

PILLARED CLAYS AS ADSORBENTS FOR SOME ACID DYES♦

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Abstract: This paper is dealing with the obtaining of some pillared smectites (SmP) and with the assessment of their adsorptive affinity for several azoic acid dyes, used for leather and fur dyeing. Three SmPs were obtained by the reaction between a native Na-smectite (Sm) and partially hydrolyzed solutions of: AlCl_3 (PAC), FeCl_3 (PFC) and $\text{Fe}_2(\text{SO}_4)_3$ (PFS). The adsorption capacity of three acid dyes – *Acid yellow 166*, *Acid Red 337* and the *Acid Green 73 1:2 Cr-complex*, was determined at $\text{pH} = 5.5$, over a $25 \div 300$ mg/L dye concentration range and adsorbent dosage of 2 g/L. The minimal metal/Sm ratios required for a permanent pillaring effect are: 3 mmol Al/g Sm and 4 mmol Fe/g Sm, respectively. The adsorbents efficiency decreases in the order: Sm-PAC > Sm-PFC > Sm-PFS, while the dyes adsorption capacity decreases as follows: Yellow > Green > Red. The maximum uptake was of 232 mg Yellow dye/g Sm-PAC and the minimal uptake was of 28.35 mg Red dye/g Sm-PFS. The S-shaped experimental adsorption isotherms confirm the SmPs mesoporous solids behaviour.

Keywords: *colored wastewater, adsorption, pillared clays, acid dyes*

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INTRODUCTION

Synthetic dyes are extensively used in different processing industries such as textile, leather, printing, cosmetic, drug and food. The majority of dyestuffs are used today for textiles and leather processing and most of them fall into the azo and anthraquinone classes [1].

Dyes removal from industrial wastewater is an environmental issue, due to their high organic loads, low biodegradability, toxicity [2], mutagenicity [3] and carcinogenicity [4]; even in low concentrations, color imparts an unaesthetic appearance to water.

The selection of adequate methods for effective removal of dyes from wastewaters depends on many factors: the dye chemical structure, specific behavior at different *pH* values, concentration in wastewater etc. Physicochemical, chemical and biological methods are used for dyes removal: coagulation-flocculation, oxidative degradation, precipitation, biodegradation, adsorption, biosorption. As the biological treatment shows poor effectiveness for color removal, physicochemical and chemical methods are preferred. Adsorption is the common treatment for colored wastewaters with low dye concentrations. The conventional adsorbent is the activated carbon but many other low-cost adsorbents, such as: zeolites, clays, agricultural and industrial wastes, biosorbents etc. are effective in the colored water treatment [5].

Clay minerals are well-known as natural adsorbents and used in various industrial and domestic activities. Characteristic dimensions of nanometric scale make some clays valuable substrates for the obtaining of nanostructured materials. Smectite, one of the most abundant clay minerals, is a dioctahedral 2:1 phyllosilicate which, due to its expandable lamellar structure, is amenable to intercalation reactions of “host-guest” type [6], in which different “guest” reactants are inserted in the interlayer region of the “host” mineral with the preservation of the layered structure. One class of such products is of particular interest: the pillared clays (PILCs), obtained by the intercalation of Al/Fe/Zr/Cr polyoxycations followed by calcination, when the metal polyoxycations turn into stable oxide pillars, strongly bonded to the host mineral surfaces. The oxide pillars permanently prop open the layered clay edifice and give birth to microporous or mesoporous materials, with stabilized, adjustable porosity. PILCs are mainly used as acid catalysts [7] but can be also used as selective adsorbents, due to their mesoporous solids characteristics, the porosity of which can be controlled by the interlayer pillars size and density; applications for pollution removal were reported [8].

