SORPTION AND PHOTOCATALYTIC DEGRADATION OF AZOIC DYES ON TiO$_2$-PILLARED MONTMORILLONITIC CLAY

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This paper investigated the sorption and photodegradation processes of Congo Red on TiO$_2$-pillared montmorillonitic clay and TiO$_2$-pillared montmorillonitic clay modified by surfactant intercalation. The structural properties of the TiO$_2$-pillared montmorillonitic clay and TiO$_2$-pillared montmorillonitic clay modified by surfactant intercalation indicated an enlargement of the basal spacing of the clay. The enlargement was much pronounced as the used surfactant content increased. The Langmuir – Hinshelwood model was the base for interpreting kinetics data and working out of the rate constant and reaction order. The study determined the role of photocatalysis for the removal of Congo Red; under well determined working conditions, the efficiency of the process was double as compared to the simple sorption of the dye. In the studied experimental conditions a good correlation was observed between photocatalytic activity of the TiO$_2$-pillared montmorillonitic clay and TiO$_2$-pillared montmorillonitic clay modified by surfactant intercalation and both the specific surface area and the size of TiO$_2$ crystallites values, affected by the modification route of Valea Chioarului clay.

INTRODUCTION

Reports within the last years pointed towards the presence of new xenobiotic substances in the environment as a consequence of massive utilization of chemicals for various manufacturing purposes and in day-by-day life. The incapacity of the conventional wastewater treatment techniques to fully eliminate most of the biorefractory pollutants has increased the environmental awareness with respect to set up and development of more effective treatment systems.

The effluent discharged by various textile industries contains a large number of dyes, increasing the total COD of wastewaters. Some dyes are reported to cause allergy, dermatitis, cancer and mutation in human. A strong carcinogenic potential with extremely serious consequences for the human health was ascribed to azoic dyes and their degradation products. Moreover, the persistence of colour appearance (at concentration above 1 mg·L^{-1}) in treated wastewaters prevents their re-use. Congo Red, an azoic dye, has been used in the cellulose industries (cotton textile, wood pulp and paper) to a lesser extent due to its high toxicity.

Because of stringent government legislations, it is important to remove dyes from wastewater before they are contacted with unpolluted natural water.[1]

There are several traditional chemical and biological processes for dye removal, but the application of these techniques has been restricted due to the essentially nonbiodegradable nature of dyes, which are stable to light and oxidation.[2]

Adsorption is one of the effective methods to remove coloured textile contaminants from wastewaters. A lot of clays, such as sepiolite, montmorillonite, smectite, have been investigated for this purpose.[3-5] Due to their structural properties, high chemical stability, high specific surface area and high adsorption capacity, they can be used to remove dye from effluents. The clays can adsorb organic substances either on its external surfaces or within its interlamellar spaces, by interaction with or substitution of the exchange cations in those spaces.[6]

Also, hydrotalcite-like compounds display high adsorption capacities for dye molecules and they can be very competitive with other sorbents.[7]

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Orthman *et al.* showed that hydrotalcite had an adsorption capacity toward Acid Blue 29 comparable with that of commercial activated carbon.[8]

Pillared clays prepared by exchanging polycations within the interlayer region of expandable clay minerals which, following calcinations, are transformed into metal oxide pillars fixed to the layers of the clay to yield rigid cross-linked materials.[9] A variety of inorganic oxides: Al_2O_3, ZrO_2, TiO_2, Cr_2O_3, Ga_2O_3, and mixed-metal oxides Al_2O_3-Ga_2O_3 , Al_2O_3-SiO_2 have been successfully pillared in smectites to generate high surface area catalysts.[10-12]

Romanian montmorillonite pillared with various metal compounds, possessing additional functions originating in both surface area extension and identity of the pillars, are interesting from academic and industrial point of view. TiO_2 and TiO_2-based materials have attracted growing interest because they can be used as photocatalysts for effective treatment of wastewaters polluted with toxic organic compounds.[13-16]

The aim of this work was to investigate the efficiency of TiO_2-pillared montmorillonitic clay and TiO_2-pillared montmorillonitic clay modified by surfactant intercalation for removal of an azoic dye, namely Congo Red, from aqueous solution, by adsorption and photodegradation processes.

RESULTS AND DISCUSSION

Sample characterization

The XRD data of prepared samples, related to diffracting angle θ of [001] reflection, interplanar distance d , are show in Table 1.

