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Procedia Environmental Sciences 17 (2013) 270 – 278

Procedia

Environmental Sciences

The 3rd International Conference on Sustainable Future for Human Security
SUSTAIN 2012

Color removal of reactive procion dyes by clay adsorbents

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Abstract

The adsorptions of reactive procion brilliant red H-EGXL and procion yellow H-EXL by various clay adsorbents were investigated in this research. The research showed that synthetic talc has the highest adsorption capacity for decolorization of both procion type of reactive dyes compared with other clay adsorbents. The removal efficiencies of synthetic talc relatively stable above 80% until the initial dye concentration reached at 160 mg.L⁻¹ of both reactive procion dyes when the liquid/solid ratio of 50 mL.g⁻¹. Synthetic talc and kaolin showed higher adsorption capacity under acidic condition than neutral and alkaline condition because of higher zeta potential. The adsorption isotherm of synthetic talc and kaolin were fitted by Langmuir adsorption isotherm that assumes that dyes molecule only formed monolayer over the homogenous surface of adsorbent

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Selection and peer-review under responsibility of SUSTAIN conference's committee and supported by Kyoto University; (OPIR), (GCOE-ES), (GCOE-HSE), (CSEAS), (RISH), (GCOE-ARS) and (GSS) as co-hosts.

Keywords: Color removal, reactive procion dyes, clay adsorbents, adsorption capacity, adsorption isotherm

1. Introduction

Textile industry plays an important role in the economic development in non-oil and gas sector of many developing countries. Apart from its significant role, however, textile industry also creates serious problems to environment, particularly disposal of colored dye wastewater. Dyed contaminated wastewater contains colored compound from residues of dyes and various chemical additives. Reactive dyes are extensively used in dyeing processes for coloring yarn or fabric due to their high reactivity and good color resilience [1]. However, they are harmful to aquatic environment especially for aquatic livings if they

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2.3. Batch adsorption test

Adsorption experiments were conducted by a batch method. A series of polypropylene centrifuge tube containing 1.00 g of adsorbent with 50 mL of dye solution (0-200 mg/L-1) were prepared. The tube was then shaken with a shaker typed SN-200SD (Nissin, Japan) at 150 rpm at room temperature for 16 hours to reach the equilibrium and followed by centrifugation with Avanti™ HP-25 centrifuge (Beckman Coulter, USA) at 2900 rpm for 15 minutes. Filtration was carried out to separate the filtrated and residue of adsorbents with 0.1 µm of membrane filter (Millipore, Japan). The absorbance of filtered sample was measured at peak wavelength of the dye (λ_{\max} Procion red= 535 nm, λ_{\max} Procion yellow= 418 nm) with UV-2550 UV-Visible Spectrophotometer (Shimadzu, Japan). The adsorption capacity was calculated by following the equation below:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where: q_e is the adsorption capacity, the dyes uptake by a unit weight of adsorbent (mg.g^{-1}), C_o is the initial concentration of dye (mg.L^{-1}), C_e is the residual concentration of dye (mg.L^{-1}), V is the volume of solution (L) and m is the weight of adsorbent (g) [5].

Table 1. Chemical composition of clay adsorbent.

Composition	Clinoptilolite (%)	Mordenite (%)	Sepiolite (%)	Bentonite (%)	Kaolin (%)	Synthetic talc (%)
SiO ₂	74.92	67.11	62.16	64.49	72.54	59.17
TiO ₂	0.48	0.51	0.51	0.57	0.81	0.32
Al ₂ O ₃	9.57	9.54	7.34	10.61	13.57	4.57
Fe ₂ O ₃	2.04	4.05	3.74	4.38	1.89	0.49
MnO	0.13	0.09	0.09	0.12	0.07	0.05
MgO	2.96	1.89	11.76	3.3	2.31	31.98
CaO	3.50	4.31	4.81	5.02	3.18	2.38
Na ₂ O	5.85	5.45	4.94	5.76	5.03	4.54
K ₂ O	4.33	2.08	2.14	1.77	1.32	0.99
P ₂ O ₅	0.58	0.58	0.58	0.58	0.58	0.58
SO ₃	0.34	0.33	0.32	0.54	0.96	0.31

