

A Comparative Study of the Adsorption of Acid Brown 75 and Direct Yellow 162 onto Unmodified and Surfactant Modified Granule Developed from Coal Fly Ash

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Abstract—This study aims to use unmodified fly ash (Un-G) and surfactant modified granule (Mo-G) for adsorption of two anionic dyes; acid brown 75 (AB 75) and direct yellow 162 (DY 162) from aqueous solution. The granule was prepared by wet granulation of fly ash powder. The formation of fly ash pellet occurred between 18-20 % water content and heat more than 800 °C. Coal fly ash in powder form was agglomerated into porous granule and modified with Hexadecyltrimethylammonium Bromide (HDTMA-Br), which optimal condition was 3.6 mmolL⁻¹. The adsorption capacities and the effect of temperature for anionic dyes adsorption at various contact times and adsorbate concentration were investigated. The equilibrium data were found to be well represented by the Langmuir isotherm equation. The sorptions of the aqueous anionic dyes onto the unmodified granule (Un-G) were small while the Mo-G's sorption was significantly increased. The adsorption process of AB 75 and DY 162 were endothermic.

Keywords—component; Adsorption; Anionic dye; Granulation; Fly ash

I. INTRODUCTION

Fly ash is a predominantly inorganic residue obtained from the flue gases of furnace at pulverized coal power plants. Fly ash contains trace concentrations of many heavy metals that are known to be detrimental to health in sufficient quantities [1]. Thus, storage and disposal of coal fly ash can result in releases of leached metals into soils, surface and ground water. Throughout the world, much research is being conducted on the use of waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. Therefore, follows logically that an economically viable solution to this problem should include utilization of fly ash rather than disposal in a landfill.

Coal fly ash has been used as an efficient adsorbent to replace activated carbon for adsorption of pollutants in wastewater [2-5]. However, the adsorption efficiency of fly ash for anion species is low because fly ash surface has anionic charge. Silicon oxide, lime, and metal oxide, the component of fly ash, could react with water (H₂O) give fly ash a pH somewhere between 10 and 12. Because of this, its surface is negatively charged that can be balanced by exchangeable cations. It has been demonstrated that the cationic surfactants have a great affinity to the negative

charge. This property could be applied to modify the external surface of the fly ash for improvement anion exchange capacity. The surfactant that is commonly employed to be attached on the adsorbent surface is the quaternary ammonium cations such as hexadecyltrimethylammoniumdodecyltrimethylammonium; benzyltrimethylammonium, cetylpyridinium chloride [6-8].

One major drawback in the use of fly ash is that it results in a fine particle size which makes difficulty during filtration or settling. Recently, Vinitnantharat *et al.* (2010) proposed the use of a pellet of adsorbent made from water treatment sludge for removal of fluoride [9]. However, less studies on a development of adsorbent granule form fly ash for adsorption of anionic and cationic surfactant.

The objective of this study is to investigate the adsorption potential of surfactant modified granule made from coal fly ash for removal of anionic dyes and from single solute system. The capacity of the modified fly ash granule for adsorbing anionic dyes was compared with that of an unmodified fly ash granule. Moreover, the adsorption thermodynamics and removal mechanisms of modified fly ash were investigated.

II. MATERIAL AND METHODS

A. Preparation of surfactant modified granule and adsorbates

Fly ash from Mae Moe power plant, Thailand was used as the adsorbent in this study. The chemical compositions of fly ash are: SiO₂ (52.5%), Al₂O₃ (27.9), CaO (6.27%), MgO (1.6%), Fe₂O₃ (6.3%), SO₃ (0.79%), and LOI ("loss on ignition"—the unburned carbon portion in the sample; 5.01%); according to ASTM C618, this material can be classified as class F because it contained less than 10% CaO, 5% SO₃, and 12% LOI and greater than 70% of the three main components (SiO₂, Al₂O₃, and Fe₂O₃) combined. Fly ash powder was mixed with distilled water to yield the moisture content of 18 ± 2%. The moisten fly ash was then pressed through an extruder which has a barrel into which the fly ash is forced by a screw. In the next step, It was heated in the oven at 800 ± 10 °C for 90 mins. After be heated, the granules were left at room temperature (30 ± 2 °C) to let them cool. The tabular granules were cut to a uniform size of 2.0 - 2.5 mm and then stored in the desiccators until use. The modified granules were prepared by exchanging the