The Al-pillared clays are preferred, because the main intercalation species, i.e. $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]$ or Al_{13} Keggin ion is well defined for its structure and can be obtained in a reproducible way [7]. Smectite pillaring with iron polyhydroxy oligomers is more difficult, mainly because iron is very sensitive to hydrolysis and precipitation and the hydrolysis can not be stoichiometrically controlled by the OH/Fe ratio. Fe(III) polyoxycations have not been yet well-defined, even if Fe_{3-13} oligomer and Fe_{13-33} polymer fractions were identified [9]. Preferred iron pillaring solutions are obtained starting from FeCl_3 and metal organic complexes [10], while the sulfated oxyhydroxyde complexes are scarcely used, due to the lower specific surface areas and acidity, and poor thermal stability of sulfate group [11].

Native and chemically modified clays can be used for the removal of all dye classes with industrial applications [12], provided the adsorbent surface matches the dye

molecule charge and conformation. Few works have been dedicated to the interaction between PILCs and colorants [13].

The aim of this work is to obtain several Al- and Fe(III) PILCs and to study their adsorptive affinity towards azoic acid dyes used in leather processing, in order to assess the opportuneness of such sorbent products in decolorization treatments. The adsorbent-adsorbate interaction mechanisms were assessed by means of experimental isotherms, which were modeled according to the Freundlich model.

MATERIALS AND METHODS

Materials

The substrate for the PILCs obtaining was a native Na-bentonite from Valea Chioarului deposits, 91.6% purity, with a cation exchange capacity (CEC) of 65 meq/g and Methylene Blue Index (MBI) of 352.5 mg/g. The clay fraction ($d < 2 \mu\text{m}$) was separated from the pristine mineral by plain sedimentation from aqueous suspension, followed by centrifugation of supernatant, and slurry air drying and milling.

Reagents for the obtaining of the pillaring solutions: aluminum chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, hydrogen peroxide H_2O_2 , sodium hydroxide NaOH and H_2SO_4 98%, were of synthesis grade.

Three anionic dyestuffs, provided by TFL Ledertechnik GmbH, were tested: SELLAFAST YELLOW 4GL [(CI) Acid Yellow 166, azoic dye], SELLACID RED PF [(CI) Acid Red 337, azoic dye], SELLA FAST OLIVE C-SG [(CI) Acid Green 73, 1:2 Cr complex of an azoic dye]. The proprietary products were used without preliminary purification. The dye solutions were obtained with distilled water, previously acidulated at $\text{pH} \approx 5.5$ with HCl.

Preparation of pillared smectites

The pillared smectites preparation comprised two steps: (1) the obtaining of the pillaring solutions and (2) the intercalation of the poly-oxycations into the clay interlayer, by cation exchange reactions.

The Al-based pillaring solution (PAC) was obtained by controlled hydrolysis of a 0.25M AlCl_3 solution with a 0.5M NaOH solution (molar ratio $\text{OH}/\text{Al} = 2.5$), added with a rate of 1.4 mL/min under vigorous stirring, at 80 °C. The final solution was 0.11M Al and had a $\text{pH} = 4.5$.

One Fe-based pillaring solution (PFC) was obtained by controlled hydrolysis of a 0.2 M FeCl_3 solution with a 0.4 M NaOH solution, added with a rate of 0.55 mL/min under vigorous stirring, at 45 – 50 °C. The resulting solution was 0.1M Fe and had a $\text{pH} = 2.55$. The second Fe-based pillaring solution (PFS) was obtained starting from FeSO_4 , by a procedure described in [14], which basically implies the use of the hydrogen peroxide (H_2O_2) both for the oxidation of FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$ and the subsequent partial hydrolysis, in the absence of catalysts. The pillaring solutions properties are summarized in Table 1.

The procedure for the pillared smectites obtaining was as follows: smectite suspensions of 10 % w/w in deionized water were obtained by swelling the mineral clay overnight

and completing with the required amount of water. The smectite suspension was slowly added over the pillaring solutions, under vigorous stirring, and completed with water, so that the final smectite concentration in the reaction mass was 1 % w/w. The metal/smectite ratio ranged between $0.4 \div 4$ mmol metal/ g smectite. The reaction mass was maintained under rapid mixing for 3 hours at room temperature. Each reaction product was washed for 8 times by sedimentation-decantation, with amounts of water equal to the initial reaction mass. The resulting slurry was then washed by several filtration- resuspending cycles, until the filtrate conductivity was less than 30 mS. The washing waters were collected and analyzed for the Al and Fe residual concentration, by conventional complexometric titration. The final precipitates were air-dried at 100 °C and milled. The thermal behavior of the obtained SmPs was investigated by TG analysis, performed on a MOM device with a heating rate of 10 °C/min.

