Studii şi Cercetări Ştiinţifice
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

2018, **19** (1), pp. 063 – 072

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry

ISSN 1582-540X

ORIGINAL RESEARCH PAPER

ACTIVATED ADSORPTION ON CLAY OF MICROPOLLUTANTS FROM PAPER PRINTING INDUSTRY

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Received: November, 28, 2017
Accepted: March, 14, 2018

Abstract: The paper presents a preliminary study of chemisorption onto anionic and cationic clays, in order to reduce the content of pollutants from a paper printing effluent, collected after technological step named: printing of paper fabric manufacturing. The procedure of filtration fallowed by adsorption process is an effective, fast and low cost technique for treatment of black effluent resulting from paper printing industry. The key parameters tested to achieve a high efficiency for the movement of micropollutants from printing fluid were substrate dose and contact time. The highest treatment performance was obtained for cationic substrate at *p*H = 6.80, in contact and agitated magnetically for 30 respectively 90 minutes at room temperature.

Keywords: *anionic and cationic clays, chemisorption, paper printing industry, wastewaters*

INTRODUCTION

Even if the importance of digital media has grown enormously in recent decades, paper printing continues to play a rather important role and more than 1 million tons of ink is produced in Europe annually. EuPIA (European Printing Ink Association) reported in its latest report in 2016 that even if the print market is down, there is a high demand for inks in other areas of the printing industry, for example: packaging and digital printing, with an increase of around 3 % per year. Figure 1 represents the global inks and is defined as follows: liquid inks water borne - contains flexo and watercolor inks, technological varnishes, thinners, primers and overpressure paints; liquid inks solvent borne - contains flexor and engraving solvent, printing inks, paper publishing inks, technological varnishes, overprinting paints, diluents and primers; oil based inks - includes coldset and heatset offset and sheetfed offset inks; all other inks - the rest of the inks [1].

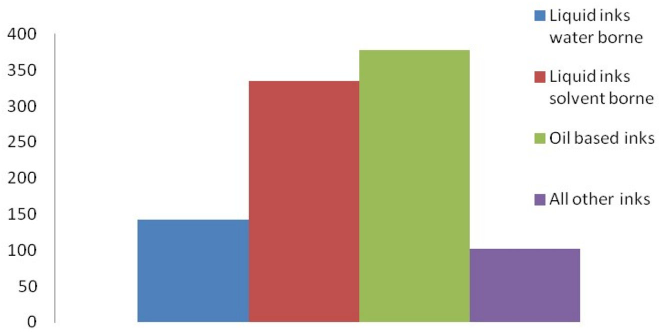


Figure 1. *Global inks European sales 2015 [1]*

The manufacture of inks used for printing on paper contain especially vegetable and colophony oils, but in most of the ink forms there are also a lot of petrochemical raw materials. The printing ink composition are composed of four types of components: colorant, binder, solvent and additives [1]. The color can be given by a pigment or dye. In order to obtain better light stability and water resistance, inorganic and organic pigments are used. They can be classified into groups based on their chemical composition [2]. The most commonly used inorganic pigments are: iron oxides, titanium dioxide, carbon black or zinc yellow. Organic pigments are synthesized from petroleum or natural gas. Other researchers show that they are in the process of coloring inks with 75 % of yellow organic pigments - yellow diarylide (PY 12), blue pigment for blue cyan is the phthalocyanine blue pigment (PB 15) and the pigment of the magenta color pigment is (PR 57:1) [3].

Black liquor is one of the main by-products of paper printing industry, which is considered as pollutant because it contains dyes, binders, solvents and additives, among others. The release of this black effluent in nature without any treatment can cause serious damages for the environment and can affect the human health. The removal of coloured effluents from printing industry discharged in different receptors or inside reuse is quite important, even if the release of dyes is in small concentrations. Even though these treatment methods appear to be effective, they have the disadvantage of being expensive due to the operating conditions and chemical reagents used.

In the present paper, in order to overcome the inconvenient of the methods already studied, we present a possible method of treating these effluents in the paper industry, namely the adsorption of pollutants on different adsorbent materials based on synthetic anionic clays and chemically modified by pillaring.

MATERIAL AND METHODS

Reagents and chemicals

All chemicals used (Sigma Aldrich, Germany) were of analytical degree and were used without any further purification: sodium hydroxide (NaOH) (99.9 %), aluminum chloride nonahydrate ($AlCl_3 \cdot 9H_2O$) (99.9 %), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium carbonate (Na_2CO_3), iron (II) chloride nonahydrate ($FeCl_2 \cdot 9H_2O$) and montmorillonite K10. The reagents were used for the Layered Double Hydroxide (LDH) precursor. Black liquor used for this study was delivery by paper manufacturer located in Bacau city, Romania, collected in a closed container and stored at -5 °C.

