¹USE OF ACTIVATED CLAYS IN THE REMOVAL OF DYES AND SURFACTANTS FROM TANNERY WASTE WATERS

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Abstract

A method is tested to reduce the pollution of effluents produced in the hide transformation process. Adsorption processes with clays could constitute a simple, selective and economical alternative to conventional physical-chemical treatments.

The adsorption capacity of natural and acid-activated bentonite and sepiolite for anionic dyes normally used in the tannery was compared with that of a conventional adsorbent such as activated carbon. Natural bentonite with a different level of acid activation was used to adsorb a non-ionic surfactant such as nonylphenol ethoxylated with 8 moles of ethylene oxide.

The capacity of sepiolite and acid-activated bentonite to adsorb anionic dyes normally used in the tannery was much greater than that of conventional adsorbents. A surfactant removal of 90 % was achieved in approximately 10 minutes because of the high affinity between surfactant and adsorbent. Natural bentonite activated with 0.5 M H₂SO₄ was the most effective adsorbent for ethoxylated nonylphenol.

Keywords: adsorption, clays, dyes, non-ionic surfactant, tannery

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1. INTRODUCTION

Present environmental legislation is very rigorous in almost all leather producing countries. Consequently, wastewater treatment is a matter of some urgency in most tanneries.

Tannery effluents are usually divided into three groups:

1. Unhairing and liming wastewater with high sulphide and lime content and high pH.
2. Tanning wastewater with high salinity and high chrome levels.
3. Retanning, dyeing and fatliquoring wastewater.

The traditional method of purification was to mix all the effluents in a big tank where some degree of chemical interaction could be expected. Nowadays, it is more usual to treat the different wastewater separately. The unhairing wastewater is treated with oxygen in the presence of manganese⁺² salt, acting as a catalyst, to transform the sulphide to sulphate; the wastewater of the tanning process, which contains chromium, is directly recycled or treated with alkali for chromium hydroxide precipitation which is subsequently re-used, and the retanning, dyeing and fatliquoring wastewater is treated with iron (II) sulphate to precipitate a high amount of proteins and organic contaminants (Heidemann, 1994). However, some contaminants such as surface active agents and fatliquors remain unaltered by a normal physical-chemical treatment (Gregori, 1994).

This scheme provides good results and has been adopted by a number of tanneries throughout the world. However, some improvements can be made to reduce the COD of effluents, mainly those of retanning, dyeing and fatliquoring.

Effluents of group 3 account for only 20 % of the COD of the full transformation process from hide to leather, whereas this figure is much higher when wet-blue leather is used as the starting material.

The aim of this work is to find a method to reduce the pollution parameters of the retanning, dyeing and fatliquoring effluents in the hide transformation process. Of all

possibilities, adsorption processes with clays could constitute a simple, selective and economically acceptable alternative to conventional physical-chemical treatments.

Clays such as bentonite and sepiolite have been largely studied since they show catalytic or adsorptive properties. As far as adsorptive properties are concerned, bentonite has been used to remove a number of chemical species: amines (Breen, 1991); organic pigments (β -carotenes) (Gonzalez-Pradas et al., 1991); cations (Ni, Zn), phenol and ketones (Stockmeyer and Kruse, 1991); phosphates (Gonzalez-Pradas et al., 1992); pesticides (Gonzalez-Pradas et al., 1993); chlorophyll (Gonzalez-Pradas et al., 1994); non-ionic contaminants (Smith and Jaffe, 1994);. Sepiolite has been used as deodorant (Ueda and Hamayoshi, 1992); and to adsorb methylene blue (Aznar et al., 1992); 4,4'-bipyridyl (Akyuz et al., 1993a); benzidine (Akyuz et al., 1993b), ammonium and ammonia (Bernal and Lopez-Real, 1993); tetrahydropyran, tetrahydrofuran and 1,4-dioxan (Breen, 1994).

2. EXPERIMENTAL

2.1 Adsorption of anionic dyes

Materials

Activated carbon provided by Merck and used as control.

Natural bentonite from deposits in the area of Cabo de Gata (located in the province of Almería, Spain).

Acid-activated bentonite prepared from the above natural bentonite by refluxing for 1 h with 0.5 N sulphuric acid. The resulting activated bentonite was washed until negative sulphate reaction and dried at 110 °C until constant weight.

Sepiolite was obtained from deposits in the area of Cabo de Gata

Acid Yellow 194 (Yellow Sellaset H, provided by TFL) is an azo 1:2 di-sulphonated Co-complex dye. The formula and the complete structure diagram are not available. A general outline of the dye structure is shown in Fig. 1 (Püntener, 1991). A solution with an initial concentration of 214.8 ppm was prepared. This dye solution showed a maximum absorbance at a wavelength of 402 nm.

