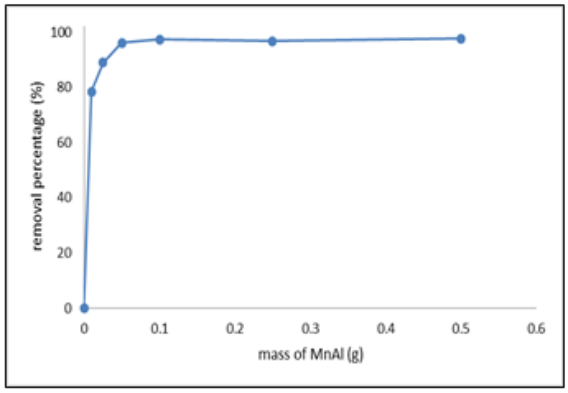

Figure 4. Removal percentage of MO at different mass of MnAl

Correlation coefficient (R^2) value for both kinetic plots (Figure 5) were used to evaluate the suitability of the models. Pseudo-first order plot shows very poor R^2 value suggesting that the adsorption of MO onto MnAl is not a pseudo-first order reaction. The adsorption process can be best described by pseudo-second order kinetic model as the R^2 value was found to be 1, indicating that the rate determining step of the system due to chemisorption mechanism involving the valency forces through electrons sharing or exchange between the MO and MnAl [23].

Isotherm models were used to evaluate the experimental data at different MnAl dosages. Two common isotherms applied including Langmuir and Freundlich models. Langmuir isotherm model assumes the monolayer adsorption takes place on homogeneous sites while Freundlich model assumes the multilayer occurs on heterogenous surface [24]. The linearized Langmuir and Freundlich equations used in this study are expressed in equations (3) [25] and (4) [26], respectively.

$$\frac{q_e}{c_e} = q_o K_L \ - \ K_L q_e \ldots\text{Eq. 3}$$

$$\log q_e = \log K_F + (1/n)\log C_e \ldots\text{Eq. 4}$$

where C_e is equilibrium concentration of MO, q_o is the amount of MO adsorbed at complete monolayer coverage, K_L is the Langmuir constant and both K_F and n are the Freundlich constants.

The R^2 value is determined to do the conformity of the validation of findings and the plots (Figure 6). Adsorption of MO favoured monolayer adsorption since the R^2 of Langmuir equation is higher than Freundlich equation. This model suggested that the adsorbent surface probably might be homogeneous. During adsorption, the mechanism occurs between the interaction of the monolayer adsorbate and the homogeneous sites of the adsorbent. Hence, when the adsorbent is fully covered by adsorbate, it will reach saturation and cannot be adsorb further [27].

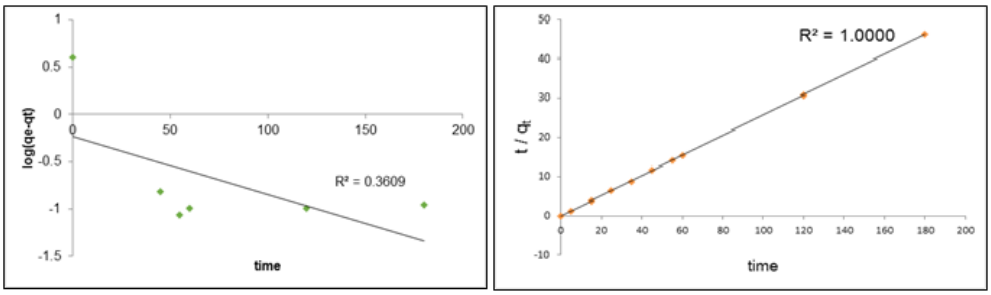

Figure 5. Fitting the experimental data in (a) pseudo-first order and (b) pseudo-second order models

