Treatment of Coloured Textile Wastewater by Activated Clay

H. BOUABDESSELAM*, S. MEDDAH, Y. BOUZIDI† and D. BOURG†

Laboratoire des Technologies de l'Environnement, ENSET, B.P. 1523
Oran El M'naouer, Algéria
Fax: (213)(41)416916; E-mail: bhassiba@yahoo.fr

Activated clay has been successfully applied for the removal of red dye H3BD in the industrial textile wastewater. Activated clay has proved its effectiveness as 98% of the dyes contained within the effluent are eliminated and the COD is reduced from 10800 ppm to 32 ppm with a neutral pH and an excellent decantability. A complete study of textile dye adsorption on acidified clay was performed changing several factors such as stirring velocity, contact time and initial concentration.

Key Words: Adsorption, Clay, Dye, Textile, Treatment, Wastewater.

INTRODUCTION

Textile industry wastewaters are highly polluted due to their strong concentration of toxic dyes. The chemical treatment based on iron or aluminium chloride gives negative results. In this case, recuperative processes such as adsorption into porous solid[1], membrane separation[2] and solvent extraction[3] may be applied. Activated carbons are among the most effective adsorbents, having high surface area per unit mass. Activated carbon exhibts high adsorption capacity for organic compounds[4–7].

In recent years, there has been increasing interest in utilizing natural clay minerals like montmorillonite, kaollinite and illite for the removal of toxic metals and some organic polluants from aqueous solutions[8–11]. The abundance of clay in most continents of the world and its low cost make it a strong candidate as an effective adsorbent for the removal of many pollutants from wastewater. Research studies have shown its ability to bind and remove pathogenic virsuses, pesticides, herbicides and other toxins[12, 13]. Recently, activated bentonite has been utilized to remove pesticides[14, 15] and synthetic dyes from aqueous solutions[16].

The aim of this work is to investigate, experimentally, in a first step, the potential of acidified clay to adsorb dye pollutants using red dye H3BD, often used by the textile industry, as a model compenent. The effects of amount of clay, contact time, agitation speed and the initial dye concentration were studied. In a second step, the

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activated clay was used as adsorbent in textile industry wastewater treatment. The wastewaster was analyzed and the effect of clay mass on COD was studied.

EXPERIMENTAL

The natural clay used for acid activation was purchased from Algerian Society ENOF.

Natural clay (25 g) used was agitated with 500 mL of 1 M sulfuric acid at 98°C for 6 h, then the mixture was cooled, filtered and washed a few times to eliminate chloride and sulphate ions and finally dried at 120°C in an oven for a few hours. The analytical results of the acid activated clay are reported in Table-1. Table-2 summarizes the methods and instruments used for the analysis of activated clay.

TABLE-1
CHARACTERISTICS OF ACTIVATED CLAY

Parameter	Value
Color	White
pH	3.42
Density	2.32 g/cm^3
Colloidality	15.5%
CEC	40 meq/100 g of clay (test of methylene blue)
	39 meq/100 g of clay (conductimeter method)
Specific surface constitution	171.5928 m^2/g. Montmorillonite, kaolinite and illite (the rate of foulness has been reduced)
Chemical composition	1.00% Fe_2O_3; 2.00% K_2O; 0.05% TiO_2; 0.07% CaO; 48.00% SiO_2; 0.10% Na_2O; 0.3% MgO; 37.00% Al_2O_3 and 12.10% L.O.F.

TABLE-2
METHODS USED FOR ANALYSIS

Parameter marks	Used method	Utilized device
Specific area	Method of BET	Micrometrics GEMINI VACPREP 061
Constitution	X-ray diffraction	Ganiometer Philips PW3710 type (radiation kα of copper, $\lambda = 1.54056$ Å).
Chemical composition	Fluorescence-RX	FRX of type P.W1404 X-RAY Spectrometer

Batch adsorption test

The red dye H3BD chosen for the adsorption study is used in the textile industry and its characteristics are shown in Table-3.

TABLE-3
CHARACTERISTICS OF THE RED DYE H3BD

Parameter	Value
State	Liquid
Temperature	12.9°C
pH	6.26
Conductivity	1.18 ms/cm
Ratio of saltiness (SDR)	0.58 g/L
Density	1134 g/L
Wavelength of absorption	570 nm

Batch adsorption experiments were carried out by allowing an accurately weighed amount of activated clay to reach equilibrum with dye solutions of known concentrations. Different weights (50 to 500 mg) of clay were added to narrow-neck bottles each containing 50 mL solution. The bottles were shaken in a temperature-controlled water bath shaker (B. Braun, model Infors AG, Bottmingen, Germany). The temperature was fixed at 20°C. The narrow-neck bottles were submitted to fast shake for 1 h followed by a further hour of slow shake. At the end of the equilibrium period, the contents of bottles were filtered, centrifuged for half an hour and the supernatant was subsequently analyzed for residual concentration of dye.