Adsorbents preparation

In this original paper is presented a chemisorption process, because the adsorption is accompanied by chemical reaction and involves the redistribution of valence electrons, requiring additional activation energy. Chemisorption is also called adsorption activated [4]. In order to obtain some clay-based adsorbents, in the present study certain chemical methods of structural modification were used, namely: intercalation of the Al^{3+} and Fe^{2+} cations in the clay structure by ion exchange and pillaring to obtain the cationic adsorbent name PILCs. The preparation of PILCs consists in the following stages: ion exchange of montmorillonite K10 with Na^{+} ion in order to obtain Na-Montmorillonite K10 (Na-MtK10), intercalation with Al^{3+}-Fe^{2+}– pillaring agent and calcination of intercalated clays [5].
For the preparation of the anionic adsorbent, LDH, the synthetic co-precipitation method at low supra-saturation at constant *p*H 7, is the most frequently used method [5 –10]. Through the pillaring process there is a change in the structure of the clay materials, its composition, as well as some properties: ion exchange capacity, adsorption capacity, specific surface and hardness [9].

UV-Vis chemisorption tests

Batch mode adsorption studies for black liquor have been carried out to investigate the effect of different parameters such as adsorbate concentrations (0.050 %, 0.025 % and 0.005 %) and sorption time (5 min, 30 min, 60 min, 90 min and 120 min). The experiments were conducted in triplicates. In Table 1 are presented the sorbents used for analysis and the abbreviations, in order to eliminate the micropollutants from printing fluid.

Table 1. *Sorbent concentration and abbreviation used*

Sorbent name	Sorbent concentration [%]	Sorbent abbreviation
Layered double hydroxides (anionic adsorbent)	0.050	LDH–a
	0.025	LDH–b
	0.005	LDH–c
Aluminium pillared clays (cationic adsorbent)	0.050	PILCs–a
	0.025	PILCs–b
	0.005	PILCs–c

The UV-Vis spectrophotometric analyses were realized, after contact time and established the concentration for each sample, using a Beckman DU-640 UV-Vis spectrophotometer. The absorbance domain was spectrophotometrically measured from 200 nm to 800 nm.

RESULTS AND DISCUSSION

The manufacturing paper industry use mixtures of various dyes, lacquer, additives, etc. producing paper printing toxic effluents. One of the environmental protection strategies consists in retaining the pollutants present in these toxic effluents, on different adsorbent materials before these wastewaters to be reversed into the environment. The use of clays as adsorbents in the retention of pollutants from liquor toxic effluents is based on the high selectivity, large sorption capacity, physical-chemical stability, advantageous kinetic features, mechanical strength and low cost.

Effect of adsorbent dose

The influence of adsorbent dose on micropollutants removal was examined at a *p*H of 6.80 working with 50 mL paper printing effluent, with different doses of adsorbents at room temperature. The reduction of pollutants content in contact with establishes sorbent dose increase as is indicated in the Figure 2.

Figure 2 shows the UV-Vis spectra of the tested solutions and the adsorption were obtained from the dyes dispersed in water in contact with anionic and cationic clay at different concentrations (0.050 %, 0.025 % and 0.005 %), using water as reference solvent. Due to the presence of anthraquinone-base of dye, a big π-conjugated planar structure generates intermolecular π-π interaction [16].

The most important chemical substances specifies of dye colors are presented at significant adsorption wavelength. The maximum adsorption (λ_{max}) at 514 nm is attributed of red chemical compounds, λ_{max} 459 nm of yellow chemical compounds and 631 nm for blue chemical substances [15].

A.

B.

