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Original Article

Removal of reactive dyes from wastewater by shale

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Abstract

Colored textile effluents represent severe environmental problems as they contain mixture of chemicals, auxiliaries and dyestuffs of different classes and chemical constitutions. Elimination of dyes in the textile wastewater by conventional wastewater treatment methods is very difficult. At present, there is a growing interest in using inexpensive and potential materials for the adsorption of reactive dyes. Shale has been reported to be a potential media to remove color from wastewater because of its chemical characteristics. In this study, shale was used as an adsorbent. The chosen shale had particle sizes of : A (1.00 < A < 2.00 mm), B (0.50 < B < 1.00 mm), C (0.25 < C < 0.50 mm), D (0.18 < D < 0.25 mm) and E (0.15 < E < 0.18 mm). Remazol Deep Red RGB (Red), Remazol Brilliant Blue RN gran (Blue) and Remazol Yellow 3RS 133% gran (Yellow) were used as adsorbates. Batch adsorption experiments were performed to investigate the effect of contact time, pH, temperature and initial dye concentration. It was found that the equilibrium data were best described by the Langmuir isotherm model, with the maximum monolayer adsorption capacities of 0.0110-0.0322 mg/g for Red, 0.4479-1.1409 mg/g for Blue and 0.0133-0.0255 mg/g for Yellow, respectively. The maximum adsorption capacity of reactive dye by shale occurred at an initial pH of 2, initial concentration of 700 Pt-Co and temperature 45°C. Reactive dye adsorption capacities increased with an increase of the initial dye concentration and temperature whereas with a decrease of pH. The fixed bed column experiments were applied with actual textile wastewater for estimation of life span. The results showed that COD and color removal efficiencies of shale fix bed column were 97% and 90%, respectively. Also the shale fixed bed columns were suitable for using with textile effluent from activated sludge system because of their COD and color removal efficiencies and life expectancy comparison using with dyebath wastewater and raw wastewater.

Keywords: reactive dyes, shale, adsorption, textile wastewater

1. Introduction

Colored textile effluents represent severe environmental problems as they contain mixture of chemicals, auxiliaries and dyestuffs of different classes and chemical constitutions. The release of color wastes into receiving water causes damage to the environment as they may significantly affect photosynthetic activity in aquatic life due to reduced light penetration. They may also be toxic to some aquatic lives because they contain metals, chlorides, etc. Reactive dyes are the most common dyes used due to their advantages, such as bright colors, excellent colorfastness and ease of application (Yang and Al-Durf, 2001; Mahony *et al.*, 2002). Elimination of dyes in the textile wastewater by conventional wastewater treatment methods is very difficult. Various methods for dye and color removal, such aerobic and anaerobic microbial degradation, coagulation and chemical oxidation, membrane separation process, electro-chemical,

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filtration, softening and reverse osmosis have been proposed from time to time (Robinson *et al.*, 2001). However, all of the methods suffered from one or another limitation and none of the processes described above were successful in removing color from wastewater completely. Adsorption is probably the simplest process for dye removal. Currently, activated carbon is believed to be the most effective adsorbent. However, high cost in production and regeneration make it uneconomical (Wang *et al.*, 2005). At present, there is a growing interest in using inexpensive and potential materials for the adsorption of reactive dyes. Shale has been reported the potential media to remove pollutants from wastewater because of their chemical characteristics and inexpensive material. This had led to a search for low-cost materials, which could be considered as adsorbents alternative to low cost adsorbent and utilization with biological treatment system. This study is aimed at investigating the adsorption of reactive dyes onto shale. Shale was used as adsorbent. The experiments were performed for different parameters, such as contact time, pH, initial dye concentration and temperature on adsorption rate of three reactive dyes Red, Blue and Yellow on shale were investigated. Langmuir and Freudlich models were used to describe adsorption isotherm. The fixed bed column experiments were applied with actual textile wastewater for estimation of life span and COD, color removal efficiencies.