RESULTS AND DISCUSSION

Clay mass: The adsorption data for the uptake of red dye *vs*. mass clay is presented in Fig. 1. The results show that using 100 mg of clay, the dye is completely removed from the solution by the sorbent. The quantity of dye adsorbed remains unchanged for any further increase in clay mass.
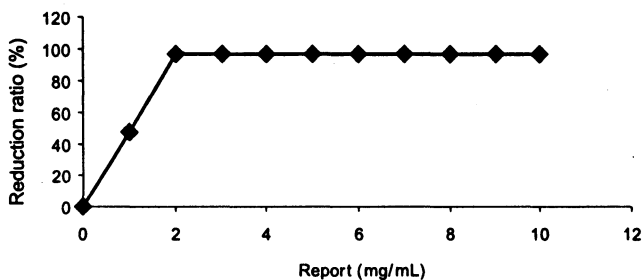

Fig. 1.   Evolution of the red dye reduction *vs*. the report clay mass/volume solution acidified clay mass

Contact time: 100 mg of acidified clay was added to 50 mL of red coloured solution with an initial concentration of 50 mg/L. The mixture obtained was put under fast agitation for 2 h; every 5 min, a little quantity of the liquid mixture was taken. These samples were filtered and analyzed by UV in order to follow the evolution of the red dye concentration (Fig. 2). At the same time pH and
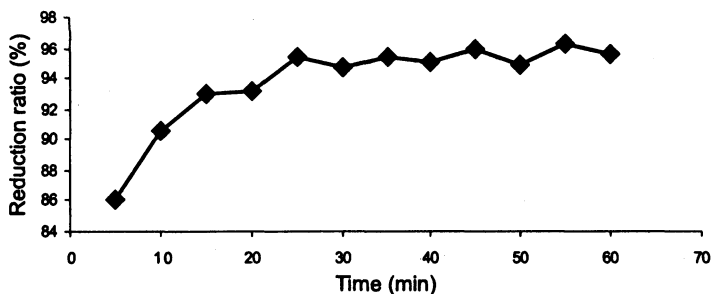

Fig. 2.   Plot of dye adsorption *vs*. square root of time

conductivities were measured (Fig. 3). The results show that the equilibrium time required for the dye adsorption onto activated clay is almost 25 min. These results
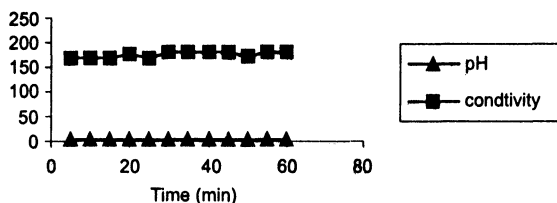

Fig.3.   Evolution of pH and conductivity *vs.* time

also indicate that the sorption process can be considered fast because the largest amount of dye attached itself to the sorbent within the first 25 min of adsorption. The pH and the conductivity remain practically constant, which deduce the phenomenon of physisorption and not one of exchange of the protonated dye (acidic environment) with the metallic cations of the natural clay[16].

Shaken speed: Some samples were prepared with 100 mg of activated clay and 50 mL of dye solution (50 mg/L) and were put under agitation during 25 min at different speeds: 250, 500, 750, 1000, 1250 and 1500 rpm. The results show that when the speed increases, the dye sorption increases (Fig. 4). Similar behaviour has been reported for the removal of cadmium from cereal waste[17].
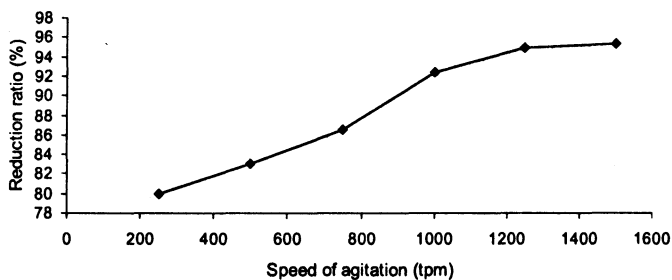

Fig. 4.   Evolution of the dye reduction ratio *vs.* speed of agitation

Initial dye concentration: Known weights of activated clay (while respecting a clay mass/dye volume equal to 2) were added to bottles containing 50 mL of solution and shaken for 25 min.

As is shown in Table-4, the adsorption of dye by activated clay increases as the initial dye concentration increases. Increasing the initial dye concentration would increase the mass transfer driving force and therefore, the rate at which dye molecules pass from the bulk solution to a particle surface. Similar behaviour has been reported recently by Benat *et al.*[18] for the adsorption of phenol by bentonite.