The crystallite TiO_2 size was estimated according to Scherrer formula:

$$L = K \cdot \lambda /(\beta \cdot \cos\theta) \qquad (1)$$

where: λ is the wavelength of the X-ray radiation ($CuK\alpha = 0.15406nm$), K is a constant taken as 0.89, β is the line width at half-maximum height, and θ is the diffracting angle of (101) reflection of anatase ($2\theta=25.39$). A full samples characterization is presented in our previous paper.[17]

Table 1

Some structural results of obtained samples

Sample	2θ	$d_{001,}$ nm	S_{BET} (m^2/g)	Ø $TiO_2,$ nm
Na-clay	7.18	1.239	32.4	-
Ti-PILC	6.08	1.459	89.3	22.2
S_1-Ti-PILC	6.23	1.416	119.5	17.1
S_2-Ti-PILC	4.63	1.904	207.9	6.6
S_3-Ti-PILC	3.60	2.451	301.4	5.8

XRD results show for TiO_2-pillared sample that the basal (001) peak around $2\theta=7$ (characteristic for parent clay) is shifted toward lower 2θ value. This result indicates an increase of the basal spacing of the clay after performing the pillaring process.

In the case of TiO_2-pillared montmorillonitic clay modified by surfactant intercalation (S_i-Ti-PILC samples) it can be seen that the basal (001) peak is considerable shifted toward lower 2θ value. These results clearly indicates an enlargement of the basal spacing of the clay. The enlargement is much pronounced as the used surfactant content increase.

The process of enlargement of the basal spacing of the clay, followed by titanium pillars formation results in an increase of specific surface area, proportional to the used surfactant content.

The small dimensions of TiO_2 crystallite has a high contribution to the specific surface area value.

Effect of pH on removal efficiency of Congo Red on monocationic and pillared montmorillonitic clay

Figs. 1 and 2 show sorption efficiency of Congo Red on the monocationic form, Na-clay, as a function of pH.

The removal efficiency was calculated by using the following relationship:

$$\eta = \left[\left(C_i - C_f\right)/C_i\right] \cdot 100 \quad [\%] \qquad (2)$$

where: C_i – dye initial concentration, $mg \cdot L^{-1}$;
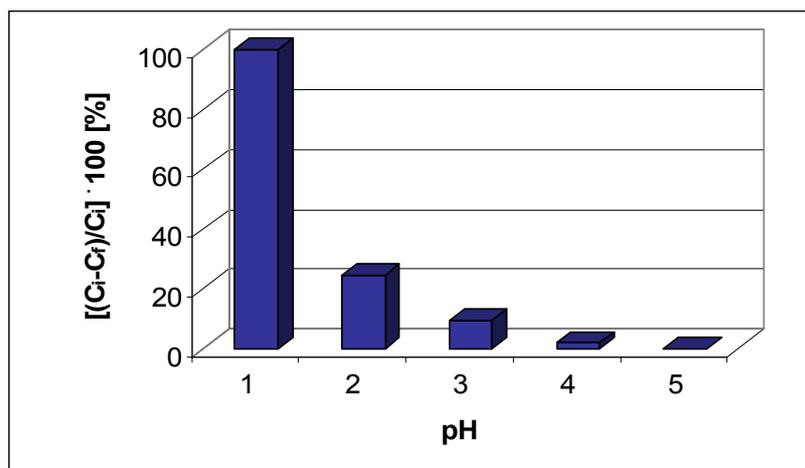 C_f – dye residual concentration after certain intervals, $mg \cdot L^{-1}$.

Fig. 1 – Variation of removal efficiency of Congo Red on Na-clay within acidic pH range:
C_i=20 mg·L^{-1}; [Na-clay]=1 g·L^{-1}; stirring=15 min.
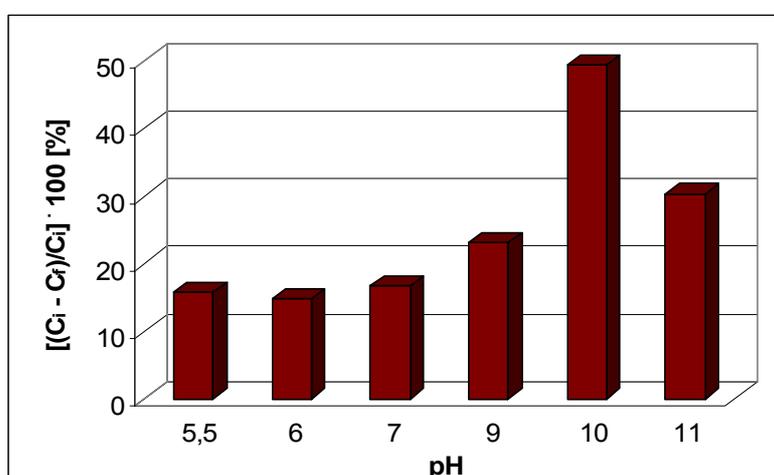

Fig. 2 – Variation of removal efficiency of Congo Red on Na-clay within basic pH range:
C_i=20 mg·L^{-1}; [Na-clay]=10 g·L^{-1}; stirring=30 min.