inorganic anion of the fly ash granules with HDTMA-Br. Ten grams of fly ash granule were treated with a HDTMA-Br solution at a concentration of 1.5 mmol L⁻¹. The mixtures were stirred at 30 ± 1 °C (above the kraft point, of is 25 °C) [10] for 48 h at 150 rpm in an incubator shaker. Then, the modified granules were separated from the solution by filtration, followed by washing with distilled water several times. Then the modified granule were dried at room temperature (30 ± 2 °C) for overnight and stored in the desiccators. The two kinds of anionic dyes used in the experiments were supplied from Modern Dye Stuff Co.,Ltd and Clariant (Thai) Co.,Ltd, which were acid brown 75 (AB 75), and direct yellow 162 (DY 162), respectively. All these dyes were of commercial grade and were used without further purification. The synthetic wastewaters were prepared by dissolving dyestuffs in deionized water to produce a stock solution of 1 g L⁻¹. Color was analyzed by American Dye Manufactures Institute (ADMI) method using Shimadzu double. All chemicals used in this work were of analytical grade.

B. Characterization of adsorbents

Scanning Electron microscopy (SEM) was used to understand the particle shape, surface texture, or morphology of the unmodified and surfactant modified granules. Samples were scattered as thin film on adhesive tape on a brass bar and coated with gold in the JEOL (JFC-1100 E Ion) sputtering device and transferred into the JEOL (JSM-6400) sample chamber at the accelerating voltage of 15-40 kV. Fourier transform infrared (FTIR) spectroscope was used for characterization of the surface functional groups of the granules. Receiving the observable adsorption spectra, fly ash samples were grounded to the average diameter around 0.5 μm and mixed with KBr (analytical grade IR) for approximately prepare a 0.5% (w/w). Then put into a manual hydraulic press at 10 tons. The sample turns into disc, diameter and thickness approximate 12.7 mm and 1 mm respectively. The spectra of the samples were measured and recorded from 4,000 to 400 cm⁻¹ on a BIO-RAD, FTS 175 spectrometer. During the process, the FTIR chamber was continuously purged with nitrogen to remove moisture. The specific surface area of the fly ash was obtained using a TriStat 3000 analyzer (Micromeritics Instrument Corp) with N₂ adsorption at - 196°C. The sample was first degassed at 200°C for 4 h. TriStat 3000 is an automated gas analyzer which contains three ports, allowing up to three samples to be analyze simultaneously. The TriStat 3000 system consists of the TriStar analyzer, a SmartPrep degasser that is used for samples preparation, a vacuum pump and a control module for entering analysis and report options.

C. Adsorption isotherm and thermodynamic study

The adsorption isotherm study was carried out via the batch method for the fly ash granule. Essentially, 150 mL of a solution containing the adsorbate with an initial concentration ranging from 5 to 50 mg L⁻¹ was mixed with 3 grams of granule in a 500 mL bottle. The granules were shaken for the contact time 0.25 – 168 hours in electrically thermostat reciprocating shaker at 150 rpm. The effect of

temperature on adsorption of AB75 and DY 162 was studied in the temperature range 30, 40, 50, and 60 °C. The amount of dyes adsorbed, q_e (mg g⁻¹) was computed by using the following expression:

$$q_e = (C_0 - C_e) \times \frac{m}{v} \quad (1)$$

In this study, two adsorption isotherm models were selected to evaluate the adsorption capacity of the adsorbent: Langmuir and Freundlich isotherms.