Application of the acid activated clay in treatment of textile industry wastewater

Analysis of the wastewater: Before proceeding to treat the textile industry wastewater, a first set of samples was taken for analysis in order to quantify and identify the pollution in wastewater by prescribed methods[19]. The results are reported in Table-5 and the follow-up of COD and the BOD is presented in Fig. 5. As shown in Fig. 5, the pollution reached its highest in the afternoon, by which time all departments have released their effluent (manufacture is finished).
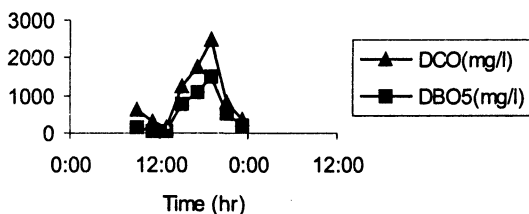

Fig. 5.   Variation of COD and BOD during 24 h

TABLE-4

EFFECT OF INITIAL DYE CONCENTRATION ON ADSORPTION
BY THE ACIDIFIED CLAY

Concentration of the solution (ppm)	Concentration of the red dye in the aqueous phase (ppm)	Concentration of the red dye in the solid phase (ppm)	Reduction ratio of the red dye (%)
10	1.96	8.04	80.40
20	2.02	17.98	89.90
30	2.34	27.66	92.20
40	2.40	37.60	94.00
50	2.44	47.56	95.12
60	3.25	56.75	94.58
70	5.37	64.63	92.32
80	4.99	75.01	93.76
90	6.43	83.57	92.85
100	5.66	94.34	94.34
150	8.89	141.11	94.07
200	19.24	180.76	90.38
250	28.53	221.47	88.58
300	42.12	257.88	85.96
400	98.90	301.10	75.27
500	182.60	317.40	63.48
600	276.00	324.00	54.00
800	475.00	325.00	40.62
1000	675.00	325.00	32.50

TABLE-5
CHARACTERISTICS OF THE FIRST SET OF WITHDRAWALS

Parameter	Norm	Withdrawals							
		1	2	3	4	5	6	7	8
Time (h)	—	09:00	11:00	13:00	15:00	17:00	19:00	21:00	23:00
Temperature (°C)	30	28.30	28.60	29.20	29.10	30.30	28.50	28.60	28.30
pH	5.5–8.5	11.22	9.77	9.78	11.08	10.88	10.72	10.86	9.37
Conductivity (μs/cm)	—	5320	2670	1260	2640	3580	1000	1000	1500
Ratio of saltiness (g/L)	—	2660	1340	630	1320	1790	1408	1460	750
SO_4^{2-} (mg/L)	—	154	101	84	180	182	182	134	120
CO_3^{2-} (mg/L)	—	371	90	47	169	187	0	191	0
HCO_3^- (mg/L)	—	615	205	183	549	512	1047	307	344
Cl^- (mg/L)	—	914	750	229	311	716	562	511	302
NO_3^- (mg/L)	—	7	7	5	11	12	6	9	5
NO_2^- (mg/L)	—	0.60	0.01	0.60	0.04	0.05	0.14	0.04	0.05
NH_4^+ (mg/L)	—	0.27	0.05	0.06	2	5.20	1.80	3.20	1
PO_4^{3-} (mg/L)	—	0.50	0.33	0.30	2	0.88	0.88	0.25	0.63
Dry residual at110°C (mg/L)	—	3660	1860	880	2390	2740	3200	2250	1130
SiO_2 (mg/L)	—	8.20	5	6	11	11.40	11.40	9	9
Acidic organic matter (mg/L)	—	104	56	16	53	74	62	46	56
Basic organic matter (mg/L)	—	35	9.10	7.90	54	67	54	43.50	53
COD (mg/L)	120	630	290	160	1260	1780	2500	830	380
BOD (mg/L)	40	176.70	69.90	45.10	781.50	1103.90	1500.30	531.50	213.0
Ca (mg/L)	—	34	43	35	20	50	43	63	67
Mg (mg/L)	—	20	53	34	35	22	69	11	23
Na (mg/L)	—	1208	557	193	506	736	598	589	293
K (mg/L)	—	12	8	7	105	104	140	33	18
Fe (mg/L)	5	0.25	1.30	2.50	0.35	0.45	0.20	1.20	2
Cu (mg/L)	3	2.40	2.50	2.30	2.40	0.37	0.31	3.20	1.80
Colour	colourless	white	white	colourless	yellow	yellow	yellow	yellow	black
Odour	odourless	bleach	bleach	u*	u	u	u	u	u

*unpleasant

A second set of samples were taken to determine the release that corresponds to the peak of pollution in the order to treat it.

Four samples were taken at intervals of 2 h: the first, after the waste release generated by scalding; the second, after the waste release generated by the hoary cloths; the third after the waste release generated by dyeing; and finally the fourth after the waste release generated by the impression.

