Organo-fly ash granule as an adsorbent for the removal of acid brown 75, direct yellow 162, and chromium (III) in single and mixed solute system

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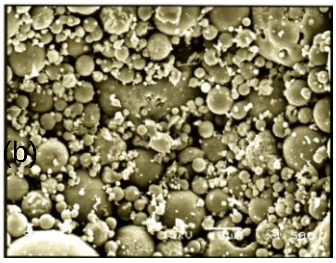
The tanning industry in Thailand is one of the country's oldest industries. Wastewater generated from this industry usually contains a mixture of several toxic chemicals, such as chromium, sulfide and leather dyes. To date, very few techniques have been report to effectively treat mixed waste containing several toxic species.

In this aspect, adsorption has gained increasing attention for applications in mixed wastewater treatment. Fly ash, in powder form, has been widely used as an adsorbent for wastewater treatment (Hsu, 2008 and Mohan and Gandhimathi, 2009). However, the development of granulated fly ash, which is more appropriate for real application, has not been investigated. Here we report a new adsorbent, organo-granule (Org-G) made from coal fly ash for removal of anionic dyes (acid brown 75; AB75 and direct yellow 162; DY162) and Cr(III) used in tanning process, from single and mixed solute system.

Org-G was prepared from dried fly ash powder at 1000 g was mixed 7.2 m*M* Hexadecyltrimetylammonium Bromide (HDTMA-Br) solution and pressed through a pellet extruder. Moistened granules were heated to 800 °C for 90 minutes, then cooled to room temperature (30 ± 2 °C). The tabular granules were cut to 2.0–2.5 mm and kept in the desiccators until use. Org-G and unmodified fly ash granule (Un-G) were compared in simultaneous experients.

Adsorbents characteristics were measured by SEM, XRD, XRF, FTIR, BET, and CEC. SEM images of Un-G particles were generally spherical in shape along with some agglomerated of particles, from 0.5 μm to 50 μm (Figure 1a) compared to Org-G particles (Figure 1b). The major components of two adsorbents were oxides of Si, Al, Ca, Fe, and various other oxides (Table 1). The XRD analysis showed that the major crystalline constituents are augnite [$Cu(Mg)(Si,Al)_2O_6$], hematite [Fe_2O_3] and anhydrite [$CaSO_4$].


(a)

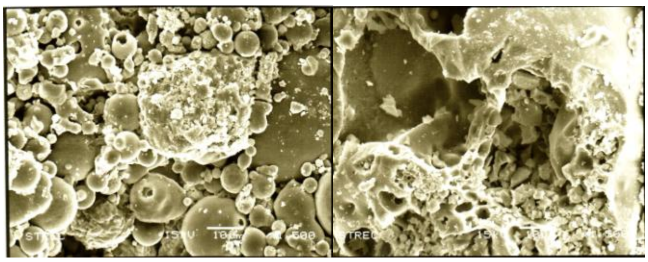

(b)

Figure 1 SEM images of (a) Un-G and (b) Org-G (x 1500 times magnification)

Table 1 The chemical composition of unmodified and organo -fly ash granule

Adsorbent	Composition (% wt)								
	SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	K_2O	MgO	Na_2O	other
Un-G	35.13	19.20	16.57	15.21	5.18	3.30	2.68	1.38	1.35
Org-G	35.18	19.24	16.55	15.03	5.36	3.37	2.69	1.36	1.22

Adsorption isotherms have been analyzed in term of Langmuir and Freundlich isotherm equations. The adsorption data were best fitted to Langmuir model (Table 2). The low of b values revealed that the energy of adsorption onto Un-G and

Org-G is low. This is a weak interaction (i.e. Van der Waals bond) such as that between molecules in liquid.