For the monocationic clay, within 1-5 pH range, the removal efficiency decreased sharply as pH increased from 1 to 5 (Fig.1). Based on literature,[18] Congo Red tends to aggregate in aqueous and organic solutions. The aggregates might have various sizes and shapes due to hydrophobic interactions between aromatic rings of dye molecules. This aggregation phenomenon is more noticed for high Congo Red concentrations, at high salinity and/or low pH. The formed aggregates (micelles) separate and precipitate onto solid surfaces. As a result, the high removal dye efficiency cannot be ascribed to the sorption capacity of the monocationic clay but to dye behaviour under strong acidic pH.

Within basic pH range, it was necessary to increase the monocationic clay concentration 10 times to have final concentrations for the dye that could be analytically determined and the maximum removal efficiency was 49% at pH = 10 (Fig. 2).

As sorption experiments within basic pH range required high concentrations of adsorbent, the dye removal efficiency on the pillared clay (Ti-PILC) and under photocatalytic conditions was investigated only within acidic pH range (Fig. 3).

The aggregation capacity of Congo Red at low pH (pH = 1) might explain the high removal efficiency on Ti-PILC (96.3%) and under photocatalytic conditions. However, a good removal efficiency of the dye resulted under the given working conditions and pH = 4 (46.7%). For that reason, the optimum pH was considered as 4.0 and used throughout all experiments, which were conducted on the synthesized samples.
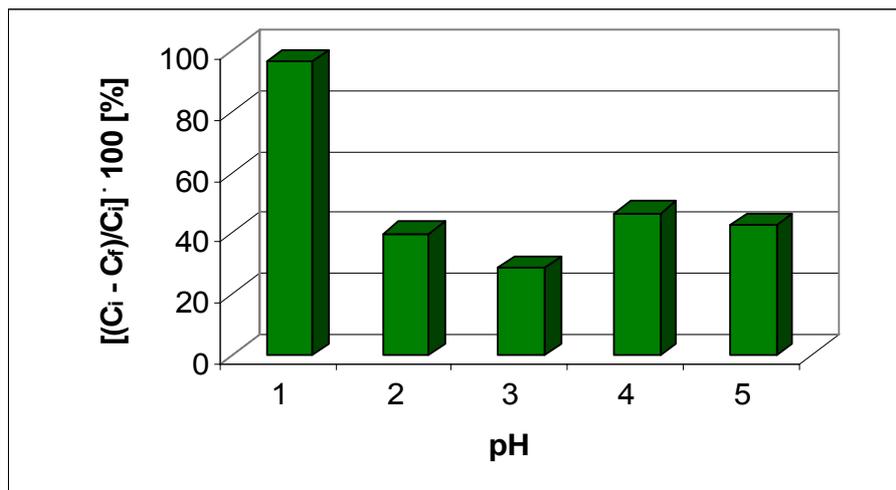
Fig. 3 – Variation of removal efficiency of Congo Red on Ti-PILC within acidic pH range and under photocatalytic conditions: C_i=20 mg·L^{-1}; [Ti-PILC]=1 g·L^{-1}; stirring =15 min.
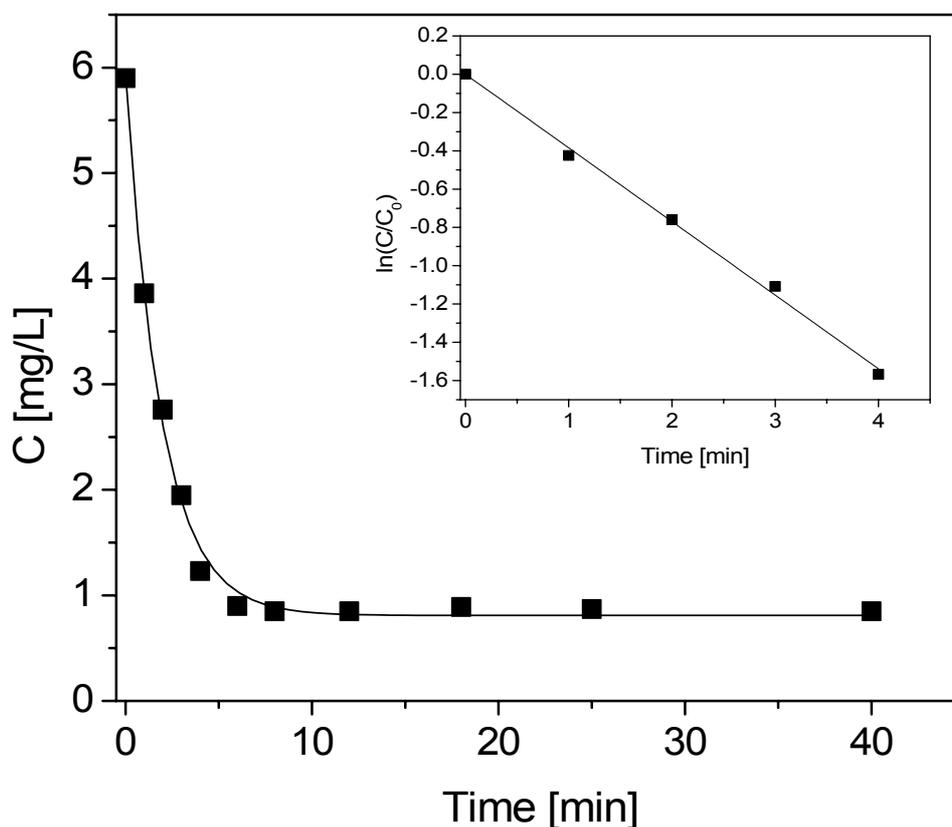