III. RESULT AND DISCUSSION

A. Characterization of adsorbents

Fly ash is a heterogeneous material consisting largely of small spheres, formed by the condensation of aluminous and siliceous glass droplets in the air. Also found in fly ash samples are irregular, porous, coke-like particles of unburned carbon material, which are often concentrated in the larger size fractions. The formation of fly ash granule occurred between 18 % water content and heat temperature 800 °C. Fig. 1 (a) and (b) show the scanning electron microscope (SEM) image of the unmodified granule at x 30 and x 1500 magnification. The SEM photograph showed fly ash particles were generally spherical in shape along with some agglomerates of particles and range in size from 0.5 μm to 50 μm.

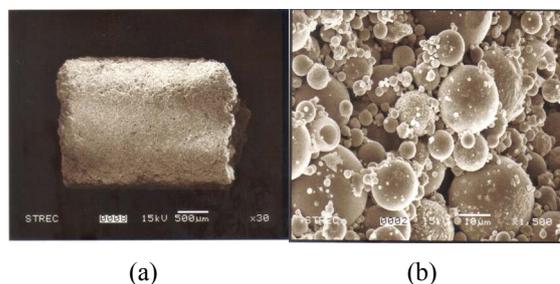


Figure 1. SEM of fly ash granule (a) x 30 times (b) x 1500 times.

The infrared spectrum for Un-G and Mo-G are illustrated in the Fig.2. The FTIR spectrum of Un-G shows a strong broad band at 3434.07 cm⁻¹ which indicates the presence of hydroxyl groups on the fly ash. The band appearing at 1098.87 cm⁻¹ is associated with Si-O asymmetric stretching vibrations. The band appearing at 780 – 790 cm⁻¹ corresponds to the quartz present in the fly ash. The intensity of the band at 462 cm⁻¹, associated in all cases with Si-O bending vibrations, is unrelated to the degree of crystallization of the material. The bands appearing between 800 and 500 cm⁻¹ are associated with the tetrahedral vibrations formed by what are known as secondary building units (SBU) and fragments of the aluminosilicate system. These bands are typical characteristic of the double or single rings (depending on the structure of the material) and/or the TO₄ (T = Si, Al) tetrahedral bonds. It can be seen from the FTIR spectrum of

Mo-G (b) that the intensity of the bands at 1000 and 1098 cm^{-1} had considerably decreased. This can be attributed to the replacement of surface Si-OH by Si-O $[(\text{CH}_3)_3\text{NC}_{16}\text{H}_{33}]$ groups. New bands at 1629 cm^{-1} appeared at are due to C-H bending vibrations corresponding to $-\text{CH}_2-$ of $-\text{N}(\text{CH}_3)_3$ group which provides evidence for the presence of HDTMA $[(\text{CH}_3)_3\text{NC}_{16}\text{H}_{33}]^+$ on the fly ash surface. A shifting to higher position of the parent peaks were observed in the Mo-G. The shifting may come from the results of physical bonding between the Al-O/ Si-O/other oxides in fly ash with highly active polar group in surfactant.

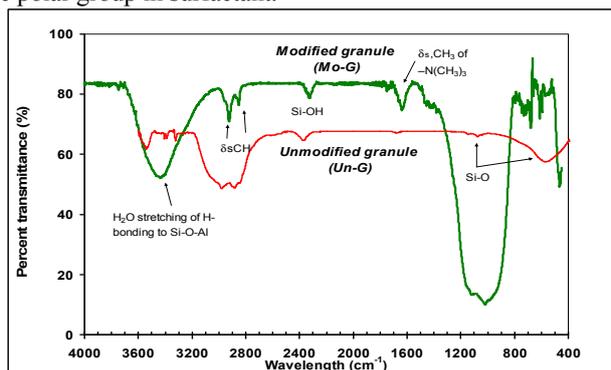


Figure 2. FTIR spectra of Un-G and Mo-G.

