BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 65 (69), Numărul 1, 2019
Secţia
CHIMIE şi INGINERIE CHIMICĂ

TEXTILE EFFLUENT DISCOLORATION BY SORPTION ONTO MESOTROPHIC PEAT

BY

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Received: February 15, 2019
Accepted for publication: March 22, 2019

Abstract. The paper presents a few laboratory tests of adsorption onto mesotrophic peat (MP) applied to decolorize a real textile effluent by using the ‘batchwise’ sorption technique. For high efficiency of textile effluent discoloration, there were tested the following operating parameters: pH (1.6 - 10.86), sorbent dose (4 - 40 g/L), temperature (5°, 25° and 45°C), and sorption time (till 24 h). The best sorption performance was obtained at high acidic pH (1.6), with MP peat dose of 20 - 40 g/L, temperature of 25°C, initial intermittent agitation (no more than 3 - 5 min), continuous sorption operating regime, a minimum contact time of 780, or 840 min, and was varied between 53.50% and 57.25% for color removal, and also 47.04% - 51.80% for COD_{Cr} removal.

To increase the textile effluent treatment degree can be applied also other physical-chemical or biological treatment steps (*i.e.* coagulation-flocculation, advanced oxidation/reduction, membrane processes as ultrafiltration, ionic exchange, etc.).

Keywords: adsorption; discoloration; textile effluent; mesotrophic peat (MP); treatment efficiency.

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1. Introduction

Commonly, from all industrial wet technological processes there are produced industrial wastewaters with different characteristics depending of the utilized raw materials' characteristics, efficiency of all operations and processes implicated in the productive technological process, or other technical services, and also operating regime and working conditions. Usually, these wastewaters must be treated before their final discharge in the urban sewer system, or inside recycling/reuse in order to fulfill the imposed quality for discharging into natural aquatic receptors (*e.g*., watercourse nearby), or urban sewer system, or inside reuse/recycling into industrial wet technological steps.

The most corresponding wastewater management strategy is selected by the environmental manager of industrial company based mainly on the cost-efficiency criteria and sustainability indicators. In this wastewater management strategy, the key role is played by the wastewater treatment system used (centralized or decentralized one), hardly influenced by the selected treatment technological steps, required equipments/installations to be used for removal of polluting species, and also of any additional hydraulic loads.

One treatment step discussed in a lot of research studies is **adsorption** (based on *physical adsorption* – van der Waals, hydrogen or hydrophobic bonds), **sorption** (based on *physical-chemical adsorption* due to van der Waals, hydrogen or hydrophobic bonds (*physical nature*) and ionic exchange and/or covalent bonds (*chemical nature*) mainly resulted in chemical sorbate - sorbent interactions as coagulation-flocculation, precipitation, chelating/complexation, oxidation, reduction, hydrolysis, or other types of simple and/or combined chemical reactions), and **biosorption** (based on essential *biological processes* (biological in nature) associated or not with other *physical-chemical processes* performed simultaneously, or consecutively in the same aquatic environment) (Șuteu *et al.*, 2012; Șuteu *et al.*, 2017; Zaharia, 2015; Zaharia and Șuteu, 2012a,b) as a treatment process with very good results in term of efficiency vs. costs, easily to be applied (Anjaneyulu *et al*., 2005; Doke and Khan, 2012; Gorduza *et al.*, 2002; Gupta and Suhas, 2009; Gupta *et al.*, 2009; Han *et al*., 2012; Hameed, 2008; Hubbe *et al*., 2012; Shih, 2012; Şuteu *et al*., 2009; Şuteu *et al*., 2010; Zaharia *et al*., 2012; Zaharia *et al*., 2014).

A natural carbonaceous adsorbent which can be applied in sorptive treatments of industrial effluents is the mesotrophic peat (MP) that can be used as efficient sorbent for different polluting species removal (*e.g.*, phenol and its derivates, color, etc.) (Zaharia, 2016) from final industrial effluents.

This paper summarizes a few experimental tests performed to evaluate the sorptive potential of mesotrophic peat (MP) especially for discoloration of a real textile effluent and reduction of its organic load, expressed as COD removal (%). The effect of different operating parameters onto sorption efficiency, in terms of color and organics (expressed as COD) removals, *i.e.* pH, adsorbent quantity, temperature and sorption time, was mainly had in view related to finding of the best conditions for highest discoloration degree (sometimes also COD removal) onto mesotrophic peat (MP) (as natural efficient alternative sorbent).