Table 2 Langmuir parameter of unmodified and organo -fly ash granule

Adsorbent	Langmuir parameters	Single-solute system			Mixed-solute system	
		AB 75	DY 162	Cr(III)	Mixed dye	Mixed Cr(III)
Un-G	Q^o (mg g^{-1})	55.87	22.22	3.87	30.21	0.50
	b	0.0003	0.0013	0.0013	0.0003	0.8818
	R^2	0.9992	0.9968	0.9980	0.9651	0.9750
Org-G	Q^o (mg g^{-1})	63.69	56.18	3.39	36.50	0.46
	b	0.0013	0.0020	0.0446	0.0274	0.6519
	R^2	0.9705	0.9888	0.9890	0.9190	0.9313

The feasibility of the sorption process was assessed by the thermodynamic parameters as shown in Table 3. The values of ∆H° for both Un-G and Org-G support the physical sorption as the predominant mechanisms. The increasing trend of adsorption with temperature is mainly due to the strongly of adsorptive forces between the active sits of Org-g and adsorbate species.

Table 3 Thermodynamic parameters of unmodified and organo -fly ash granules

Adsorbate	Parameter	Unmodified granule				Organo - fly ash granule			
		30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
AB75	∆G° (kJ mol^{-1})	21.75	22.20	22.75	23.06	19.46	19.60	19.80	19.52
	∆H° (kJ mol^{-1})	8.22	8.22	8.22	8.22	18.40	18.40	18.40	18.40
	∆S° (kJ $mol^{-1}K^{-1}$)	-44.67	-44.68	-44.99	-44.56	-3.49	-3.83	-4.32	-3.30
DY162	∆G° (kJ mol^{-1})	5.11	4.63	3.85	3.29	18.63	18.40	18.14	18.24
	∆H° (kJ mol^{-1})	-15.76	-15.76	-15.76	-15.76	23.06	23.06	23.06	23.06
	∆S° (kJ $mol^{-1}K^{-1}$)	-105.70	-105.06	-105.34	-105.63	14.61	14.87	15.22	14.47
Cr(III)	∆G° (kJ mol^{-1})	5.42	4.91	4.08	3.48	9.43	9.42	9.39	9.13
	∆H° (kJ mol^{-1})	24.07	24.07	24.07	24.07	12.23	12.23	12.23	12.23
	∆S° (kJ $mol^{-1}K^{-1}$)	-37.88	-40.09	-40.05	-40.09	9.23	8.99	8.79	9.31
Mixed dye	∆G° (kJ mol^{-1})	21.30	22.37	22.76	23.18	18.55	17.97	18.27	18.74
	∆H° (kJ mol^{-1})	9.83	9.83	9.83	9.83	15.98	15.98	15.98	15.98
	∆S° (kJ $mol^{-1}K^{-1}$)	-37.88	-40.09	-40.05	-40.09	-8.47	-6.37	-7.10	-8.30
Mixed Cr(III)	∆G° (kJ mol^{-1})	1.42	0.58	0.55	0.37	2.31	2.09	2.10	1.26
	∆H° (kJ mol^{-1})	11.19	11.19	11.19	11.19	11.77	11.77	11.77	11.77
	∆S° (kJ $mol^{-1}K^{-1}$)	32.22	33.88	32.92	32.49	31.22	30.92	29.94	31.59

These results show that the Un-G have little affinity for anionic dyes, but in contrast, the Org-g shows significant sorption of anionic dyes from both single and mixed-solute system. The sorption of dyes may occurred via partition mechanisms because AB75 and DY162 has sulfonic groups and has an anthraquinone ring in its molecular structure and the resultance the Org-G have low surface areas and act as partitioning media in the sorption (Xu and Boyd,1995).

The slight decrease of the Cr (III) removal capacity for modified granule indicated that the sorbed HDTMA-Br blocked sorption sites for Cr (III). Job's method of continuous variation was used to determine the stoichiometry of the complex in solutions. The complex only occurred between Cr (III) and AB 75 at 0.88 of mole fraction of AB 75, indicative of a 1:4 for the Cr:AB 75 complexes $[Cr\ (AB\ 75)_4]^{3+}$. The formation of complex was shown to affect the adsorption capacity in mixed solute system. For mixed solute system, the lower efficiencies registered for Cr(III) and anionic dyes can be the result of a competitive adsorption mainly among these ions.

References

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