B. Adsorption isotherm

The Langmuir isotherm model assumes the uniform energies of adsorption onto the adsorbent surfaces. Furthermore, the Langmuir equation is based on the assumption of the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent where all sorption sites are identical. The Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (2)$$

where Q_o is the amount of adsorbate at complete monolayer coverage (mg g^{-1}), which gives the maximum sorption capacity of sorbent and K_L or b (L mg^{-1}) is the Langmuir isotherm constant that relates to the energy of adsorption. Fig. 3 presents the Langmuir sorption isotherms of AB 75 and DY 162 in single solution onto Un-G and Mo-G.

The Freundlich expression is an empirical model and assumes a heterogeneous energetic distribution of the active sites on the adsorbate surface with interactions between the adsorbed molecules. The linear form of Freundlich isotherm is represented by the equation

$$\log q_e = \log K_F + \log C_e \quad (3)$$

where q_e is the amount of adsorbate adsorbed per unit weight of the sorbent (mg g^{-1}), C_e is the equilibrium concentration of adsorbate in solution (mg L^{-1}), K_F is a

measure of adsorption capacity and $1/n$ is the adsorption intensity.

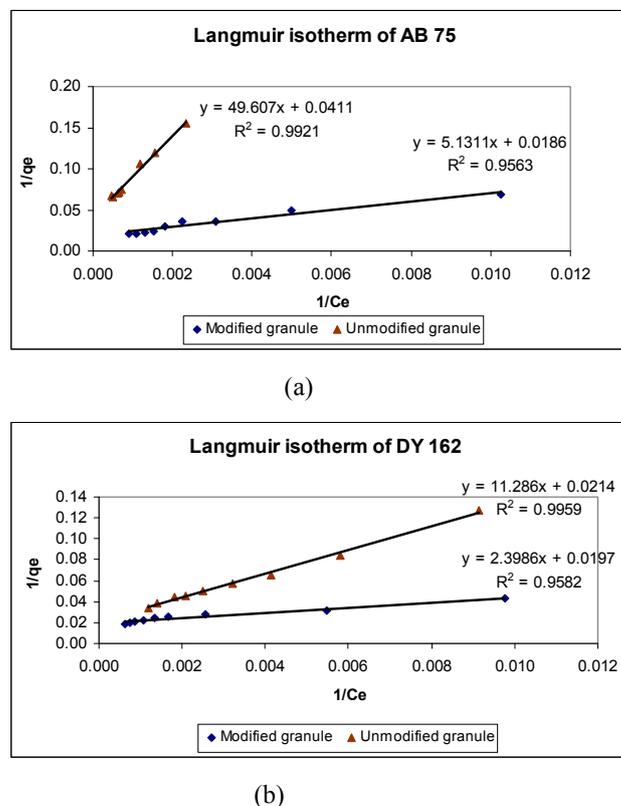
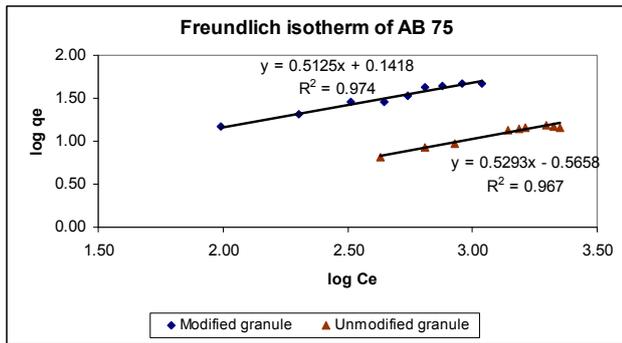
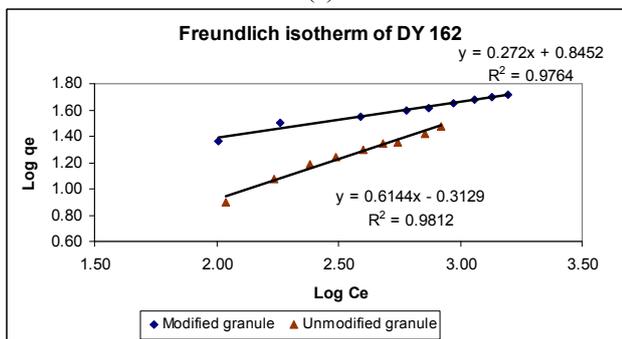