Fig. 4 – Kinetics curve for photocatalytic degradation of Congo Red on Ti-PILC sample; Inset: detail of the linearized kinetics plot; Conditions: [Ti-PILC]=1 g·L^{-1}; C_i=6 mg·L^{-1}.

Kinetics of photodegradation

Kinetics curve for photocatalytic degradation of Congo Red on Ti-PILC sample is presented in Fig. 4.

The photocatalytic degradation of several dyes over TiO$_2$-pillared clays obeys the Langmuir – Hinshelwood kinetics given by equation 3:[19]

$$r = -\frac{dC}{dt} = k \cdot \frac{K \cdot C}{1 + K \cdot C} \tag{3}$$

where: r - the rate of dye degradation, mg·L^{-1}·min^{-1};

k - the rate constant, min^{-1};

C - the dye concentration, mg·L^{-1};

K - the adsorption coefficient, L·mg.$^{-1}$

Under the conditions of the adsorbent excess, from the kinetics point of view, an apparent first-order model can be assumed (eq. 4):

$$\ln(C_t / C_0) = -k' \cdot t \qquad (4)$$

where: k' – the pseudo-first-order rate constant, min^{-1} (Table 2).

Table 2

Kinetics characteristics

Kinetics model	k', min^{-1}	Correlation coefficient, R^2
Pseudo-first order rate	$3.85 \cdot 10^{-1}$	0.9970

Photodegradation and adsorption experiments

Influence of pillaring by TiO$_2$ on dye adsorption

To study the influence of pillaring by TiO$_2$, two sets of kinetics experiments were carried out by using the monocationic clay (Na-clay) and TiO$_2$-pillared montmorillonitic clay (Ti-PILC) under the following working conditions: dye initial concentration –20 mg·L^{-1}; adsorbent concentration –0.4 g·L^{-1}.