2. Experimental

2.1. Materials and Reagents

Reagents: Sulfuric acid (H_2SO_4,) of 0.1N and concentrated (98%, Merck KGaA, Germany); sodium hydroxide (NaOH; Chemical Company, Iași, Romania) of 0.1N; potassium acid phthalate, calibration COD_{Cr} reagent (Fluka Analytical, Sigma-Aldrich Chemie GmbH); $K_2Cr_2O_7$ (Chemical Company, Romania), aqueous solution of 0.25N; mercury (II) sulfate, specific $HgSO_4$ catalyst (Fluka Analytical, Sigma-Aldrich Chemie GmbH), and silver sulfate (Ag_2SO_4), chloride inhibitory (Fluka Analytical, Sigma-Aldrich Chemie GmbH). All reagents were of analytical purity.

Adsorptive material: *mesotrophic peat*, commercial product as fertile soil for vegetal plants/crops, characterized by pH=6.6-7.0, being purchased from Matecsa Ker.Es Kért kft (Hungary), prepared in a special mode: (1) washing few times with distilled water, followed by solid separation, and its dried in air, at room temperature; (2) heating in a oven at 250°C, until a constant weight, and (3) cooling followed by final solid sample mortared, and sifted through a sieve of 1 mm mesh (Zaharia, 2016).

Real wastewater: textile effluent collected from a final collector basin after the textile finishing processing of cotton fabrics (dyeing and rinsing stages – dyeing bath containing two azo dyes – Orange 16 and Red 198, tenside, pH buffer, binders other electrolytes, anti-crust and reduction agents), characterized also in other author research reports (Zaharia, 2015; Zaharia, 2018; Zaharia and Șuteu, 2013) by COD_{Cr} of 665 mg O_2/L, pH of 7.38, color of ca 205 - 2276 HU (depending on working pH), synthetic detergents of 2.5 mg/L, extractable substances of 25 mg/L, etc. The flow of dyestuff bath was of 3.70 m^3/day and the textile operator had a production of around 15,000 linear meters of cotton fabrics per day (*i.e.* 4,615 kg cotton fabrics/day) (Zaharia *et al*., 2012a; Zaharia *et al*., 2014; Zaharia, 2015; Zaharia, 2018). The estimated flow of textile effluent was of 18 - 20 m^3/day.

2.2. Analysis Methods

Color determination. It can be expressed by absorbance related to a blank with distilled water, measured at three standard characteristic wavelengths (SR ISO 7887-97) as: 436, 525, and 620 nm, especially at 436 nm for industrial wastewaters (*apparent color* in supernatant, or *real color* in filtrate), or Hazen color index (Hazen units - HU, *i.e.* an absorbance of 0.069 at 456 nm corresponds to 50 HU) (Zaharia and Şuteu, 2013; Zaharia, 2016; Zaharia, 2018). The absorbance measurements were performed at a VIS SP-830 Plus spectrophotometer, Metertech Inc.

COD-Cr determination. It was performed by using the spectrophotometer-based method, consisting in absorbance measurement at 600 nm (A_{600}) with SP-830 Plus spectrophotometer (Metertech Inc.) of treated sample by 2h-oxidation at 150°C (oxidation in concentrated H_2SO_4 medium with $K_2Cr_2O_7$ 0.25N, in the presence of specific catalyst - $HgSO_4$, and chloride inhibitory agent - Ag_2SO_4; COD is appreciated from the specific calibration curve and linear regression equation, plotted with experimental data working with potassium acid phthalate as COD-Cr calibration reagent solution (Zaharia, 2016; Zaharia, 2018).

PH measurement. It was done directly at HACH One Laboratory pH meter.

2.3. Adsorption Working Methodology

There were performed laboratory scale set-up adsorption tests by using the 'batchwise' technique. Therefore, in each conical flask of 100 mL it was added a specific amount of mesotrophic peat (MP) (0.1 - 2.0 g) and 50 or 25 mL of textile effluent, at different temperatures (5°C, 25°C and 45°C) controlled with a thermostated assembly.

The adjustment of textile effluent pH was done with HCl 0.1 N or NaOH 0.2 N.

After a corresponding adsorption time (*t*) and/or 24 h, the supernatant COD_{Cr} and its apparent color were determined after the sorbent separation by sedimentation.

The discoloration degree, or color removal, and also COD removal were calculated by using the relation (1):

$$R(\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad (1)$$

where: C_0 and C_t are the initial and residual (after *t* adsorption time) color, or COD_{Cr} of supernatant [HU, or mg O_2/L].