Figure 3. Plot of Langmuir adsorption isotherm of (a) AB 75 and (b) DY 162 (Condition: adsorbent dosage: 3 g/150 ml, pH: 4 ± 0.1 , agitation speed: 150 rpm, initial concentration: 5-50 mgL^{-1})

The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The values of $1/n$ and K_F for the sorbent were calculated from the slope and the intercept of the linear plot of $\log q_e$ vs. $\log C_e$. Fig. 4 presents the Freundlich sorption isotherms of AB 75 and DY 162 in single solution onto Un-G and Mo-G. For solid-liquid system, adsorption isotherm is important in description of adsorption behavior. In this work, Langmuir isotherm models were used to describe the relationship between the amount of dyes adsorbed and its equilibrium concentration in solution for four temperatures (30, 40, 50, and 60 $^{\circ}\text{C}$). To evaluate the adsorption of anionic dyes by Mo-G, the isotherm studies were performed at the constant equilibrium pH value of 4 ± 0.1 . The uptake of AB 75 and DY 162 increased with increasing the initial concentrations. The sorption of dyes and chromium by Mo-G fit very well with the Langmuir isotherm model because the straight line graph is obtained when these data are plotted with the coefficient of determination (r^2) for each set of the linearized data exceeding 0.95. Mo-G showed a higher agreement with Langmuir isotherm, indicating that monolayer adsorption being more dominant. The low values of b indicate that physical interactions are the main binding forces of AB75 and DY162 by Un-G and Mo-G.



(a)



(b)

Figure 4. Plot of Freundlich adsorption isotherm of (a) AB 75 and (b) DY 162 (Condition: adsorbent dosage: 3 g/150 ml, pH: 4 ± 0.1 , agitation speed: 150 rpm, initial concentration: 5-50 mgL⁻¹)

The maximum adsorption capacities (Q^0) at various temperatures increased in the order $60 > 50 > 40 > 30$ °C. This suggests that the adsorption process of AB 75 and DY 162 was endothermic. It can be concluded that temperature can increase the kinetic energy of the dye molecules and, hence, enhanced the mobility of the dye ions. The adsorption coefficient, K_F that is related to the apparent energy of sorption, It indicates the affinity of adsorbent to the chromium and dye ions. The low of K_F values showed that the energy of adsorption onto Mo-G granule is low. This is a weak interaction (i.e. Van der waals bond) such as that's between molecules in liquid.

C. Effect of temperature and thermodynamic study

Thermodynamic parameters reflect the feasibility and spontaneous nature of the process. Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°), and standard entropy (ΔS°) changes during the adsorption process were calculated using (4), (5) and (6) at different temperatures (30, 40 and 50 and 60 °C) at 50 mg L⁻¹. The Gibbs free energy change, ΔG° , can be determined by the following equation:

$$\Delta G^\circ = -RT \ln K_L \quad (4)$$

where K_L is the Langmuir constant, R the universal gas constant (8.314 JK⁻¹mol⁻¹), and T is the absolute temperature (°K). The relationship between Gibbs free energy change (ΔG°), entropy (ΔS°) and enthalpy change (ΔH°) is expressed as

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (5)$$

Eq. (11) can be expressed in its linear form as

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear plot of $\ln K_L$ vs $1/T$. The results of thermodynamics parameters are shown in TABLE I.