2. Materials

2.1 Shale

The raw shale were used as untreated adsorbent in this study was obtained from The Siam Cement Public Company Limited, Saraburi Province, Thailand. Shale was studies without any pretreatment and was crushed and washed with distilled water and dried using hot air oven at 105°C for 24 hours. The particle size of shale was measured by dry sieving into five different sizes. The chosen shale had particle sizes of: A ($1.00 < A < 2.00$ mm), B ($0.50 < B < 1.00$ mm), C ($0.25 < C < 0.50$ mm), D ($0.18 < D < 0.25$ mm) and E ($0.15 < E < 0.18$ mm). The physical characteristics of shale and method analysis were shown in Table 1. The major chemical compositions of shale were carried out by using an energy dispersive X-ray spectrometer (Oxford ED, 2000). They were 57.80% SiO_2, 17.20% Al_2O_3 and 11.80% CaO. Many studies were found that the absorbent which contained Si and Al give a high adsorption capacity of reactive dye (Basava Rao and Ram Mohan Rao, 2006; Ozacar and Sengil, 2003).

2.2 Reactive dyes

Remazol Deep Red RGB (Red), Remazol Brilliant Blue RN gran (Blue) and Remazol Yellow 3RS 133% gran (Yellow) were used as adsorbate in this study were obtained from DyStar Thai Co., Ltd. Thailand. The synthetic reactive dye wastewater with 600 mg/l was prepared by dissolving 0.6 g of reactive dye in 900 ml of distilled water; 40 g of NaCl were added at room temperature and the mixture was stirred until complete dissolution; the solution was heated to 60°C and 1.5 g of NaOH were added; the mentioned temperature was maintained for 2 hrs, with the addition of 2 g of Na_2CO_3 after the first hour; the solution was cooled to room temperature and distilled water was added to complete the volume.

3. Experiments

3.1 Batch studies of adsorption

Batch adsorption experiments were performed as a function of contact time, pH, temperature and initial dye concentration. The conditions of batch experiment are shown in Table 2. Adsorption isotherm studies were carried out at five different shale mass (1, 2, 4, 6 and 8 g). A series of 250 ml Erlenmeyer flask containing 200 ml of dye solution and required amount of shale were mixed using the shaker at constant agitation speed of 150 rpm. The sorbent was then separated by filtration. The filtrated dye concentrations were measured with spectrophotometer at 465 nm.

3.2 Fixed bed column studies

Fixed bed column studies were conducted using plastic columns having as shown in the schematic diagram in Figure 1. The columns were packed with different particle size of shale on supporting layer of glass wool at the bed depth of 30 cm. Three types of actual textile wastewaters were used in this experiment were obtained from textile industry in Prachinburi Province, Thailand. The first one was dyebath wastewater was collected from dyeing process, the second one, raw textile wastewater which was collected from the equalizing tank after preliminary process, and the last

Table 1. Physical characteristics of shale

characteristic	Shale A	Shale B	Shale C	Shale D	Shale E	method
Size (mm)	1.00-2.00	0.50-1.00	0.25-0.50	0.18-0.25	0.15-0.18	ASTM E11
Bulk Density (g/cm^3)	1.253	1.236	1.189	1.165	1.156	ASTM D2854
Porosity(%)	34.00	34.00	33.00	33.00	33.00	ASTM D2854
Permeability (m/d)	657.504	476.978	127.035	32.801	23.634	ASTM D2468
BET Surface (m^2/g)	3.063	3.742	3.787	4.200	5.117	B.E.T method

Table 2. Condition of batch experiments

Parameter	Contact time	Adsorption isotherm	pH	Temperature	Initial dye concentration
shale	A-E	A-E	A-E	A-E	A-E
Initial dye concentration (Pt-Co)	700	700	700	700	100, 200, 400, 600, 700
Shale dose (g)	1	1, 2, 4,6, 8	1	1	1
pH	10.5	10.5	2, 4, 6, 8, 10, 12	10.5	10.5
Contac Time (hrs)	6, 12, 24, 48, 72, 96, 120	72	72	72	72
Temperature (°C)	32±0.2	32±0.2	32±0.2	30, 35,40, 45	32±0.2
rpm	150	150	150	150	150
Volume ofdye solution (ml)	200	200	200	200	200

Table 3. Chemical composition of actual textile wastewater

Chemical composition	Unit	Mean±SD		
		dyebath wastewater	raw textile wastewater	effluent from AS
COD	mg/l	45500±182.00	2600±3.78	750±1.67
BOD	mg/l	5±0.00	520±0.47	25±0.04
SS	mg/l	45±0.73	130±0.85	90±0.33
TDS	mg/l	45000±123.00	5600±6.54	4800±15.00
Color	Pt-Co	2502000±500.00	2105±13.00	420±3.00