3. Results and Discussion

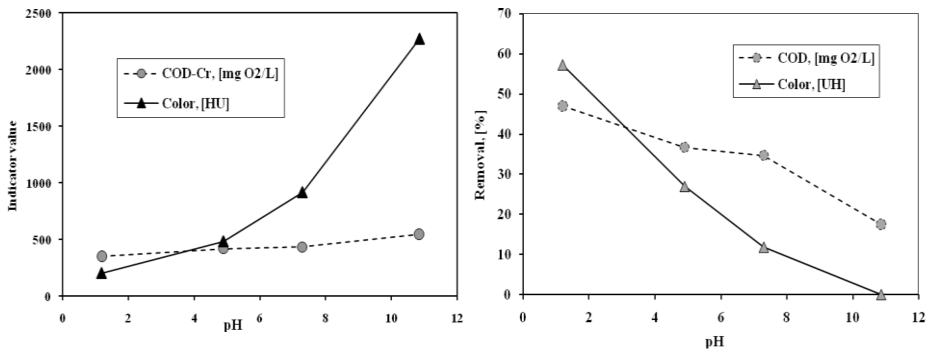
Into other author previous studies (Zaharia, 2015; Zaharia, 2016; Zaharia, 2018; Zaharia and Şuteu, 2013) there were established a few principal operating parameters that must be had in view for the adsorption/sorption process of different organic species onto adsorptive materials, especially 'low cost' adsorptive materials.

In this study it was proposed the variation field for each studied operating parameters (*i.e.* initial pH of textile effluent, sorbent dose, temperature, and contact time) of sorption process onto mesotrophic peat (MP), and determined the highest efficiencies in color, or COD removal associated with its corresponding operating parameters for high treatment efficiency.

3.1. Influence of Initial pH of Textile Effluent in Sorption onto MP Peat

The influence of initial pH of textile effluent in the sorption onto MP was examined using 0.5 g of MP sorbent at room temperature, and working with 25 mL of textile effluent (*i.e.* a sorbent dose of 20 g/L of MP).

The experimental results are illustrated in Fig. 1.



a *b*

Fig. 1 – Influence of initial pH *vs.* color and COD removal in the textile effluent sorption onto MP peat (20 g/L sorbent; 24 h of sorption).

The treated effluent quality indicators (COD_{Cr}, color) after the adsorption onto MP had values lower more than 1.21 - 1.89 (COD), or 0 - 4.7 (color) times in comparison with un-treated effluent, but still very high related to the imposed maximum permissible limits for safe discharge in aquatic receptor (*i.e*. 125 mg O_2/L, or 50 HU), or even inside reuse (meaning around 352.16 mg O_2/L (pH 1.2) and 548.62 mg O_2/L (pH 10.86) for COD, or 205.36 HU (pH 1.2) and 2275.893 (pH 10.86) for color).

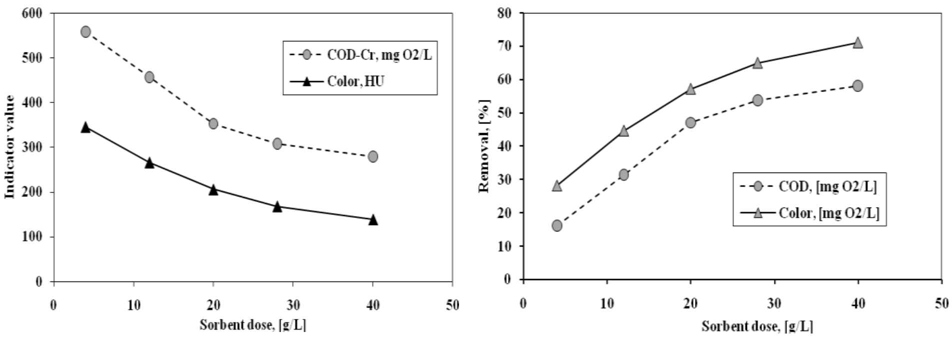
The removals were varied significantly with initial pH value of textile effluent (after pH adjustment at certain pH value) between 17.50-47.04% COD, or 0-57.25% color (*e.g.*, for pH of 10.89 the color removal was not possible, and additional color was introduced in effluent at higher pH values as a result of sorbent degradation, but good color removal of 50.30-57.25% was performed at pH of 1.2 in comparison with 26.96% at pH of 4.90 and 11.83% at pH of 7.3).