The plots of variation of Congo Red residual concentration (Fig. 5) show that the monocationic clay does not adsorb the dye. On the contrary, for the TiO$_2$-pillared clay, the dye concentration decreased by time, the removal efficiency was 20%.
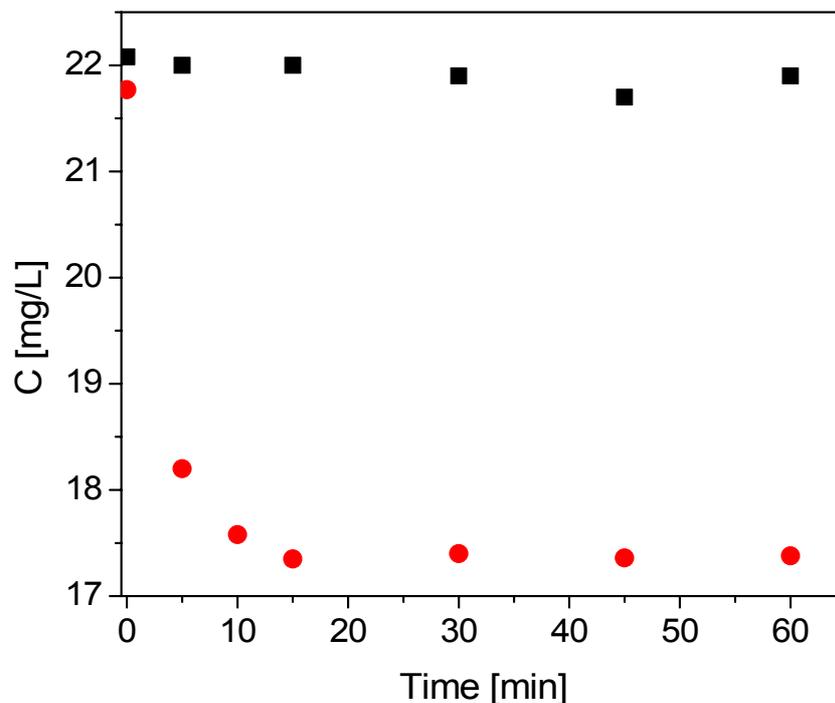

Fig. 5 – Variation of Congo Red concentration by time: C$_i$=20 mg·L^{-1}; ■ – [Na-clay] = 0.4 g·L^{-1}; ● – [Ti-PILC] = 0.4·g L^{-1}.

Influence of photocatalysis on the removal efficiency of Congo Red

To highlight the effect of photocatalysis on dye removal efficiency as compared to adsorption, several kinetics experiments were carried out by using the pillared clay (Ti-PILC). The initial working conditions were as follows: dye solution concentration - 20 mg·L^{-1}; initial pH of solution – 4; adsorbent concentration – 0.4 g·L^{-1}.

Fig. 6 shows the results as kinetics plots. On the pillared clay (Ti-PILC), in the absence of UV irradiation (in dark), the retention of Congo Red occurred, but the efficiency was low (about 20% after 60 minute), while UV irradiation led to efficiency of about 40%. Thus, photocatalysis practically doubled the removal efficiency.
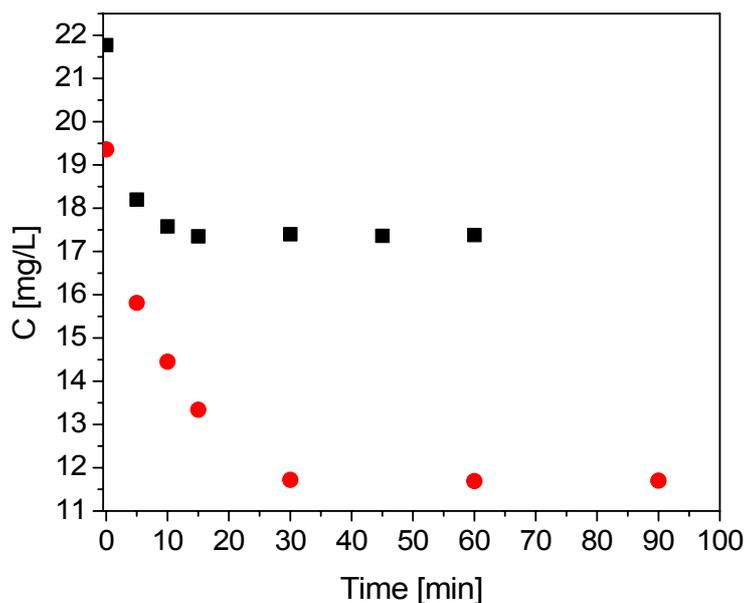
Fig. 6 – Variation of Congo Red concentration by time under the following conditions:
[Ti-PILC] = 0.4 g·L^{-1}; ■ – Congo Red on Ti-PILC, in the absence of UV radiation (in dark);
● – Congo Red on Ti-PILC, photocatalytic process.

Influence of surfactant concentration used for intercalation prior to pillaring by TiO$_2$

To get data concerning the optimum surfactant concentration required to modify the clay to increase efficiency, three clay samples were studied for surfactant intercalation by using surfactant/clay ratios within 0.059 – 0.298 g CTAB/g clay range. Fig. 7 shows the removal efficiency of Congo Red on the pillared clay (Ti-PILC) as compared to three clay samples modified by intercalation of surfactant. The concentration of the dye solution was 20 mg·L^{-1}.