3. Result and discussion

3.1. Adsorption capacity

Adsorption capacity is defined as adsorption mass of adsorbate per unit mass of adsorbent and commonly used as parameter to determine the potential adsorbent [6]. High adsorption capacity with low equilibrium concentration of adsorbate means the adsorbent has a good ability for the adsorbate separation. Fig. 2 and Fig. 3 show that synthetic talc has the highest adsorption capacity for removal both procion brilliant red H-EGXL and procion yellow H-EXL followed by kaolin and other clay adsorbents. The difference in specific surface area, typical ion exchange characteristic and electro-kinetic behavior of

surface net charge between adsorbent, and dye molecule determined the capacity of each adsorbent for removal of procion dyes. In this research specific surface area was measured by methylene blue adsorption [7] as also the cation exchange capacity. Hang and Brindley (1969) reported that methylene blue adsorption method can be applied for specific surface area measurement of clay mineral which gave no significantly different result compared with standard of Brunauer-Emmett-Teller (BET) method [8]. Another benefit from this method is its efficiency in both cost and time of measurement. Anion exchange capacity was measured by NO_3^- adsorption method while electrical behaviour of zeta potential was analyzed with Zeta potential analyzer type ZC-2000 Zeecom (Microtec, Japan).

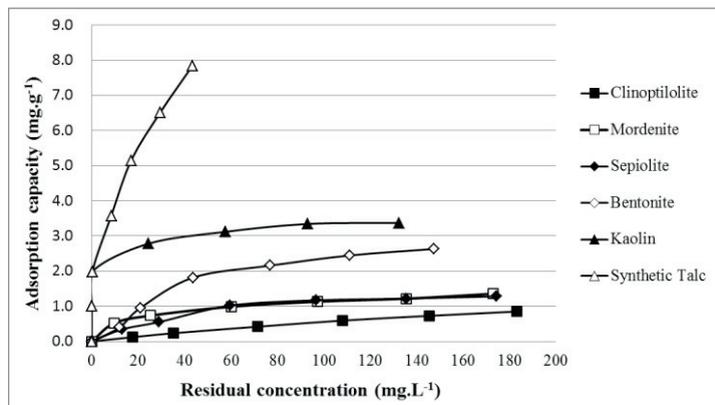


Fig. 2 Adsorption capacity for procion brilliant red H-EGXL removal on various clay adsorbents at neutral pH condition

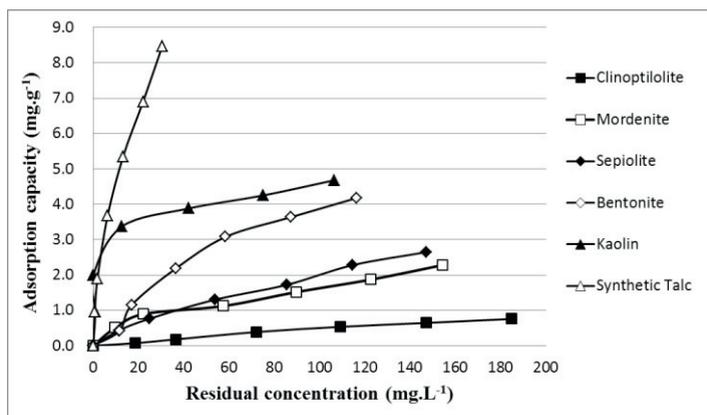


Fig. 3 Adsorption capacity for procion yellow H-EXL removal on various clay adsorbents at neutral pH condition