Table 1. Pillaring solutions characteristics

SmP	Pillaring solution characteristics
Sm-PAC	AlCl ₃ basified with NaOH at 80 °C; 0.11M Al ; OH/Al = 2,5 :1 ; NaOH adding rate : 1.4 mL/min ; final pH = 4.5 ; 14 days ageing
Sm-PFC	FeCl ₃ basified with NaOH at max. 50 °C; 0.1M Fe ; OH/Fe= 2 :1 ; NaOH adding rate : 0.55 mL/min ; final pH = 2.55 ; 24 h ageing
Sm-PFS	Fe ₂ (SO ₄) ₃ basified at max. 50 °C; 2.37M Fe ; basicity = 13.8 % ; final pH = 1.6 ; 24 h ageing

Adsorption tests

Batch adsorption experiments were performed at 25 °C. A series of flasks, containing 100 mL dye solutions of increasing concentration from 25 to 300 mg/L and 2 g/L clay-based adsorbent, were stirred with a magnetic stirrer for 4 hours. After overnight equilibration, the supernatant was collected by centrifugation and the residual dye concentration was determined photocolormetrically on a FEK-56M-Y4.1 photocolormeter, at wavelengths of 400, 540 and 630 nm for the yellow, red, and olive dyes, respectively. The difference between the dye concentration before and after the sorption process was used to obtain dye sorption data and isotherms. The experimental data were processed according to the Freundlich sorption isotherm and the model kinetic parameters were obtained.

RESULTS AND DISCUSSION

The main problem with the pillaring solutions is accidental precipitation during basification with direct alkali addition; precipitation in pillaring solutions was avoided only when the prescribed temperature and alkali adding rate were observed (see Table 1) under continuous vigorous stirring. The slower adding rate of the alkali solution for the obtaining of the PFC pillaring solution (0.55 mL/min) is consistent with the higher hydrolytic sensitivity of iron, compared to aluminum. The use of H₂O₂ in acid protected medium for the PFS obtaining avoided local precipitation, which is commonly associated with the basic metal salts solutions precipitation.

The minimal metal/Sm ratios required for a permanent pillaring effect were: 3 mmol Al/g Sm and 4 mmol Fe/g Sm, which corresponds to 1400 % and 1800 % satisfaction degrees of the smectite CEC, respectively. When lower metal/clay ratios were used, unreacted clay separated at the bottom of the reaction vessel during the first washing-sedimentation cycles. Washing is a very important phase, because hydrolysis of the inserted cations continues in aqueous media after the cation-exchange reaction. Flocculation and sedimentation are improved after each settling-decantation cycle, which confirms the development of the hydrolytic – polymerization processes after the insertion of the polyoxocation species into the clay interlayer spaces.

Aluminum concentration in the washing waters was equal to zero, while residual iron concentration showed 95 – 98 % retention of iron in the smectite interlayer.

The obtaining of the SmP was limited to the conventional pillared clays [7], i.e. the air-dried intercalation products, without further calcination, in order to preserve the porosity and the “card-stack” structure of the intercalated product as much as possible.

Profiles of the TGA curves are shown in Figure 1. The Sm-PFS was heated up to 500 °C, to avoid the platinum crucible attack by the sulfate groups. All diagrams have similar shapes for all the three SmP inorganic-inorganic intercalates and show weight loss of 8.7 % for Sm-PAC, 8.2 % for Sm-PAC and 5 % for Sm-PFS. These figures, together with the inflection points at 125 °C and 700 °C are consistent with the inorganic nature of the products and indicate mainly the hydration and hydroxylation water removal.