Acid Blue 349 (Blue Sellaset H, provided by TFL) corresponds to the following formula: Chromate (3-), bis [6-[(5-chloro-2-hydroxy-4-nitrophenyl)azo]-5-hydroxy-1-

naphthalenesulfonato(3-)]-, trisodium (Fig. 1). A solution with an initial concentration of 216.3 ppm was prepared. This dye solution showed a maximum absorbance at a wavelength of 585 nm.

Acid Red 423 (Red Sellaset H, provided by TFL) is a monoazo 1:2 di-sulphonated Cr-complex dye. Its formula and structure diagram are unspecified. A general outline of the dye structure is shown in Fig.1 (Püntener, 1991). A solution with an initial concentration of 223.5 ppm was prepared. This dye solution showed a maximum absorbance at a wavelength of 516 nm.

Adsorption

A total of 100 cm³ of the mentioned solutions was added to a given amount of each adsorbent in stoppered bottles. The bottles were shaken for three hours at 25 °C. After shaking, the amount of unadsorbed dye was determined at the wavelength of maximum absorbance. The amount of adsorbed dye was calculated from the difference between initial and final concentrations.

The adsorption capacity, R, was calculated by applying the following equation:

$$R (\%) = [(C_0 - C) / C_0] \times 100 \quad (1)$$

where C₀ is the initial concentration of the dye and C is the equilibrium concentration.

The analysis of variance was applied to the results of adsorption capacity to assess the significant differences between the adsorbents.

The adsorption isotherm of the SELLA FAST Brown H dye (provided by TFL) on bentonite activated with 0.5 N H₂SO₄ was studied. A given amount of the dye was dissolved in 500 ml distilled water and different amounts of acid-activated bentonite were added. After shaking for three hours at 25 °C and settling overnight, the dye concentration from the supernatant was measured. The formula and the structure diagram of the dye are not available, although its dyeing characteristics are similar to those of the other studied dyes and it belongs to the same family.

The experimental results have been fitted to the Langmuir model (Kipling, 1975; Matthijs and De Henau, 1985) and to the Freundlich model (Adamson, 1982; Garcia et al., 2002):

$$\text{Freundlich: } X = K_f C^n \quad (2)$$

$$\text{Langmuir: } C/X = 1/bX_m + C/X_m \quad (3)$$

where:

X = mg of dye adsorbed per kg of adsorbent

C = equilibrium concentration in the solution (mg/l)

K_f = value of X at $C = 1$ mg/l

n = slope of the isotherm

X_m = retention capacity of the clay (mg/kg)

b = parameter related to the retention energy

The least squares method was used to calculate the parameters K_f and n of the Freundlich equation and the parameters b and X_m of the Langmuir equation.

2.2 Adsorption of non-ionic surfactants

Materials

The adsorbent used in these experiments was natural bentonite of a particle size of 75 μm (Volcangel, provided by BENESA, Bentonitas Especiales), which was activated with three concentrations of sulphuric acid: 0.1; 0.5 and 2.0 M (B01, B05 and B20).

Nonylphenol ethoxylated with 8 moles of ethylene oxide (Fluiderm S, provided by Inquímica) was studied. A solution with an initial concentration of 2400 mg/l was prepared.

Different amounts of surfactant were added to known amounts of acid-activated bentonite so that the relation between g of surfactant and g of adsorbent varied from 0.1 to 1.0 in a total volume of 0.250 l. After shaking for 3 hours at 25 °C and settling

overnight, the concentration of the surfactant from the filtered supernatant was determined by measuring its absorbance at 220 nm.

The experimental results were fitted to the Freundlich and Langmuir equations as mentioned above. The adsorption capacity as a function of the adsorbent was determined by applying Eq 1.

A 1-g portion of bentonite 01 was dispersed in 1 l solution containing 1 g of nonylphenol ethoxylated with 8 moles ethylene oxide (Fluiderm S, provided by Inquímica). Samples were taken at time intervals, filtered and analysed for surfactant concentration with a Perkin Elmer UV-VIS Spectrophotometer, to study the adsorption kinetics. All the experiments were carried out at 25 °C.

3. RESULTS AND DISCUSSION

3.1 Adsorption of anionic dyes

Table 1 shows the adsorption capacity (as defined by Eq. 1) of the adsorbents with Acid Yellow 194, Acid Blue 349, Acid Red 423.

The analysis of variance was applied to the results of adsorption capacity to assess the significant differences between the adsorbents. Table 2 shows mean values, standard errors and significance level of differences between the adsorbents. The sepiolite (97.9 %) and the bentonite activated with sulphuric acid 0.5 N (84.9 %) showed the highest adsorption capacity. The difference in adsorption capacity between the adsorbents was significant at 5 % level.

Fig. 2 shows the adsorption isotherm of the SELLA FAST Brown H dye using bentonite with an acid activation level of 0.5 N as adsorbent.