After only ten minutes, the dye removal efficiency increased from 25.4% in the presence of Ti-PILC to 42.7% in the presence of 0.059 g surfactant/g clay (S$_1$-Ti-PILC). After the same time interval, the dye removal efficiencies on S$_2$-Ti-PILC and S$_3$-Ti-PILC samples were similar, which concluded that a concentration of 0.29 g surfactant/g clay was not justified.
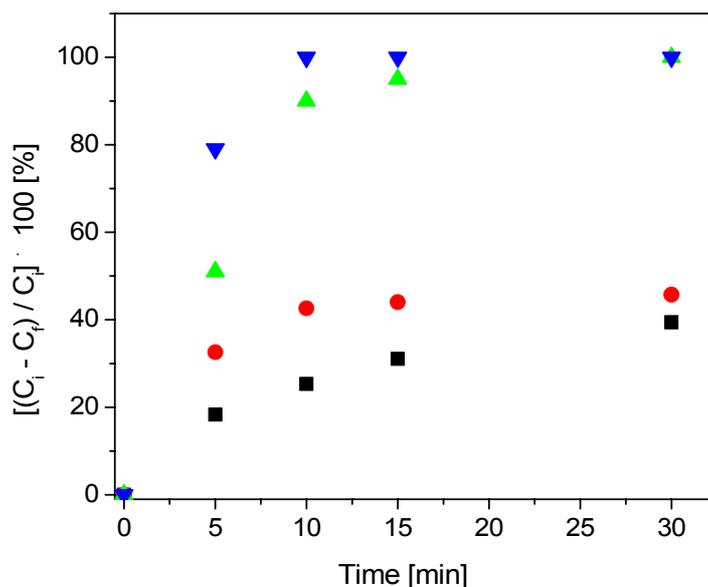

Fig. 7 – Variation of Congo Red removal eficency under the following conditions:
■ – [Ti-PILC] =0.4 g·L^{-1}; ● – [S$_1$-Ti-PILC] =0.4·g L^{-1}; ▲ - [S$_2$-Ti-PILC] =0.4 g·L^{-1};
▼ – [S$_3$-Ti-PILC] =0.4 g·L^{-1}.

Influence of the photocatalytic material concentration on photocatalytic efficiency

To get data concerning the influence of the photocatalytic material concentration on the maximum removal efficiency of the dye, parallel experiments were carried out by using two of the samples modified by intercalation with surfactant and pillaring by TiO_2 at two different concentrations: 0.4 g·L^{-1} and 1 g·L^{-1}. Fig. 8 shows the efficiencies for the two systems under different solid/liquid ratios.
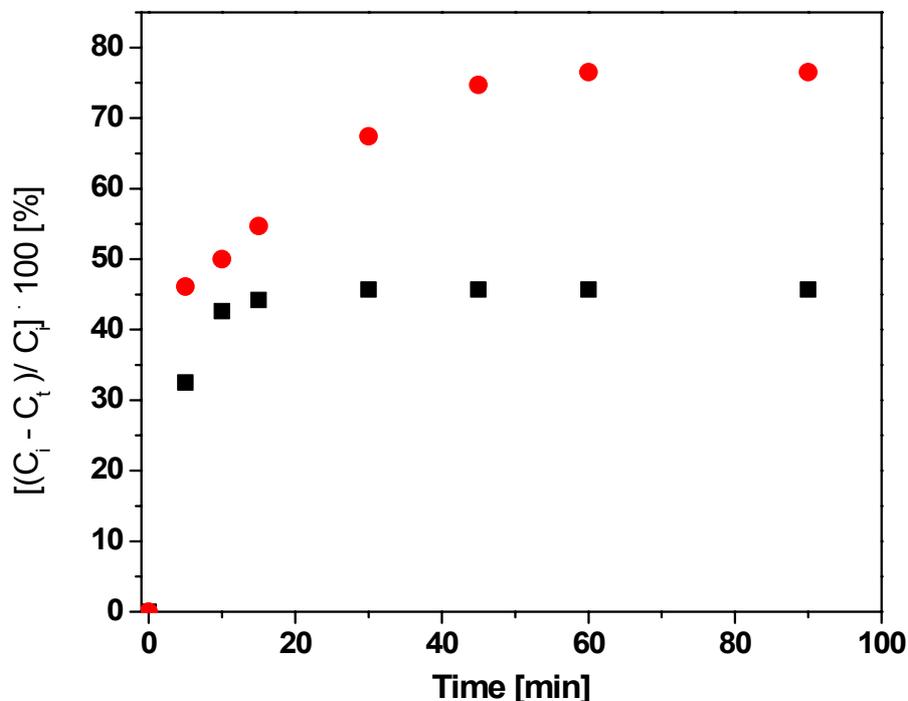
Fig. 8 – Variation of Congo Red removal eficency under the following conditions:
● - [S$_1$-Ti-PILC]=1 g·L^{-1}; ■ - [S$_1$-Ti-PILC]=0.4 g·L^{-1}.