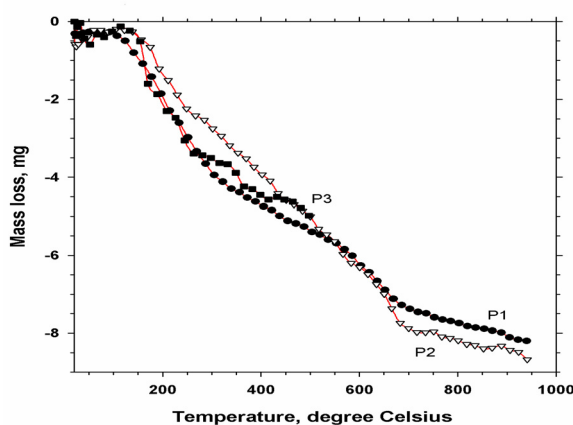


Figure 1. The TGA curves for SmPs:

● P_1 – Sm-PFC; ■ P_2 – Sm-PAC; ▽ P_3 – Sm-PFS; Sample mass = 100 mg

Experimental sorption isotherms, grouped after the adsorbent type, are given in Figures 2, 3 and 4, respectively. The S-shape of the sorption isotherms confirms the mesoporous solids characteristics of the obtained products. The sorptive affinity of the three SmPs decreases in the order: Sm-PAC > Sm-PFC > Sm-PFS, while the dyes adsorption capacity decreases as follows: Yellow > Green > Red, irrespective of the adsorbent type. These observations suggest that the SmPs efficiency depends both on the structural and surface properties of the adsorbent and the dye chemical structure. The Al-Sm has the most opened-up and regular layered structure, due to the well-defined Al-Keggin intercalated cations and due to the mild pH conditions in which the cation exchange – intercalation processes took place. At $pH = 4.5$, the acid attack upon the

mineral substrate is minimal and the tactoids integrity is preserved. Fe-based pillaring solutions contain a wider range of poly-oxycationic species, which lead to less-defined porosity. The PFS-Sm poor efficiency may be due to the extreme acidic conditions of the intercalation process; at $pH = 1.6$, the acidic attack on the octahedral layer of the mineral tactoids determines the mineral amorphisation, which results in poor regularity of the intercalated edifice. The pillaring effect is also diminished by the higher volumes of the sulfated poly-oxycations [11], which can not enter the interlayer region. Dyes adsorption on the SmP products involves both mineral – dye interactions and dye – dye interactions. The experimental isotherms shape shows a three-phase sorption process: firstly, strong mineral surface and pillars – dye interactions take place, when the active, positively charged sites are occupied by the dyes anions; then, the adsorbed dye molecules orientate themselves to find advantageous positions and allow other dye molecules to enter the pores, through hydrophobic dye – dye interactions, until the pores are filled.