Table 2 shows that bentonite has the largest specific surface area than other clay adsorbents. Although bentonite has large specific surface area, it is categorized as a cationic exchanger [6]. Ion exchange could not take place on the bentonite-procion dyes system because procion dyes are anionic type. In addition, zeta potential analysis showed that bentonite was more negatively charged than synthetic talc and kaolin. Reactive anionic dyes have negative surface charge due to the presence of sulfonic groups (SO_3^-) on the dyes compound [9]. On the other hand, although synthetic talc has a specific surface area smaller than bentonite, this material has $0.0257 \text{ meq.g}^{-1}$ of anion exchanges capacity. Accordingly, synthetic talc

removed procion reactive dyes by physical adsorption and ion exchange mechanism. While kaolin has more positive net charge compared to the synthetic talc and bentonite, and has 0.0301 meq.g⁻¹ of anion exchange capacity even though its specific surface area is very small compared to the synthetic talc, bentonite and other adsorbents. Clinoptilolite, mordenite and sepiolite were categorized as cationic exchanger in which only physical adsorption occurred during the adsorption of reactive procion dyes.

Table 2. Characteristic of clay adsorbent. Condition: 10 mg.L⁻¹ of each adsorbent for zeta potential analysis at neutral condition at room temperature. Anion exchange capacity was analyzed at around pH 9-10 due to the washing effect by NaOH before NO₃⁻ adsorption.

Adsorbents	Methylene blue adsorption method		Ionic type	Zeta potential (mV)
	Specific surface area (m ² .g ⁻¹)	Cation exchange capacity (meq.g ⁻¹)		
Clinoptilolite	68.37	0.1326	Cationic exchanger [10]	-59.676
Mordenite	129.23	0.1373	Cationic exchanger [11]	-73.251
Sepiolite	305.06	0.1498	Cationic exchanger [12]	-50.697
Bentonite	724.49	0.1500	Cationic exchanger [6]	-58.315
Kaolin	2.18	0.0700	Anion exchange capacity: 0.0301 meq.g ⁻¹	-37.324
Synthetic talc	156.91	0.1499	Anion exchange capacity: 0.0257 meq.g ⁻¹	-53.560

3.2. Removal ratio

Removal ratio (R) was calculated to investigate the percentage of dye removal as the increasing of initial dyes concentration. Removal ratio was calculated following the equation 2.

$$R = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (2)$$

Where: *R* is the removal ratio (%), *C_o* is the initial concentration of dyes (mg.L⁻¹) and *C_e* is the residual concentration of dyes (mg.L⁻¹). Table 4 shows that the removal ratio of procion brilliant red H-EGXL from 40-200 mg.L⁻¹ of initial dyes concentration while Table 5 shows removal ratio of procion yellow H-EXL. As shown in Table 3 the removal ratio of procion brilliant red H-EGXL by synthetic talc has the highest percentage than other adsorbents. At the 40 mg.L⁻¹ of procion brilliant red, the removal ratio of synthetic talc and kaolin reached over 90%. Bentonite is able to remove 46.62% of procion brilliant red due to the large specific surface area which is different from other cationic exchanger clay adsorbent. The same result was also shown in Table 4 for the removal of reactive procion yellow H-EXL in which synthetic talc has the highest removal ratio. The removal ratio of clay adsorbent slightly decreases with increasing initial dyes concentration. The removal ratio of synthetic talc is relatively stable over 80% until the dyes concentration reached 160 mg.L⁻¹ both procion brilliant red H-EGXL and procion yellow H-EXL. Laksono (2009) reported that textile materials absorb dyes partially during the dyeing process and the rest (2-50%) will still remain in the dyeing effluent [3]. Roanne (2010) formulated that 0.89-1.12 g.L⁻¹ of procion dyes is required for coloring 0.227 kg of cotton lint depending on the desired color brightness [13]. From the average dyes that remain in the effluent and the using of dyes during the dyeing process,

around 288.5 mg.L^{-1} of dyes will still remain in the effluent. According to the removal ratio, 1.00 g of synthetic talc could remove 78.10% of procion brilliant red H-EGXL and 84.67% of procion yellow H-EXL at 200 mg.L^{-1} of initial dyes concentration. Thus, the exact amount of necessary adsorbent can also be estimated.