For S$_1$-Ti-PILC sample at a concentration of 0.4 g·L^{-1}, the removal efficiency increased in the first 30 minutes reaching 45.7% and then it remained constant. At a higher concentration, 1 g·L^{-1}, after 30 minutes, the removal efficiency was 67.4% and after 60 minutes it increased to 76.5%.

It followed that for the same duration, the increase of the photocatalytic material concentration, *i.e.*, increase of catalytic surface area, led to the increase of removal efficiency.

EXPERIMENTAL

Materials

The starting clay was obtained from Valea Chioarului zone, Roumania. Chemicals such as hydrochloric acid, titanium tetraisopropoxide and cethyl-trimethylammonium bromide (CTAB) were supplied from Merk. Congo Red, which is the sodium salt of diphenyl-4,4'-bis azo-2-naphthylamine-1-1 sulphonic acid-4 ($C_{32}H_{22}N_6Na_2O_6S_2$) was purchased also from Merk (Fig. 9).
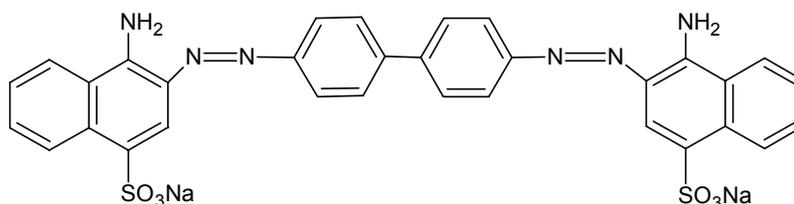
Fig. 9 – Structure of Congo Red.

Sample preparation

The Roumanian montmorillonite - starting material - had the following chemical composition (wt%): SiO$_2$-72.87; Al$_2$O$_3$-14.5; MgO-2.15; Fe$_2$O$_3$-1.13; Na$_2$O-0.60; K$_2$O-0.60; CaO-0.90; PC-5.70. Its mineralogical composition consisted of kaolinite, illite, montmorillonite and nontronite, besides small quantities of feldspar–albite and quartz. The determined cationic exchange capacity was 82meq/100g.

The monocatonic form (sample Na-clay) was prepared as follows: the clay was mixed with NaCl aqueous solution (1M) under S/L ratio = 1/10 and stirred for 3 hours at room temperature. The procedure was repeated three times to add fresh NaCl aqueous solution. The as-prepared clay was separated by vacuum filtration and washed until it was free of chloride (determined by $AgNO_3$ solution).

Preparation of pillaring solution

0.9 mM of titanium tetraisopropoxide was hydrolised with 1M hydrochloric acid under magnetic vigorous stirring for 3 hours. The quantities of HCl and titanium tetraisopropoxide were calculated in order to obtain a molar ratio $[Ti]/[H^+] = 1 : 4$.

Preparation of TiO₂-pillared montmorillonitic clay (sample Ti-PILC)

The pillaring solution was added, drop by drop, to the suspension of Na-clay (1%) in order to obtain a ratio equal to 1mM Ti per gram of clay. The suspension was stirred for 2 hours at room temperature. After vacuum filtration and washing several times with deionised water, the obtained solid

was dried at 70°C for 24 hours. In view of the pillaring process finalization, the samples were calcined at 550°C, for 4 hours, with a growth temperature rate of 1°C/min.

Preparation of TiO₂-pillared montmorillonitic clay modified by surfactant intercalation (S$_i$-Ti-PILC)

The surfactant modified Ti-PILC was synthesized as follows: 1g Na-clay was first dispersed in about 120 mL distilled water and then CTAB was added. The quantities of added CTAB were 0.2, 0.5 and 1 from CEC of the clay. The reaction mixture was stirred for 10 hours at 80°C. All products were separated by centrifugation and washed until free of bromide anions with distilled water and dried at 70°C for 48 hours. In view of both the surfactant elimination and the pillaring process finalization, the samples were calcined at 550°C, for 4 hours, with a growth temperature rate of 1°C/min, using an oven type Nabertherm. The dried solid was re-suspended in distilled water in order to obtain 1% suspension of surfactant modified clay. This suspension was treated with pillaring solution in order to obtain 1mmol Ti per gram of solid. Table 3 shows the synthesized samples.