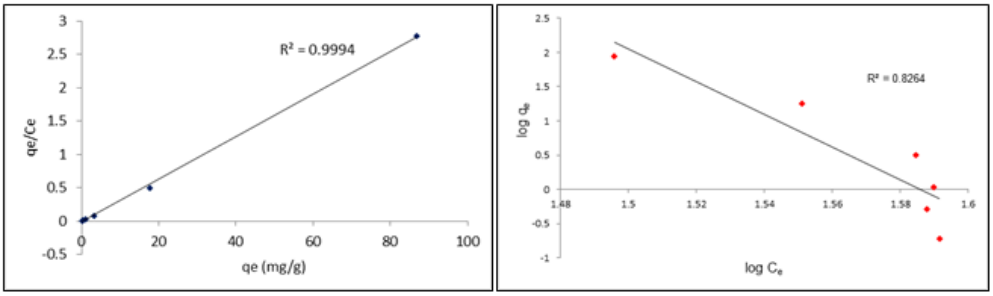

Figure 6. Fitting the experimental data in (a) Langmuir and (b) Freundlich isotherms

IV. SUMMARY

The LDH has potential to be used as an adsorbent in the removal of anionic dye from aqueous solution. The experimental data shows the removal percentage of MO dye by MnAl can reach almost 100% with the optimum mass of 0.100 g. The kinetics data fitted well with the pseudo-second order (R^2=1) while the mechanism of adsorption for MO dye is govern by monolayer adsorption as it is fitted with Langmuir model with the R^2 of 0.9994.

V. ACKNOWLEDGMENT

The authors are grateful to the Ministry of Higher Education Malaysia for the funding of this research (FRGS 59179) and Universiti Malaysia Terengganu for providing research facilities and supports.

[1] Sharma, S., Kalpana, Arti, Shweta, Suryavathi, V., Singh, P. K., Ramesh, Shipra & Sharma, K. P. 2007. Toxicity Assesment of Textile dye Wastewater Using Swiss Albino Rats. *Australasian Journal of Ecotoxicology*. vol. 13, pp. 81-85.

[2] Malik, A. & Grohmann, E. 2012. Environmental Protection Strategies For Sustainable Development. Strategized For Sustainability. Springer, New York.

[3] Zubair, M, Daud, M, McKay, G, Shehzad, F, Al-Harith, MA. 2017. Recent progress in layered double hydroxides (LDH)-containing hybrids as adsorbents for water remediation. *Applied Clay Science*, vol. 143. pp. 279-292.

[4] Goh, K. H., Lim, T. T. & Dong, Z. L. 2008. Application of LDH For Removal of Oxyanions: A Review. *Water Research*. vol. 42, pp. 1343-1368.

[5] Ji, H, Wu, W, Li, F, Yu, X, Fu, J and Jia, L. 2017. Enhanced adsorption of bromate from aqueous solutions on ordered mesoporous Mg-Al layered double hydroxides (LDHs). *Journal of Hazardous Materials*, vol. 334, pp. 212-222

[6] El Hassani, K, Beakou, BH, Kalnina, D, Oukani, E, Anouar, A. 2017. Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: A comparative study. *Applied Clay Science*, vol. 140, pp. 124-131.

[7] Villegas, J. C., Giraldo, O. H., Laubernds, K. & Suib, S. L. 2003. New layered double hydroxides Containing Intercalated Mn Oxide Species: Synthesis and Characterization. *Inorg. Chem.*, vol. 42, pp. 5621 - 5631.

[8] Bi, B., Xu, L., Xu, B., & Liu, X. 2011. Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media. *Applied Clay Science*, vol. 54, pp. 242247.

[9] Teixeira, T. P. F., Aquina, S. F., Pereina, S. J. & Dias, A. 2014. Use of Calcined Layered Double Hydroxide For the Removal Of Color And Organic Matter From Textile Effluents: Kinetic, Equilibrium and Recycling Studies. Brazilian *Journal of Chemical Engineering*. vol. 31(1), pp. 19-26.

[10] Chequer, F., Rodrigues de Oliveira, G., Ferraz, E. & Cardoso, J. 2013. Textile Dyes: Dyeing Process and Environmental Impact. INTECH.

[11] Zaharia, C., Suteu, D., Muresan, A., Muresan, R. & Popescu, A. 2009. Textile Wastewater Treatment By Homogenous Oxidation With Hydrogen Peroxide. *Environmental Engineering and Management Journal*. vol. 8(6), pp. 1359-1369.

[12] Narita, E., Uchiyama, H., Aisawa, S. & Umetsu, Y. 2000. Synthesis and Thermal Decomposition Behavior Of Mn-Al Layered Double Hydroxide. *Clay Science*. vol. 39(4), pp. 197-206.