The behavior of color sorption onto MP, mainly due to residual dye content and other colored compounds present in textile effluent as residuals or degradation compounds, may be correlated with the sorbent surface charge which is significantly influenced by effluent pH.

At high acidic pH (pH < pH_{ZC}; pH_{ZC} (MP) ≈ 3.80 - 4.20) the sorbent surface is positively charged and is available to strong electrostatic interactions with anionic groups of used textile dyes, together with van der Waals, hydrogen and hydrophobic bonds that permitted the accumulation of textile colored organics at external surface of MP matter.

3.2. Effect of Adsorbent Dose in Effluent Sorption onto MP Peat

The influence of adsorbent dose in color removal was examined at pH of 1.20 working with 25 mL textile effluent, with different doses of MP (0.1 - 1 g), and room temperature. The increase of color and COD removal (*R*, [%]) with sorbent dose increasing (from 4 g/L till 40 g/L) is shown in Fig. 2.



a *b*

Fig. 2 − Influence of sorbent dose *vs.* color and COD removal in the sorption onto MP (pH=1.20; 24 h of sorption).

The best value of 57.249% for color removal, or 56.198% for COD removal indicating the highest adsorptive MP capacity was obtained with 40 g/L of MP, but these values are closed to those performed with 20 g/L and 28 g/L that is why it can conclude that maximal removal percentages of 47.044-57.249% for color and 53.503-56.298% for COD were performed for a MP concentration in range of 20-40 g/L. The most recommended sorbent dose for no exceeding sorbent consumption was in range of 20 - 28 g/L of MP.

3.3. Effect of Temperature in Effluent Sorption onto MP Peat

The capacity of MP to remove color, or the discoloration degree at normal un-treated effluent pH (7.30) and sorption favorable pH (1.20), at three different temperatures (5°C, 25°C, and 45°C), was determined using a sorbent dose of 24 g/L (*i.e.* 0.6 g MP per 25 mL of textile effluent).

The influence of temperature against the colored species sorption efficiency onto MP peat is shown in Fig. 3 in terms of residual color (Fig. 3*a*) and color removal (Fig. 3*b*).

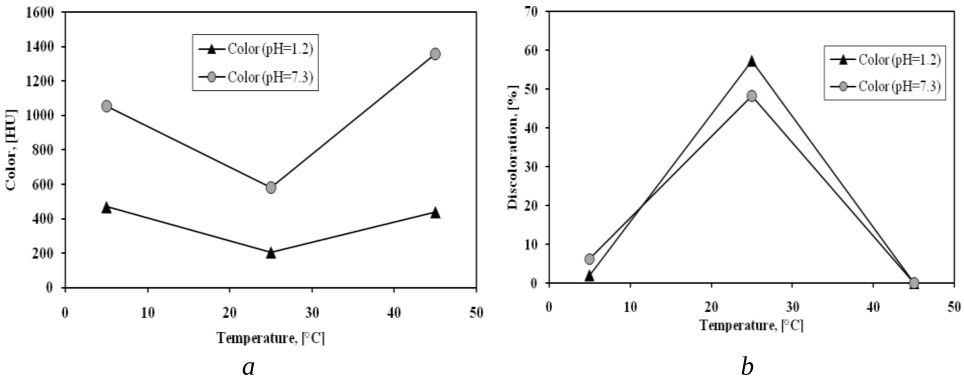


Fig. 3 – Influence of temperature *vs.* color removal (discoloration degree) in the adsorption onto MP (24 g/L sorbent; 24 h of sorption).

Fig. 3 shows the influence of temperature increasing in high acidic conditions (pH=1.20) toward the color value (Fig. 3*a*) in treated textile effluent and also textile effluent discoloration degree at two pH values (pH 1.2 and 7.3) (Fig. 3*b*). After 24 h of sorption (sorption equilibrium being always attained) the maximal removals of 57.249% and 48.349% for color were performed at 25°C in high acidic pH, and also neutral pH.

No color removals were performed at 45°C, and lower removals were obtained at cold temperature (5°C) in range of 2.045 - 6.196%, that is why no clear suggestion about an exothermic process of colored species sorption onto MP peat can be concluded without further advanced investigations.

3.4. Effect of Contact Time in Effluent Sorption onto MP Peat

An important operating parameter in continuous effluent treatment regime is the contact time between sorbent – textile effluent for highest removals of color and organics (COD_{Cr}). This operating parameter also permits the elucidation of adsorption kinetics and isotherm, and selection of corresponding operating parameters in practice for normal, or critical and sometimes special operating cases. Therefore, it was studied the influence of sorption time onto the textile effluent discoloration working without (initial textile effluent pH, pH=7.38) and with pH adjustment at the recommended adequate high acidic operating pH (1.2), using a sorbent dose of 24 g/L, at room temperature (around 22-25°C).