The results of analysis of these different wastewaters are shown in Table-6.

These results show that the most polluted wastewater (highest COD) is that corresponding to the descending of dyeing. The dyes used contribute to the increase of COD.

TABLE-6
CHARACTERISTICS OF THE SECOND SET OF WITHDRAWALS

No. of sample	1	2	3	4	Norm
Temperature (°C)	26	43.60	23	23.10	30
pH	11.71	10.28	9.65	8.20	5.50–8.50
Potential (mV)	−282	−213	−165	−83	—
Conductivity (ms/cm)	6.33	5.60	5.40	5.60	—
Rate of saltiness (g/L)	3.44	3.03	2.92	3.03	—
Turbidity NTU	672	1242	5250	862.5	—
MIS (mg/L)	50	100	150	50	—
COD (mg/L)	1840	6040	10800	800	120
BOD (mg/L)	511	1677	3000	222	33
Phenol (mg/L)	1.37	2.97	24	1.26	0.50
NH_4^+ (mg/L)	1.971	1.80	20.20	0.65	—
Sulphates (mg/L)	323	531	2300	522	—
Chlorides (mg/L)	> 125	> 125	> 125	> 125	—
Cu (mg/L)	0.62	1.92	17	1.92	3
Zn (mg/L)	0.70	5.21	7.15	0.74	5
Cd (mg/L)	1.69	1.32	2	0.49	0.20
Odour	bleach	bleach	dye	dye	odourless
Color	white	yellow	dark green	blue	colourless

Method of wastewater treatment

To optimize the operative conditions of treatment, several samples (50 mL) of the third most contaminated release were treated. Each sample was subjected to fast agitation for 25 min with a weight varying from 10 to 300 mg of acidified clay. Then the crude was filtered and centifuged for 1 h. The supernatant was analyzed by measuring the COD. This operative method has been applied in two

cases, undecanted (Fig. 6) and decanted (Fig. 7) wastewater. In the *latter case*, before clay treatment, 100 mL of wastewater was left to decant for 10 min; then 50 mL of surpernatant was analyzed; its COD became 700 ppm and then treated as described previously. Fig. 6. shows an irregularity in the percentage of COD
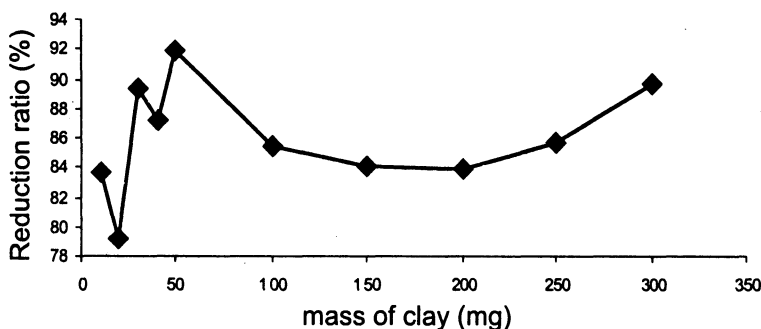
Fig. 6.   Evolution of COD reduction ratio of undecanted wastewater after treatment according to the acidified clay weight

reduction. In spite of that, the ratio of adsorption reached 91.85%; the COD value stays outside the industrial wastewater norms. Fig. 7. (showing after treating the decanted wastewater) shows that the percentage of COD reduction increases with the increase of clay. 97% of reduction in COD was reached with 50 mg of clay mass, to stabilize them.
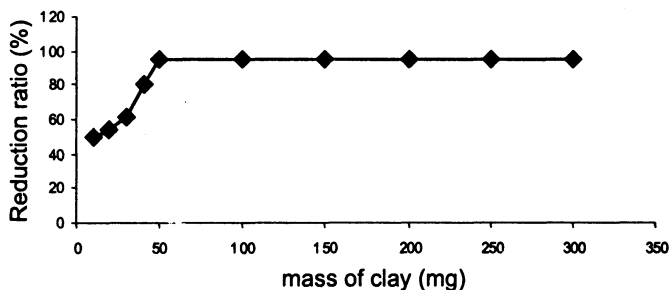
Fig. 7.   Evolution of COD reduction ratio of the decanted wastewater after treatment according to acidified clay weight

In this case, the COD value obtained is 35.05 ppm which is in conformity with the industrial waste norm (120 ppm).

Conclusions

The potential of acid activated clay to adsorb dye from aqueous solution was assessed. The adsorption capacity increased with an increase in shaken speed and initial dye concentration. Its utilization in the treatment of dye-contaminated wastewater shows its high adsorptive capacity. The COD was reduced from 10800 ppm to 35 ppm. What is more, the dye was completely eliminated and it permitted perfect decantation, as the pH of the wastewater treated was practically neutral.

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