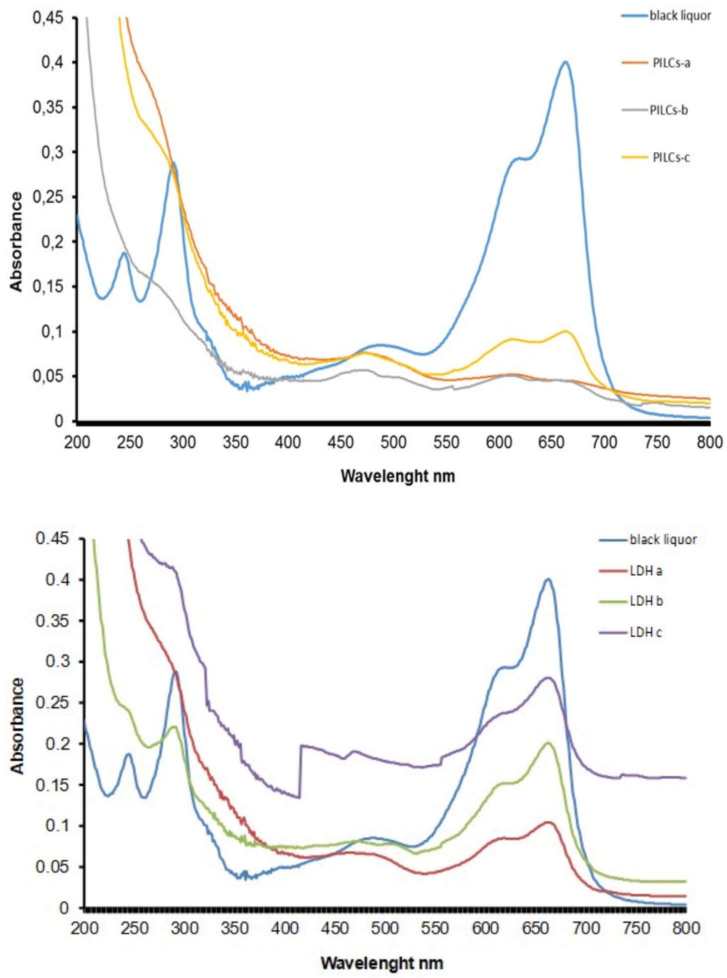


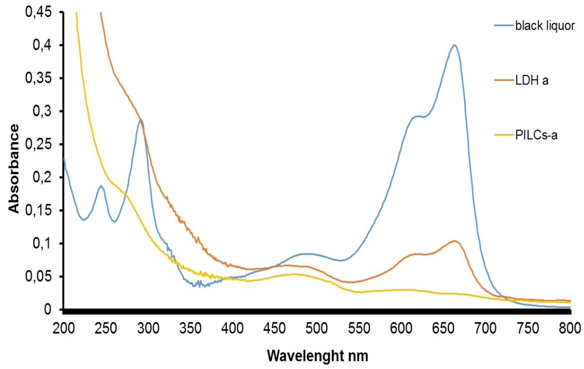
Figure 2. *UV-Vis spectra of black liquor with different amounts of cationic (A.): PILCs–a, PILCs–b, PILCs–c and anionic (B.): LDH–a, LDH–b, LDH–c substrates*

The highest treatment performance was obtained for cationic substrate at *p*H = 6.80, PILCs–a and PILCs–b at 0.050 % and 0.025 % concentrations, with a yield of 94 % after being in contact and agitated magnetically for 5 minutes at room temperature.

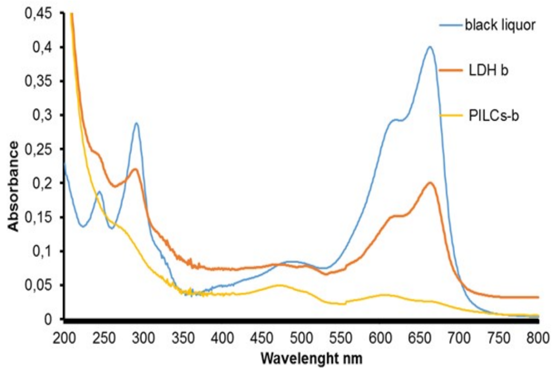
Influence of different adsorbents: anionic versus cationic clay

As can be seen in Figure 3, at all tested concentrations, the cationic adsorbent had significant results, a yield of 94 % after only 5 minutes of being in contact with pollutants and magnetic stirring.

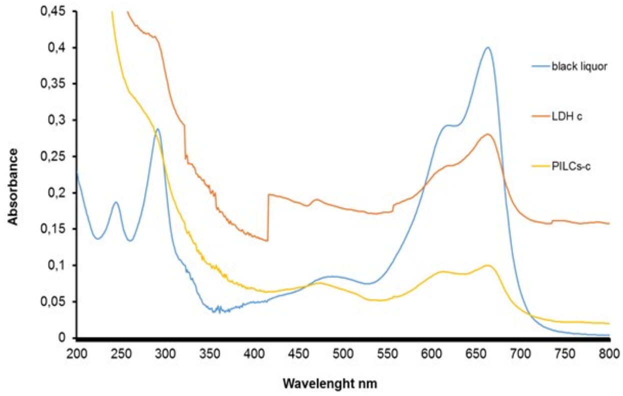
The cationic clays present a high affinity for aromatic chemical structures present in black liquor, due to the presence of Al^{3+} or/and Fe^{2+} cations. Clay minerals possess a high adsorption capacity towards several classes of dyes and their adsorption capabilities are comparable to those activated carbons. The adsorption performance of studied substrates depends strongly on class of dye. Also, the efficiency of adsorption system depends on the *p*H [17]. The variation of *p*H leads to the variation of ions exchange at surface, being an important property for mineral clay.