It is obvious from ΔH° of this study that physisorption takes part in adsorption process in which the adsorbate adheres to the surface only through weak intermolecular interactions. The positive value of ΔH° suggested the endothermic nature of adsorption. The Gibbs free energy change, ΔG° , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. The value of ΔG° is positive, which indicates the non-spontaneous adsorption system. Entropy change (ΔS°) is a measure of the disorder present in a system. The positive value of ΔS° reflects the affinity of the Mo-G for the AB 75 and DY 162 and suggests some structural changes in adsorbate and adsorbent [11].

TABLE I. THE OVERALL THERMODYNAMIC PARAMETER

Adsorbate	Temperature (°C)	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (KJ mol ⁻¹ K ⁻¹)
AB 75	30	15.01	17.71	8.92
	40	15.50	17.71	7.07
	50	15.16	17.71	7.91
	60	14.82	17.71	8.69
DY 162	30	12.82	29.18	53.99
	40	12.48	29.18	53.37
	50	12.39	29.18	52.15
	60	11.05	29.18	54.45

D. Adsorption capability of unmodified and surfactant modified granule

Adsorption of AB 75 and DY 162 on Un-G and Mo-G from single solute system was compared. The equilibrium data were processed according to the well-known Freundlich and Langmuir isotherms. The maximum adsorption (Q^0) value calculated from the Langmuir isotherm model for the AB 75 and DY 162 sorption by Un-G and Mo-G adsorbents can be seen in Fig. 5. The comparisons of the Freundlich constant

(K_F) for Un-G and Mo-G are exemplified in Fig. 6. The results from Langmuir isotherm demonstrate that the Un-G have little affinity for anionic dyes, in contrast, the modified granule shows significant sorption of anionic dyes from single solute system. The Q^0 values found in sorption of AB 75 and DY 162, on Mo-G are about two times higher than that adsorbed for Un-G.

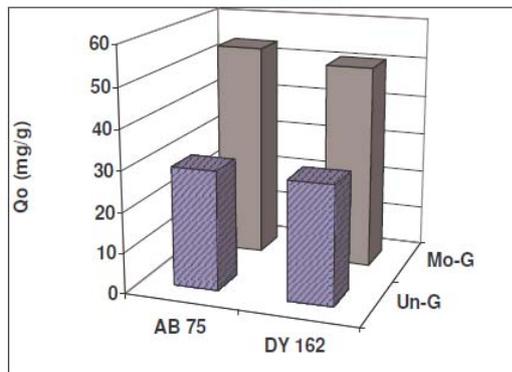


Figure 5. Comparison of the maximum adsorption (Q^0) value calculated from Langmuir model for the AB 75 and DY 162

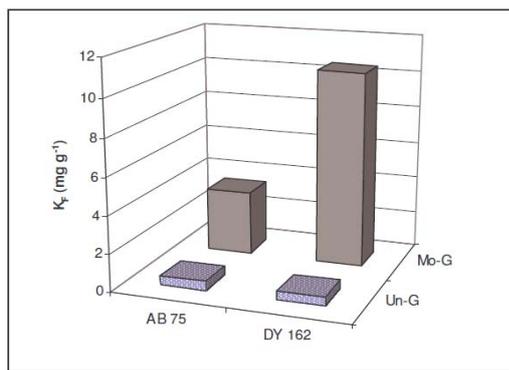
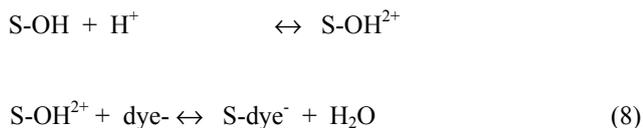


Figure 6. The K_F (Freundlich constant) values for the adsorption of AB 75 and DY 162 by Un-G and Mo-G

As shown in Fig. 6, it also reveals that the modified granule adsorbed more anionic dyes than the unmodified one. The ability of the Mo-G to sorb anionic dyes is due to the anion exchange at the positive sites brought about by the reversed charged resulting from the HDTMA double layer onto the fly ash surface. Because AB 75 and DY 162 have sulfonic groups ($-\text{SO}_3^-$) in its molecular structure exist in water as the anion form, the Mo-G is able to sorb AB 75 and DY 162 by the anion exchange and ligand exchange as follows:
Electrostatic attraction:



Ligand exchange:



where S is the surface of the unmodified fly ash granule.