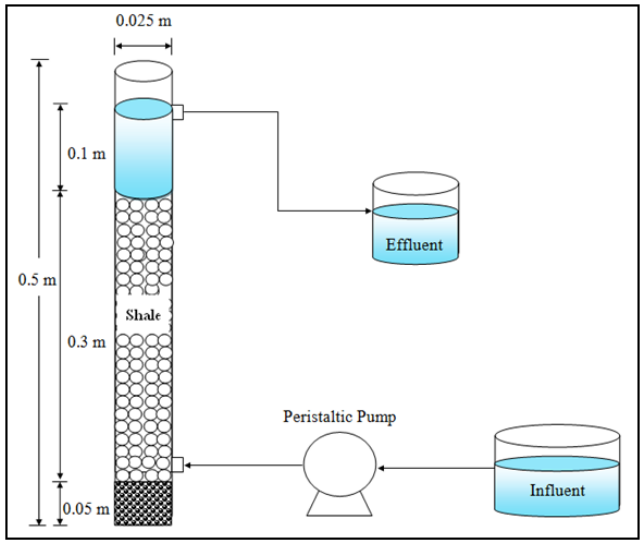

Figure 1. Schematic diagram of the column study

one, effluent from AS which was collected from storage tank after passing activated sludge treatment system. The compositions of actual textile wastewaters were shown in Table 3. The fixed bed columns were loaded with actual textile wastewaters which up-flow mode at hydraulic loading rate of 2.939 m^3/m^2-d. They were operated until COD and color concentrations of outlet were equal with 95% of inlet concentrations.

4. Results and Discussion

4.1 Batch studies of adsorption

4.1.1 Effect of contact time

As shown in Figure 2, the dye adsorption capacities of shale were increased with an increasing of the contact time. The adsorption capacity of shale was quite rapid in the first 48 hrs, then gradually increased with the prolongation of contact time. After 72 hrs of contact, no obvious variation in dye adsorbed was examined. The rate of removal was higher in the beginning due to larger surface area available of adsorbent. After that, the rate of dye uptake was controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles (Amin, 2008). Based on these results, 72 hrs was taken as optimum contact time in each batch adsorption experiments.

4.1.2 Adsorption isotherms

Langmuir and Freundlich isotherms are used to describe, and are represented by Equation (1) and (2), res-

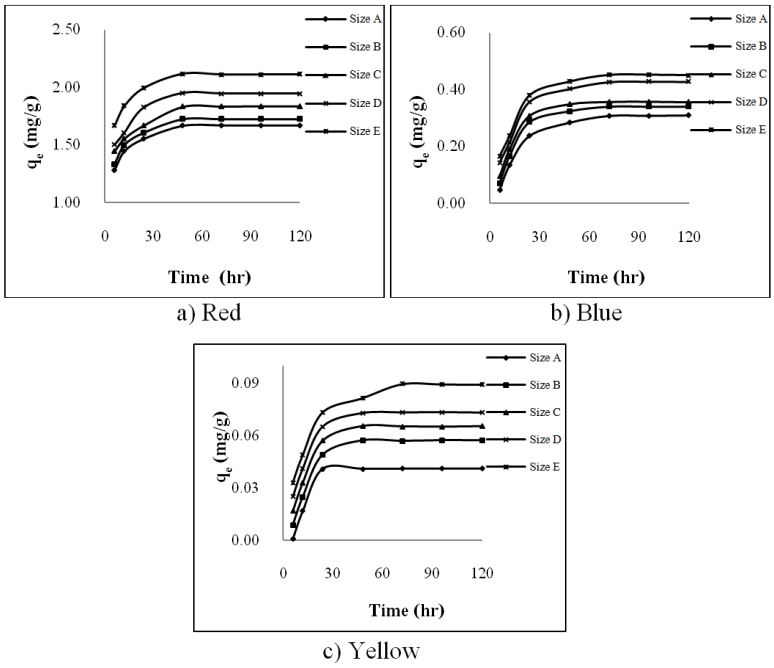

Figure 2. Effect of contact time on adsorption of Red, Blue and Yellow dyes onto shale: Initial reactive dye concentration 700 Pt-Co; Adsorbent dosage 1 g/ 200 ml; pH 10.5; room temperature

pectively.