***A**-LDH–a versus PILCs–a (0.050 %)*



***B**-LDH–b versus PILCs–b (0.025 %)*



***C**- LDH–c versus PILCs–c (0.005 %)*

Figure 3. *UV-VIS spectra of black liquor with different substrates*

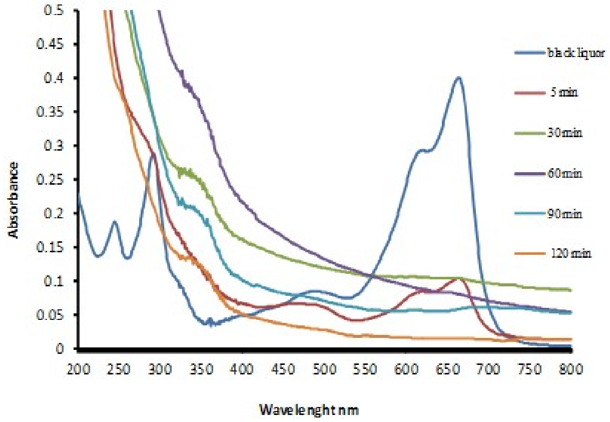
In the present study, these properties are confirmed for cationic sorbent, at *p*H of 6.80 and make the difference between anionic versus cationic substrates.

Influence of contact time

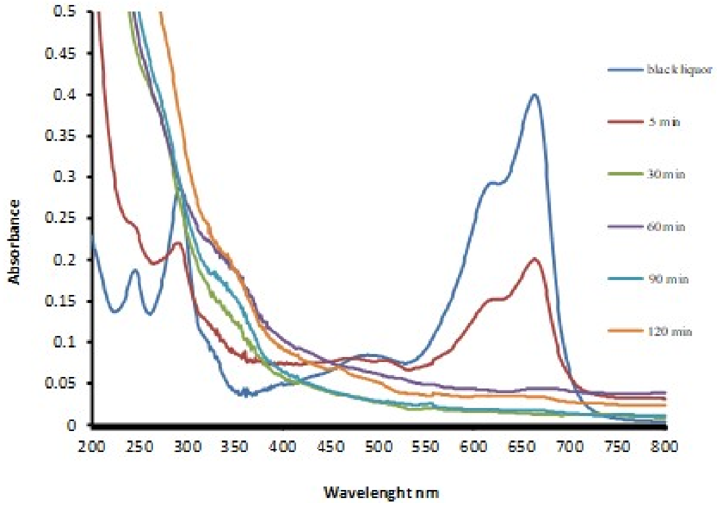
The contact time of sorbent - paper printing effluent (sorption time) is an important parameter for obtaining color removal, for elucidation of the mechanism, and for the choice of optimum operating parameters.

For this reason, the influence of this parameter into the paper print effluent of *p*H 6.80, using different sorbent doses, at room temperature was tested.

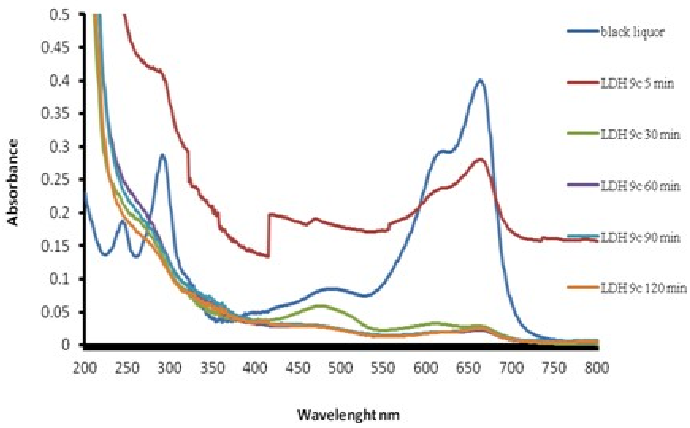
The effect of sorption time versus micropollutants removal by sorption on clay materials is presented in Figure 4 and 5.