Table 3

Samples preparation conditions

Sample	Aqueous clay suspension (wt %)	Surfactant content (g CTAB/g clay)	Added Ti content (mmolTi/g clay)
Na-clay	-	-	-
Ti-PILC	1	-	1
S$_1$-Ti-PILC	1	0.059	1
S$_2$-Ti-PILC	1	0.149	1
S$_3$-Ti-PILC	1	0.298	1

Sample characterization

XRD powder patterns were collected on a BRUKER D8 Advance instrument using CuKα1 radiation (Ni filter, CuKα = 0.15406nm, 40 kV and 50 mA).

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption using a Nova 2200 Schimadzu instrument. The specific surface area was calculated by using the standard Brunauer Emmett and Teller method on the basis of the adsorption data.

Effect of pH on removal efficiency of Congo Red on monocationic and pillared montmorillonitic clay

All adsorption and photocatalytic experiments were carried out under magnetic stirring at 25º C. The photocatalytic tests used a 12W Vilber Lourmat UV lamp with Hg 6W-254nm tube.

The pH experiments were carried out under the following working conditions: samples of 0.05 g of Na-clay and TiO₂-pillared montmorillonitic clay respectively (Ti-PILC) were contacted with 50 mL solutions having initial concentration of 20 mg·L^{-1} Congo Red. The pH was carefully adjusted by adding a small amount of dilute HCl or NaOH, by using an Inolab pH meter. The experiments over pillared material were carried out under photocatalytic conditions.

Kinetics of photodegradation

For the kinetics study of Congo Red photodegradation, parallel samples of 0.05 g Ti-PILC each, were contacted with 50 ml solution having initial concentration of 6 mg·L^{-1}, under magnetic stirring and influence of UV radiations. After certain intervals, the samples were centrifuged to separate solid phase. Then, the residual concentration of Congo Red in the solution was determined.

Photodegradation and adsorption experiments

The photodegradation and adsorption experiments were carried out on montmorillonitic clay changed into monocationic form (Na-clay), TiO₂-pillared montmorillonitic clay (Ti-PILC) and TiO₂-pillared montmorillonitic clay modified by surfactant intercalation (S$_i$-Ti-PILC).

The removal efficiency of Congo Red was scrutinized by taking into consideration the following aspects: the influence of pillaring the monocationic form by TiO₂ on adsorption, influence of photocatalysis as compared to adsorption in dark, influence of surfactant concentration used to modify the clay, influence of the photocatalytic material concentration and solid/liquid ratio.

Congo Red concentration in the aqueous solution was determined spectrophotometrically, at 498 nm, using a Varian Carry 50 UV-VIS spectrophotometer.

CONCLUSIONS

The experimental results show that for Congo Red photocatalytic degradation, the optimum value of pH is 4.0, due to the fact that the aggregation phenomenon based on hydrophobic interactions between aromatic rings of dye molecules was removed.

The structural and adsorptive properties of the TiO_2-pillared montmorillonitic clay and TiO_2-pillared montmorillonitic clay modified by surfactant intercalation indicated an enlargement of the basal spacing of the clay. The enlargement is much pronounced as the used surfactant content increase. The process of enlargement of the basal spacing of the clay, followed by titanium pillars formation results in an increase of specific surface area, proportional to the used surfactant content. The small dimensions of TiO_2 crystallite has a high contribution to the specific surface area value.

The removal efficiency of Congo Red was scrutinized by taking into consideration the following aspects: the influence of pillaring the monocationic form by TiO_2 on adsorption, influence of photocatalysis as compared to adsorption, influence of surfactant concentration used to modify the clay, influence of the photocatalytic material concentration and solid/liquid ratio. The Langmuir – Hinshelwood model was used for interpreting kinetics data.

In the studied experimental conditions a good correlation was observed between photocatalytic activity of the TiO_2-pillared montmorillonitic clay and TiO_2-pillared montmorillonitic clay modified by surfactant intercalation and both the specific surface area and the size of TiO_2 crystallites values, affected by the modification route of Valea Chioarului clay.

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