Langmuir isotherm: $$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{Qb}\frac{1}{C_e} \quad (1)$$

Freundlich isotherm: $$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (2)$$

The model fits to the results of all investigated dyes were assessed based on the values of the determination coefficient (R^2) of the linear plot. Table 4 showed the R^2 values of the Langmuir model were greater than that of the Freundlich model for the adsorption of all investigated dyes. This indicates that the adsorption of all investigated dyes on shale particles was better described by the Langmuir model than

Table 4. Langmuir and Freundlich isotherm constants for adsorption of three reactive dyes on shales

Shale	Dye	Langmuir Isotherm			Freundlich Isotherm		
		Q(mg/g)	K	R^2	n	K_f(mg/g)	R^2
A	Red	0.0110	0.0434	0.9978	0.0683	5.236×10^{-21}	0.9625
B		0.0202	0.0441	0.9963	0.0869	1.718×10^{-16}	0.9845
C		0.0218	0.0447	0.9979	0.0895	5.728×10^{-16}	0.9685
D		0.0252	0.0448	0.9991	0.0925	2.075×10^{-15}	0.9512
E		0.0322	0.0449	0.9960	0.1121	7.533×10^{-13}	0.9718
A	Blue	0.4479	0.0050	0.9961	0.3105	1.355×10^{-7}	0.9900
B		0.5291	0.0050	0.9987	0.3459	7.619×10^{-7}	0.9876
C		0.9397	0.0044	0.9933	0.4335	1.694×10^{-5}	0.9705
D		1.0392	0.0043	0.9939	0.4352	1.884×10^{-5}	0.9804
E		1.1409	0.0043	0.9990	0.4496	2.875×10^{-5}	0.9889
A	Yellow	0.0133	0.0462	0.9798	0.0673	8.375×10^{-21}	0.9983
B		0.0165	0.0468	0.9846	0.0730	4.036×10^{-19}	0.9945
C		0.0207	0.0478	0.9822	0.0786	1.233×10^{-17}	0.9966
D		0.0245	0.0485	0.9757	0.0841	1.982×10^{-16}	0.9946
E		0.0255	0.0488	0.9835	0.0844	2.661×10^{-16}	0.9929

the Freundlich model. Langmuir isotherm assumes monolayer coverage of sorbate onto sorbent. The values of Q and b were calculated as shown in Table 4. The maximum adsorption capacity of Red, Blue and Yellow dye solutions were found in range of 0.0110-0.0322 mg/g, 0.4479-1.1409 mg/g and 0.0133-0.0255 mg/g respectively. The maximum adsorption capacity of reactive dye onto shale was lower than the value presented in the literature for the commercial activated carbon (1.80-3.48 mg/g) (Amin, 2008). As the low cost adsorbent, shale has advantage than activated carbon because they are without pretreatment.

4.1.3 Effect of pH

As shown in Figure 3, the adsorption capacity decreased with increasing of pH values for all dyes solutions. The equilibrium pH on adsorption of reactive dyes onto shale is pH 2. Adsorption of reactive dyes onto shale is the electrostatic interactions between the adsorbent and dye molecules, Adsorption increases due to increasing of electrostatic attraction between negative charged dye molecules and positive charged active group of adsorbent (Ozacar and Sengil, 2003). In the aqueous solution, the sulphonate groups of reactive dyes (D-SO_3Na) are dissociated and converted to anionic dye ion. Shale is material with amphoteric character. Thus, depending on the pH solution, their surfaces might be positively or negatively charged, which have a direct influence on electrostatic interactions. The pH affected adsorption of Blue more than Red and Yellow dye.

4.1.4 Effect of Temperature

As shown in Figure 4, the adsorption capacity of Red, Blue and Yellow dye on shale increased with increasing of the temperatures. The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution (Al-Qodah, 2000; Karaoglu *et al.*, 2010).

4.1.5 Effect of initial reactive dye concentrations

As shown in Figure 5, the reactive dye adsorption capacities of shale increased with increasing of the initial reactive dye solutions. Initial concentration provides an important driving force to overcome all mass transfer resistance of the reactive dye between the aqueous and solid phases (Karaoglu *et al.*, 2010). Hence a higher initial concentration of dye will enhance the adsorption process.