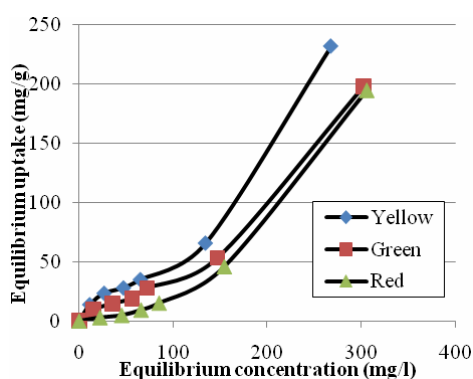


Figure 2. Dyes sorption isotherms on Sm-PAC

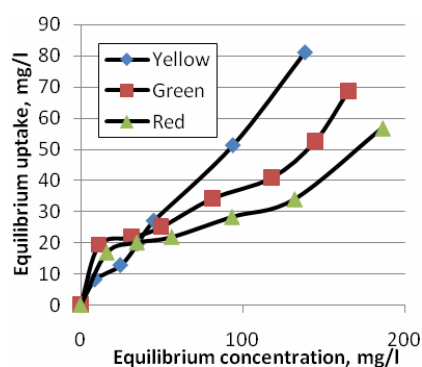


Figure 3. Dyes sorption isotherms on Sm-PFC

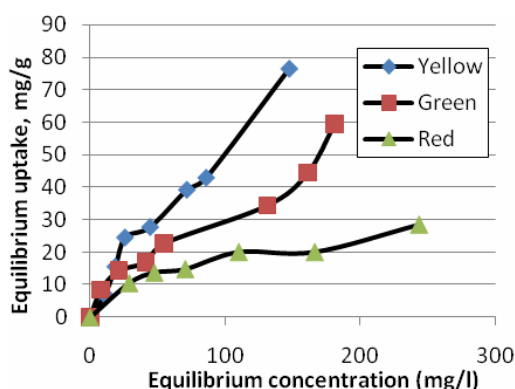


Figure 4. Dyes sorption isotherms on Sm-PFC

The maximum experimental uptake was of 232 mg Yellow dye/g Sm-PAC and the minimal uptake was of 28.35 mg Red dye/g Sm-PFS. Comparing to other clay-based adsorbent, such as *organoclays* which can retain up to 583 mg/g Yellow, 270 mg/g Red, and 609 mg/g Green, respectively [15], these figures are lower but still satisfactory. Organoclays exhibit higher uptakes due to the adsorbent – adsorbate hydrophobic interactions, but pillared clays are more environmentally friendly than organically modified minerals and can be easily tailored for targeted adsorbates.

Sorption on the SmP products was modeled according to the Freundlich isotherm:

$$X = K \cdot C^{1/n} \quad (1)$$

where: X – dye uptake on the adsorbent, at equilibrium (mg/g); C – dye concentration in solution, at equilibrium, (mg/L) , and K and n are the model parameters. From the linearized form of Eqn. (1), the model parameters and the correlation factors, R^2 were calculated, as shown in Table 2.

Table 2. *Freundlich isotherm parameters and model correlation coefficients*

Dye	Sm-PAC			Sm-PFC			Sm-PFS		
	K	n	R^2	K	n	R^2	K	n	R^2
Yellow	2.297	2.82	0.906	2.349	2.083	0.966	2.252	3.861	0.949
Green	2.712	1.257	0.930	1.569	0.603	0.853	1.780	1.175	0.959
Red	5.285	0.223	0.967	1.55	0.69	0.855	3.706	1.934	0.989

The correlation coefficient (R^2) values indicate that the experimental data fitted satisfactorily to the proposed adsorption isotherm, taking into account that the sorption experiments were carried out over a wide range of dye concentrations. The distribution coefficient (K) values are consistent with the dyes tendency to be retained onto the adsorbent. The $n > 1$ coefficients show favorable conditions for adsorption.

Modeling by more complex isotherms involving more coefficients requires the determination of some coefficients from other considerations, provided thermodynamical data are known for the given adsorbate.

CONCLUSIONS

Chemical modifications of certain clay varieties through straightforward experimental procedures lead to porous materials with selective adsorptive properties.

The Romanian native Na-bentonite is amenable to chemical transformations through host-guest reactions with Al and Fe-based polyoxycations resulting in porous products from the pillared clay class.

The effectiveness of pillared smectites as adsorbents for acid azoic dyes depends both on the structure of the adsorbent and the targeted pollutant: adsorbent products with well-defined porosity and well preserved lamellar structure, such as Sm-PAC exhibit higher adsorbate uptake than the Fe-pillared products. The adsorption capacity of the tested dyes decreased in the order: Yellow > Green > Red, irrespective of the adsorbent type. The maximum adsorption capacity was of 232 mg Yellow dye/g Sm-PAC and the minimal uptake was of 28.35 mg Red dye/g Sm-PFS.

The adsorbent – adsorbate interaction involves both substrate – dye electrostatic interactions and dye – dye hydrophobic interactions. The sigmoidal shape of the experimental isotherms confirms the mesoporous solids behaviour of the tested materials.

Treatment of low-concentration colored wastewater with pillared smectites can be an eco-friendly alternative to other advanced treatment techniques, provided a suitable contact technique is put into practice and the interference with other pollutants possibly present in the water is not significant.

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