[13] Mamat, M., Kusrini, E., Yahaya, A.H., Hussein, M.Z. & Zainal, Z. 2013. Intercalation of Anthranilate Ion Into Zinc-Aluminium Layered Hydroxide. *International Journal of Technology*. vol. 1, pp. 73-80.

[14] Wang, LY, C. Li, M. Liu, D. G. Evans, X. Duan, 2007. Large continuous, transparent and oriented self-supporting films of layered double hydroxides with tunable chemical composition. *Chem. Commun*. vol. 43. pp. 123-125.

[15] Ayawei, N., Ekubo, A.T., Wankasi, D. & Dikio, E.D. 2015. Synthesis and Application of Layered Double Hydroxide for Removal of Copper In Wastewater. `International Journal of Chemistry`. vol. 7(1), pp. 122-132.

[16] Kloprogge, JT, L. Hickey, R. Trujillano, M. J. Holgado, M. S. San Romn, V. Rives, W. N. Martens, R. L. Frost. 2006. Characterization of intercalated Ni/Al hydrotalcites prepared by the partial decomposition of urea, Cryst. *Growth Des*. vol. 6, pp. 1533-1536.

[17] Sing, K.S.W., Everett, D.H, Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. and Siemieniewska, T. 1985. Reporting Physisorption Data for Gas/Solid Systems with Special

Reference on the Determination of Surface Area and Porosity. *Pure Appl. Chem.*, vol. 57(4), pp. 603-619.

[18] Choy, J-H., Jung, J-S., Oh, J-M., Park, M., Jeong, J., Kang, Y-K. Han, O-J. 2004. Layered Double Hydroxide As An Efficient Drug Reservoir For Folate Derivatives. *J. Biomaterials*, vol. 25, pp. 3059-3064.

[19] Asari, R., Mamat, M., Abdullah, M.A.A. Mohamed Zuki, H., 2015. Kinetic study of palm oil adsorption onto acetylation treated oil palm mesocarp fiber. *Journal of Applied Sciences Research*, vol. 11(24), pp. 22-26.

[20] Mary, P.P., Subraman, M. Jeevitha., 2015. Adsorption of copper (II) ions from aqueous solution on carbons from morinda citrifolia bark. World Journal of Pharmaceutical Research, vol. 4(5), pp. 1246-1253.

[21] Qiu, H, Lu, L. V., Pan, B. C., Zhang, Q. J., Zhang, W. M. & Zhang, Q. X. 2009. Critical Review in Adsorption Kinetic Model. J Zhejiang Univ Sci A. vol. 10(5), pp. 716-724.

[22] Husin, N.I., N.A. Abdul Wahab., N. Isa and R. Boudvill, 2011. Sorption Equilibrium and Kinetics of Oil from Aqueous Solution Using Banana Pseudostem Fibers. Proceedings of *International Conference on Environment and Industrial Innovation (IPCBEE)*, vol. 12, pp. 177-182.

[23] Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. *Process Biochemistry*, vol. 34, pp. 451465.

[24] Ansari, R. and Mosayebzadeh, Z., 2010. Removal of Eosin Y, an Anionic dye, from aqueous solutions using Conducting Electroactive Polymers. *Iranian Polymer Journal*, vol. 19(7), pp. 541 551.

[25] Li, Q., Yue, Q.Y., Sun, H.J., Su, Y. & Gao, B.Y., 2010. A comparative study on the properties, mechanisms and process design for the adsorption of non-ionic or anionic dyes onto cationic-polymer / bentonite. *Journal of Environmental Management*, vol. 91, pp. 1601-1611.

[26] Mittal, A., Kaur, D., Mittal, J., (2009). Batch and Bulk Removal of a Triarylmethane Dye, Fast Green FCF, from Wastewater by Adsorption Over Waste Materials. *Journal of Hazardous Materials*, vol. 163. pp. 568 577.

[27] Crini, G. 2008. Kinetic and Equilibrium Studies On The Removal of Cationic Dyes From Aqueous Solution By Adsorption Onto A Cyclodextrin Polymer. *Dye and Pigments*. vol. 77, pp. 415-426.