On the contrary, the unmodified granule having a net negative charge in the structure tends to repulse the anion form of dyes.

IV. CONCLUSION

The results show that the agglomeration method is suitable for the production of fly ash granule, which are distributable and improve the usage and quality of granule raw material. The sorption of batch adsorption study showed that the modified granule made from coal fly ash was able to remove the anionic forms of contaminants in aqueous solution. The modification of fly ash granule with HDTMA enhance adsorption capacity of anionic dyes (AB 75 and DY 162) is due to the anion exchange and partition mechanism. The isothermal data could be well described by Langmuir models. The adsorption capacities of dyes and chromium have been increased with increasing solution temperature from 30 to 60 °C. An increase in temperature is concurrent with an increase in molecular kinetic energy thus increasing the mobility of the adsorbate. This results increased removal of anionic dyes. The adsorption process of AB 75 and DY 162 were endothermic in nature.

ACKNOWLEDGMENT

The authors would like to thank the technical supports from School of Energy, Environment and Materials and Technology, King Mongkut's University of Technology Thonburi. Funding for this research was provided by The Joint Graduate School of Energy and Environment, Thailand.

REFERENCES

- [1] F. Goodarzi, "Characteristics and composition of fly ash from Canadian coal-fired power plants" *Fuel*, vol. 85, pp. 1418-1427, 2006.
- [2] J. X. Lin, S. L. Zhan, M. H. Fang, X. Q. Qian, and H. Yang, "Adsorption of basic dye from aqueous solution onto fly ash". *Journal of Environmental Management*, vol. 87, pp. 193-200, 2008.
- [3] T. C. Hsue, "Adsorption of an acid dye onto coal fly ash", *Fuel*, vol. 87, pp. 3040-3045, 2008.
- [4] N. Dizge, C. Aydinler, E. Demirbas, M. Kobya, and S. Kara, "Adsorption of reactive dyes from aqueous solutions by fly ash" *Journal of Hazardous Materials*, vol. 150, pp. 737-746, 2008.
- [5] S. Mohan and R. Gandhimati, "Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent". *Journal of Hazardous Materials*, vol. 169, pp. 351-359, 2009.
- [6] M. Rožic, Đ I. Šipušić, S. Miljanić, L. Čurković, and J. Hrenović, "Sorption phenomena of modification of clinoptilolite tuffs by surfactant cations" *Journal of Colloid and Interface Science*, vol. 331, pp. 295-301, 2009.
- [7] Z. Li, T. Burt, R. S. Bowman, "Sorption of Ionizable Organic Solutes by Surfactant - Modified Zeolite" *Environmental Science and Technology*, vol. 34(17), pp. 3756-3760, 2000.
- [8] A. Özcan, Ç. Ömeroğlu, y Erdoğan, and A. S. Özcan, "Modification of bentonite with a cationic surfactant: an adsorption study of textile dye reactive blue 19" *Journal of Hazardous Materials*, vol. 140, pp. 173-179, 2007.
- [9] S. Vinitnantharat, S. Kositchaiyong, and S. Chiarakorn, "Removal of fluoride in aqueous solution by adsorption on acid activated water

- treatment sludge". *Applied Surface Science*, vol. 256, pp. 5458-5462, 2010.
- [10] P. Malakul, S. Saengchote, and D. A. Sabatini, "Development of Surfactant-Modified Adsorbents (SMADs) from Naturally Occurring Materials for Wastewater Treatment". *Thai Environmental Engineering Journal*, vol.18 (2), pp. 1-13, 2004.
- [11] V. K. Gupta, "Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent" *Industrial & Engineering Chemistry Research*, vol. 37, pp. 192-202, 1998.