Table 3. Removal ratio of procion brilliant red H-EGXL removal.

Initial dye concentration (mg.L^{-1})	Removal ratio (%)					
	Clinoptilolite	Mordenite	Sepiolite	Bentonite	Kaolin	Synthetic talc
40	10.50	35.74	26.49	46.62	98.62	98.62
80	9.67	23.97	24.74	44.81	69.01	89.08
120	9.17	18.20	18.82	35.39	51.53	85.54
160	8.43	14.58	14.58	30.03	41.32	81.24
200	7.86	12.95	12.21	25.77	33.23	78.10

Table 4. Removal ratio of procion yellow H-EXL removal.

Initial dye concentration (mg.L^{-1})	Removal ratio (%)					
	Clinoptilolite	Mordenite	Sepiolite	Bentonite	Kaolin	Synthetic talc
40	8.72	44.47	37.78	57.21	99.33	94.83
80	9.67	28.01	32.52	54.36	84.05	91.82
120	8.95	25.27	28.69	51.23	64.65	88.90
160	8.13	23.40	28.49	45.43	53.09	86.16
200	7.66	22.87	26.50	41.80	46.80	84.67

3.3. Adsorption capacity as the effect of initial pH condition

The adsorption capacity as the effect of initial pH condition was investigated. Kaolin and synthetic talc were selected as the adsorbents and reactive procion brilliant red H-EGXL dye was used as an adsorbate. Initial pH condition was set at acidic, neutral and alkaline condition (3.1, 6.4 and 10.2) by pH control reagent of NaOH and HCl solution. As shown in Figure 4, the adsorption capacity of synthetic talc and kaolin was higher under acidic than neutral and alkaline conditions. Table 5 shows that under acidic condition, the removal ratio of kaolin reached 100% at 60 mg.L^{-1} of initial dyes concentration. While the removal ratio of synthetic talc was still over 95%; even the initial dyes concentration reached 200 mg.L^{-1} . In adsorption application pH strongly influences the adsorption capacity by changing the amount of H^+/OH^- adsorption [14]. Figure 5 shows that surface charge of synthetic talc and kaolin was more positive under acidic condition, and it increased their adsorption capacity. The similar trend was also reported, in which synthetic talc removed anionic dye of C.I Acid Orange 7 and C.I Reactive Red 3 was more effective under acidic condition [15].

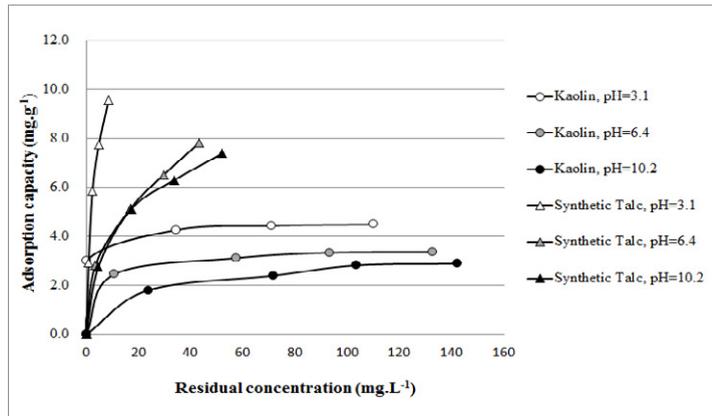


Fig. 4 Adsorption capacity for procion brilliant red H-EGXL removal as the effect of initial pH condition

Table 5. Removal ratio of procion brilliant red H-EGXL removal as the effect of initial pH condition.