4.2 Fixed bed column studies

4.2.1 COD removal efficiency

The average COD removal efficiency of three actual textile wastewater increased with the decreasing of particle size of shale as shown in Table 5. The removal efficiencies of COD for shale A-E were in range of 97.31-99.14% for dyebath wastewater, 98.428-99.336% for raw textile wastewater and 98.201-98.529% for effluent from AS. The life expectancy of column systems for removal COD of shale A-E increased with the decrease of particle size of shale. The life expectancy of systems for removal COD of shale A-E were in range of 218.18-239.70 min for dyebath wastewater, 420.09-472.19 min for raw textile wastewater and 1190.00-1245.96 min of effluent from AS**.** These results indicated that the utilization of shale adsorption with effluent from AS could be extended the life

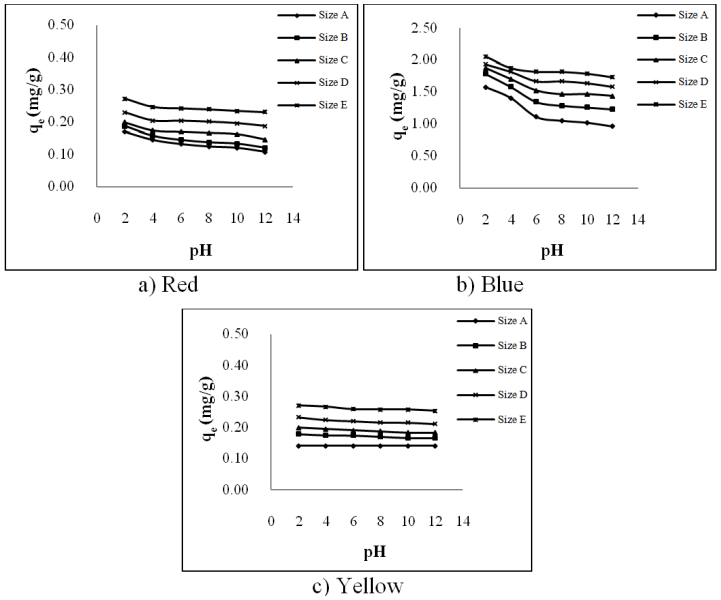

Figure 3. Effect of pH on adsorption of Red, Blue and Yellow dyes onto shale: Initial reactive dye concentration 700 Pt-Co; Adsorbent dosage 1 g/ 200 ml; room temperature; contact time 72 hrs.

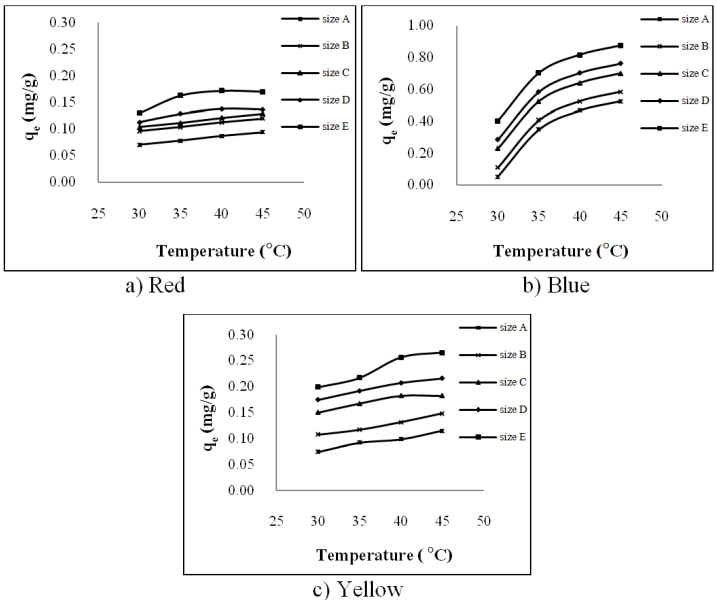

Figure 4. Effect of temperature on adsorption of Red, Blue and Yellow dyes onto shale: Initial reactive dye concentration 700 Pt-Co; Adsorbent dosage 1 g/ 200 ml; pH 10.5; contact time 72 hrs.