According to the classification of Giles et al. (1960), the isotherm seems to be of the H type, indicating that the dye molecules have such a high affinity for the bentonite surface that they are completely adsorbed in a dilute solution. The adsorbed dye anions form a monolayer with the sulphonate groups as close as possible to the adsorbent

surface. An excess of protons are probably adsorbed during the acid activation process. Sulphate groups are then counterions which compensate for the positive surface charges. An exchange between the sulphate ions by the adsorbed dye anions may take place. A similar mechanism was described in the adsorption of sulphonated dyes by chromatographic alumina pre-treated with hydrochloric acid (Cummings et al., 1959).

The K_f value of the Freundlich equation (Table 3) indicates that the acid-activated bentonite has a very strong adsorption capacity for anionic dyes in diluted solutions. The X_m value of the Langmuir equation also indicates that the studied clay possesses a very high retention capacity so that these materials are very useful in removing anionic dyestuffs from tannery waste waters.

3.2 Adsorption of non-ionic surfactants

Fig. 3 shows the adsorption isotherms of the non-ionic surfactant on three acid activated bentonites. The isotherms are of S type, of the classification of Giles et al. (1960). This indicates that the adsorption is promoted at enhanced surfactant concentration. This behaviour is explained by interactions between surfactant molecules. This adsorption is cooperative which implies a side-by-side association between adsorbed molecules.

Langmuir isotherm could not be fitted to the experimental data. The Freundlich equation provided much better results (Table 4). The acid treatment strongly attacks the clay structure. It was observed that the adsorption properties went through a maximum with the concentration of the added acid. This maximum corresponded to the activation treatment with 0.5 M H_2SO_4 , which showed the highest K_f value.

Fig. 4 shows the adsorption kinetics of the non-ionic surfactant on bentonite activated with 0.1 M H_2SO_4 . Equilibrium was reached after 30 minutes. This result again indicates a high affinity of surfactant molecules for the active sites of the bentonite.

4. CONCLUSIONS

- The capacity of acid-activated bentonite and sepiolite to adsorb anionic dyes normally used in the tannery is very high. These clays could be successfully applied at industrial scale to clean the waste waters of dyeing processes. The dye molecules

have such high affinity for the acid bentonite surface that they are completely adsorbed from dilute solution. The adsorbed dye anions form a monolayer with the sulphate groups as close as possible to the adsorbent surface. An excess of proton ions are probably adsorbed in the acid activation process. Sulphate groups of the sulphuric acid are then counterions which compensate for the positive surface charges. An exchange between the sulphate ions by the adsorbed dye anions may take place.

- The non-ionic surfactant was removed at 90 % in 10 minutes due to the high affinity between surfactant and adsorbent. The isotherms are of S type (cooperative adsorption) which implies a side-by-side association between adsorbed molecules, promoting the adsorption.
- Bentonite activated with 0.5 M H₂SO₄ was the most effective adsorbent.

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Table 1. Adsorption of anionic dyes

Adsorbent	Adsorption Capacity, R (%)		
	Acid Yellow 194	Acid Blue 349	Acid Red 423
Activated carbon	49.2	68.2	26.3
Natural bentonite	24.9	92.7	29.1
Acid-activated bentonite	71.1	98.4	85.2
Sepiolite	98.6	99.9	95.2

Table 2. Adsorption of anionic dyes. Mean values, standard errors and significance level of differences between the adsorbents

Adsorbent	Adsorption capacity (%)
Activated carbon	47,9 ± 9,9
Natural Bentonite	48,9 ± 9,9
Acid-activated Bentonite	84,9 ± 9,9
Sepiolite	97,9 ± 9,9
Significance level of differences	5 %

Table 3. Parameters of the Freundlich and Langmuir equations for the adsorption of SELLA FAST Brown H dye by acid-activated bentonite

Equation	K _f (mg/kg)	n	X _m (mg/kg)	b	r ²
Freundlich	20.417	0.486	---	---	0.996
Langmuir	---	---	360.505	1.48 x 10 ⁻²	0.996

Table 4. Parameters of the Freundlich equation for the adsorption of non-ionic surfactants

Sample	K_f (mg/kg)	n	r^2	R (%)
B01	204	1.56	0.972	93.6
B05	891	1.27	0.998	93.3
B20	192	1.38	0.966	86.9

B01: bentonite activated with 0.1 N sulphuric acid

B05: bentonite activated with 0.5 N sulphuric acid

B20: bentonite activated with 2.0 N sulphuric acid

Figure 1. Structure of the dyes. **A:** Outline of the yellow SELLASET H dye structure. **B:** Structure of the blue SELLASET H dye. **C:** Outline of the red SELLASET H dye structure

Figure 2. Adsorption isotherm of SELLA FAST Brown H dye by bentonite activated with 0.5 N H₂SO₄

B01: bentonite activated with 0.1 N sulphuric acid

B05: bentonite activated with 0.5 N sulphuric acid

B20: bentonite activated with 2.0 N sulphuric acid

Figure 3. Adsorption isotherms of ethoxylated nonylphenol by acid-activated bentonites

Fig. 4. Adsorption kinetics of ethoxylated nonylphenol by bentonite activated with 0.1 M H₂SO₄