The influence of sorption time vs. color removal, or discoloration degree by sorption onto MP peat is shown in Fig. 4.

The results were indicated a highest discoloration degree of 57.429% at pH of 1.20, or 48.349% at pH of 7.38 after 24 h of sorption. The minimal necessary sorption time for equilibrium establishment is of 780, or 840 min.

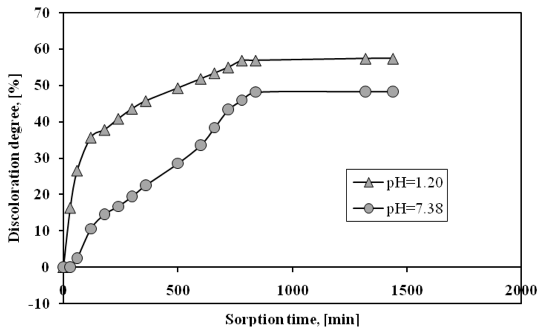


Fig. 4 – Influence of sorption time *vs.* discoloration degree in sorption onto MP peat (24 g/L sorbent; room temperature).

The sorption equilibrium establishment is explainable by the occupation of the large number of vacant available surface sites by molecules of dyes or other colored species during all stages of sorption (*physical* – colored species accumulation at external surface of MP peat by van der Waals bonds or hydrophobic interactions, and *chemical* - ionic exchange and/or electrostatic interactions dependent on sorbent surface charges at different pH values, or other covalent links).

4. Conclusions

A few laboratory scale set-up sorption tests applied for real textile effluents were performed for high removals of color and COD_{Cr} onto MP peat.

The sorption was dependent of the tested operating parameters such as initial effluent pH, sorbent dose, sorption time, and temperature. The best pH value for the color and COD_{Cr} removals was found at very high acidic pH (1.2). Both color and COD_{Cr} removals were increased with the increasing of sorbent dose (MP peat).

The sorption equilibrium at very acid and neutral pH was attained after 780 or 840 minutes, respectively. The sorption performance was studied also for different sorption operating parameters at 24 h.

No clear and concluding results were performed concerning the sorption mechanism type onto MP peat related to sorption thermal effect: it is possible to be an exothermic process. Effluent discoloration by sorption onto MP peat was not possible at high temperature (45°C) possibly due to sorbent degradation and release of colored species, and very low at temperature of 5°C.

The highest value of color removal was in range of 53.503 - 57.429% after 24 h of continuous sorption into static regime at pH of 1.20 and temperature of 25°C. Before final discharge of treated textile effluent in different aquatic receptors, it is necessary a neutralization step.

These sorption tests suggested that MP peat can be used as natural alternative sorbent for discoloration of textile effluents. These tests will continue with others for elucidation of sorption mechanism type and sorption behavior at different external pressures and load variations, but also with modeling and optimization of sorption onto MP peat applied for real textile effluents.

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DECOLORAREA UNUI EFLUENT TEXTIL PRIN SORBŢIE PE TURBĂ MEZOTROFICĂ

(Rezumat)

Lucrarea prezintă câteva teste de sorbție pe turbă mezotrofică (MP) aplicate la scară de laborator pentru decolorarea unui efluent textil real folosind tehnica adsorbției în regim static. Pentru obținerea unei eficiențe ridicate de decolorare a efluentului textil au fost testați următorii parametri operaționali: pH-ul (1,6 - 10,86), doza de sorbent (4 - 40 g/L), temperatura (5°, 25° și 45°C) și timpul de sorbție (până la 24 ore). Cea mai bună performanță a fost obținută la pH puternic acid (pH 1,6), cu o doză de turbă MP de 20 - 40 g/L, la temperatura de 25°C, cu agitare intermitentă inițială (nu mai mult de 3 - 5 minute), în regim continuu de operare, timp de contact minim de 780 sau 840 minute, și a variat între 53,50% și 57,25% pentru reținerea culorii și respectiv 4,04% - 51,80% pentru reținerea CCO_{Cr}-ului.

Pentru mărirea gradului de epurare a efluentului textil pot fi aplicate de asemenea alte trepte fizico-chimice sau biologice de epurare (*i.e.* coagulare-floculare, oxidare/reducere avansată, procese de membrană precum ultrafiltrarea, schimbul ionic, etc.).