A- *Anionic adsorbent LDH– a*



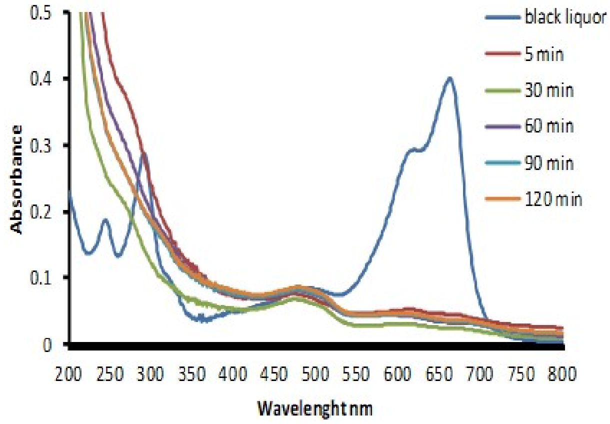
B- *Anionic adsorbent LDH–b*



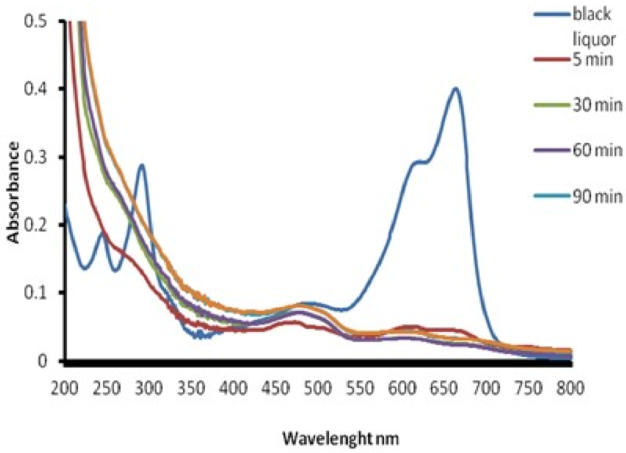
C- *Anionic adsorbent LDH–c*

Figure 4. *Influence of sorption time vs. color removal of black liquor with anionic adsorbent (LDH) at different sorption time (5 min, 30 min, 60 min, 90 min and 120 min)*

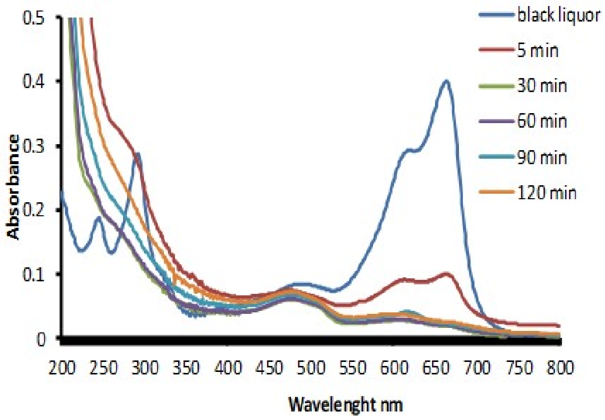
In the adsorption system, sorption time is a significant physico-chemical process parameter. In most of dye-clay adsorption system, the contact time possess a positive effect with the increase of the amount of dye adsorbed by clay.



A *- Cationic adsorbent PILCs – a*



B*- Cationic adsorbent PILCs –b*



C*- Cationic adsorbent PILCs –c*

Figure 5. *Influence of sorption time vs. color removal of black liquor with cationic adsorbent (PILCs) at different sorption time (5 min, 30 min, 60 min, 90 min and 120 min)*

As depicted in Figure 4 and Figure 5, the decrease of the absorption band intensities of black liquor from paper industry indicates that the dyes are chemisorbed by cationic clay more than anionic clay.

CONCLUSIONS

Physical, chemical, and biological pre-treatment technologies are available and can be employed to remove micropollutants from paper printing industry such as chemical oxidation, coagulation, adsorption, aerobic and anaerobic microbial degradation, membrane separation, etc. This study presents a dye removal from aqueous solution such as adsorption, in presence of natural or synthetic clay. One of the advantages of using clays as adsorbents is the layered structure of the clay allows expansion (swelling) when contacted with water, which exposes an additional mineral surface capable pollutants adsorption.

The present study showed the applicability of chemisorption method in the treatment of black liquor from paper industry. Chemisorption can be considered as a suitable alternative to existing methods for the treatment of black liquor.

The obtained results emphasize the difference between cationic and anionic clays in adsorption of micropollutants presents in paper printing industry. The cationic substrate presents the highest capacity to adsorb aromatic chemical compounds at *p*H of 6.80 and at work concentration from 0.050 % to 0.025 %.

The adsorption using clay as adsorbents is recommended for the treatment of water or wastewater.

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