Initial dye concentration (mg.L ⁻¹)	Removal ratio (%)					
	Kaolin			Synthetic talc		
	pH=3.1	pH=6.4	pH=10.2	pH=3.1	pH=6.4	pH=10.2
60	100.00	82.16	60.37	98.46	94.20	92.26
120	71.21	52.02	40.15	98.00	85.85	85.60
160	55.55	41.81	35.34	96.99	81.52	78.92
200	44.96	33.73	28.93	95.71	78.35	73.94

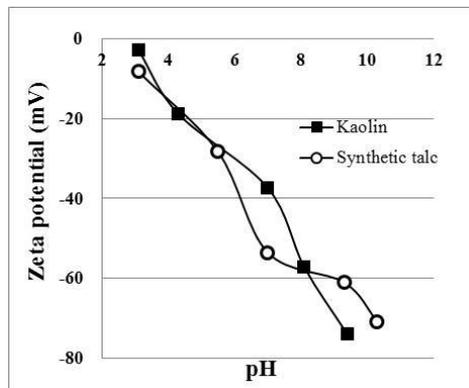


Fig. 5 Dependency of zeta potential of kaolin and synthetic talc on pH variation

3.4 Adsorption isotherm as the effect of initial pH condition

Adsorption isotherm is determined to predict the mechanism occurring during the adsorption process, especially the distribution of dye molecule over the surface of adsorbent [6]. Langmuir and Freundlich isotherm are often used to determine the adsorption isotherm. The Langmuir and Freundlich adsorption isotherm are expressed as the following equation (3) and (4), respectively [5].

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \quad (3)$$

$$\frac{x}{m} = K_f C_e^{1/n} \quad (4)$$

Where: x/m is the adsorption capacity (mg.g^{-1}), a and b are the empirical of Langmuir constant, C_e is the final concentration of dyes when equilibrium reached (mg.L^{-1}). K_f is the Freundlich capacity factor ($\text{mg.g}^{-1})(\text{L.mg}^{-1})^{1/n}$, and $1/n$ is the Freundlich intensity parameter. Table 6 summarized the isotherm parameter at different initial pH condition. As shown in Table 6, experimental data fitted well both the Langmuir and Freundlich isotherms regardless of pH fitness for the Langmuir isotherm assuming the reactive procion brilliant red H-EGXL molecule formed monolayer over homogenous adsorbent surface and no further adsorption occurred when the equilibrium was reached [2].

Table 6. Freundlich and Langmuir isotherm parameter for procion brilliant red H-EGXL.

Adsorbents	pH	Freundlich isotherm parameter			Langmuir isotherm parameter		
		1/n	K_f ($\text{mg.g}^{-1})(\text{L.mg}^{-1})^{1/n}$	R^2	q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2
Kaolin	3.1	0.05	3.65	0.97	4.51	1.20	1.00
	6.4	0.13	1.82	0.99	3.51	0.19	1.00
	10.2	0.27	0.76	0.98	3.35	0.04	0.99
Synthetic talc	3.1	0.53	3.31	0.97	12.92	0.33	1.00
	6.4	0.40	1.70	1.00	9.35	0.09	0.97
	10.2	0.41	1.52	0.99	8.84	0.09	0.99

4. Conclusion

The adsorptions of reactive procion brilliant red H-EGXL and procion yellow H-EXL by various clay adsorbents were investigated in this research. The result showed that the adsorption capacity of Synthetic talc is the highest of all other adsorbents due to the physical adsorption and anion exchange mechanism. The removal ratio of synthetic talc reached over 80% for both procion dyes removal until the initial dyes concentration reached at 160 mg.L^{-1} when liquid/solid ratio was of 50 mL.g^{-1} . As the effect of initial pH condition the adsorption capacity of synthetic talc and kaolin increased under acidic condition due to a more positive charge of zeta potential. Kaolin could remove 100% of 60 mg.L^{-1} of procion brilliant red at pH 3.1, while synthetic talc could maintain the removal ratio over 90% and even dye concentration at 200 mg.L^{-1} . Both Langmuir and Freundlich models regardless of initial pH condition expressed the adsorption

isotherm of procion brilliant red H-EGXL to synthetic talc and kaolin. The fitness for Langmuir isotherm implied that dye was regulated by monolayer adsorption mechanism.

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