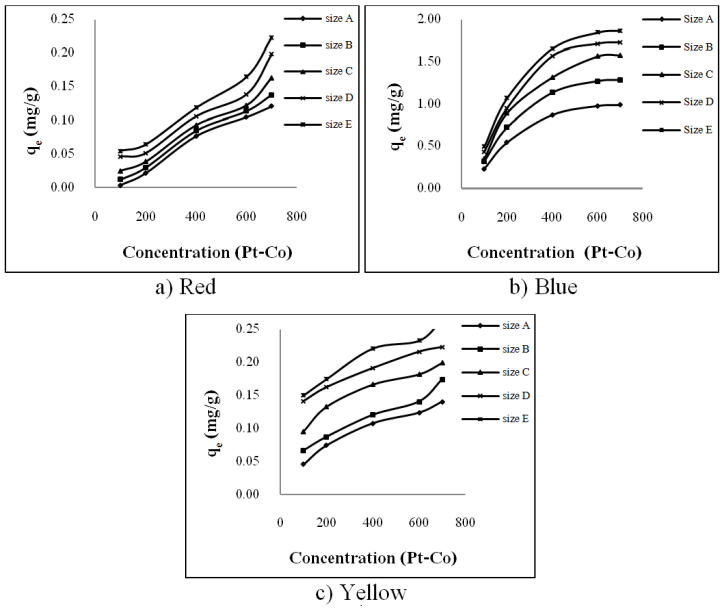

Figure 5. Effect of concentration on adsorption of Red, Blue and Yellow dyes onto shale: Adsorbent dosage 1 g/ 200 ml; pH 10.5; room temperature; contact time 72 hrs.

span of fixed bed column.

4.2.2 Color removal efficiency

The average color removal efficiency of three actual textile wastewater were increased with decreasing particle size of shale as shown in Table 5. The removal efficiencies of color for shale A-E were in range of 91.512-98.805% for dyebath wastewater, 98.449-98.983% for raw textile wastewater and 94.969-95.147% for effluent from AS. The life expectancy of systems for removal color of shale A-E increased with decreasing of particle size of shale. The life expectancy of systems for removal color of shale A-E were in range of 109.51-130.62 min for dyebath wastewater, 192.131-194.558 min for raw textile wastewater and 786.67-913.68 min of effluent from AS. These results indicated that the utilization of shale adsorption with effluent from AS could be extended the life span of fixed bed column.

Table 5. Removal efficiency of shale with various type of wastewater

Type of wastewater	Composition	Removal efficiency (%)(Mean±SD)				
		A	B	C	D	E
dyebath wastewater	Color	91.512±4.796	98.445±4.452	98.578±4.400	98.734±3.345	98.805±3.070
	COD	97.309±5.977	98.221±4.814	98.846±3.014	99.050±2.456	99.136±2.232
raw textile wastewater	Color	98.449±1.646	98.674±1.008	98.912±2.200	98.960±0.202	98.983±0.134
	COD	98.428±2.156	98.428±2.156	98.619±1.826	98.661±1.834	99.336±1.314
effluent from AS	Color	94.969±0.505	95.088±0.168	95.147±0.000	95.147±0.000	95.147±0.000
	COD	98.201±0.000	98.529±0.002	98.529±0.002	98.529±0.002	98.529±0.002

5. Conclusions

The present investigation showed that shale was a promising adsorbent for the removal of reactive dyes from aqueous solutions over a wide range of concentrations. The adsorbed amounts of reactive dyes reached a maximum at equilibrium within 72 hrs. Equilibrium data was best described by the Langmuir isotherm, with the maximum monolayer adsorption capacities of in range of 0.0110-0.0322 mg/g for Red, 0.4479-1.1409 mg/g for Blue and 0.0133-0.0255 mg/g for Yellow, respectively. The maximum adsorption capacities of reactive dyes by shale occurred at an initial pH of 2, initial concentration of 700 Pt-Co and temperature 45°C. Reactive dye adsorption capacities increased with increasing of the initial dye concentration and temperature whereas decreasing of pH. For the fixed bed system, the average COD and color removal efficiency were higher than 97% and 90%, respectively, for all actual textile wastewater. The utilization of shale adsorption with effluent from AS could be extended the life span of fixed bed column longer than dyebath wastewater and raw textile wastewater. The results of this study will provide information on the utilization of shale as low-cost adsorbent to remove COD and color from textile wastewater.

Acknowledgements

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