AGRICULTURE WASTES USED AS SORBENTS FOR DYES REMOVAL FROM AQUEOUS ENVIRONMENTS

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Abstract

This paper presents the preliminary experimental results of the use of some agro-industrial wastes (corncob, sunflower seed shells) as sorbents for Methylene Blue dye removal from aqueous environments. There were studied the main factors with high influence on the dye sorption process: temperature, sorbent amount, solution pH, dye concentration, and contact time. The results indicate that these materials have a good potential to remove the studied dye, and can be used as adsorbents into a treatment of industrial textile effluents before recycling or reuse, or discharging into the sewage system.

Key words: corncob, sunflower seed shells, sorption, Methylene Blue dye, wastewater.

Due to the new directions imposed by the concept of Sustainable Development, the Integrated Management of Solid Wastes is an important key issue, mainly because of the potential negative effects against environment of wastes production and uncontrolled storage. The agro-industrial processing gives high and diverse quantities of solid wastes that can be valorized both into digestion processes, and/or recoveries of useful products. Newly, some of them were tested for their adsorptive potential for a series of pollutants from industrial wastewaters. Assurance of the quality of water resources is representing a demand and a need of our days in conditions of reductions of the natural resources. In this context, there are important to be applied some efficient technologies and procedures for industrial effluent treatment in order to reuse the treated effluent in the technological process or to protect the urban wastewater sewage system or different emissaries that receive the treated wastewater discharges.

The dyeing effluents resulted from different industries (i.e. textile and leather industry, paper processing, chemical synthesis, foods, cosmetics) are characterized by a load with dyes not very higher but generating serious problems because of their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens (i.e. benzidines). Also, the dye presence can significantly affect photosynthesis activity and reduce light penetration, thus affecting the growth of plants and impacting on invertebrate and other forms of wildlife; dyes can cause allergy, dermatitis, skin irritation, cancer and mutations in human bodies (Suteu D. et al., 2007). Due to their aromatic structures these compounds are more stable, no biodegradable and difficult to be removed from wastewaters. There are some processes that have been employed in order to remove dyes, such as adsorption, chemical flocculation, membrane filtration, ion exchange, advanced oxidation (chlorination, ozonation) and biological procedures (Anjameyly, Y. et al., 2005; Babu, R. et al., 2007; Crini, G., 2006; Crini, G. et al., 2008; Forgacs, E. et al., 2004; Suteu, D. et al., 2009a).

Although the traditional decolourization methods such as coagulation-flocculation, sorption on activated carbon, polymeric and mineral sorbents (e.g. peat, fly ash and coal, wood chips, silica gel, corncob, barley etc.), filtration, reverse osmosis, conventional chemical oxidation (i.e. oxidation with hydrogen peroxide, sodium hypochlorite and other chemical agents), ion exchange and biodegradation can remove organic pollutants from wastewater to certain extent, they are mostly inefficient to degrade stable aromatics such as synthetic dyestuffs because of the complex polyaromatic structure and recalcitrant nature of dyes (Zaharia, C. et al., 2009). Often, the effectiveness of these methods depends on the dye types in wastewaters and, therefore their particular application is restricted (Solozhenko et al., 1995; Zaharia ,C. et al., 2009).

Frequently applied treatments for decolourization of textile effluents consist of integrated processes involving various combinations of physical, chemical and biological processes that are efficient but not cost effective (Azbar et al., 2004; Zaharia, C., 2006; Zaharia, C. et al., 2009).

The recent studies were indicating that sorption is one of the best methods for wastewater treatment in term of the best efficiencies vs. costs. One of the advantages that impose this method is represented by the possibility to use large and different categories of adsorbents that can be selected also considering the dyes structure. In practice sorption is limited to the accumulation of organic compounds at an interface liquid-solid or the dispersion away from interfaces depending on their relative strength of attraction for themselves or for the solvent (i.e. the use of activated carbon for the removal of non-polar dissolved compounds).

The removal of organic dyes by adsorption onto low-cost materials has recently become the subject of considerable interest (i.e. a potentially simple and economic 'end-of-pipe' solution to the challenges set by new legislation covering effluent discharges, especially textile effluents) (Grau, P., 1991; Bousher, A. et al., 1997; Zaharia, C., Suteu, D., 2009; Zaharia, C., Suteu, D., 2010).

This paper continues our studies concerning the utilizations of ligno-cellulose materials (i.e. agriculture wastes) as low-cost sorbents for decolourization of different textile effluents that contain synthetic textile dyes with a high molecular weight (Suteu, D. et al., 2008; Suteu, D. et al., 2009b; Suteu, D. et al., 2010a; Suteu, D. et al., 2010b; Suteu, D. et al., 2010).

The literature presents numerous and diverse results for different kinds of dye sorption studies onto different types of ligno-cellulosic materials. Some of them are synthetized into *table 1*.

In this context, new other dye sorption studies will be performed in order to understand and explain the basic sorption principles. Moreover, this paper presents the experimental results of the influence study of some operating variables of Methylene Blue (cationic dye) sorption from aqueous media onto corncob and sunflower seed shells.

This study was made in order to establish the preliminary conditions necessary to study the equilibrium, kinetic, thermodynamic and optimization of the sorption process and also to establish the most indicated conditions for developing this method into real case studies of textile effluents.

Table 1

Comparison of sorption capacity for some dyes of different lignocellulosic materials as sorbents

Dyes	Sorbent	q, mg/g	Ref
Acid Blue 324 Acid Green 25 Acid Green 27 Acid Orange 7 Acid Orange 8 Acid Orange 10 Acid Red 1 Acid Blue 80	mango seed	12.8 8.6 12.6 17.3 15.2 8.3 11.2 9.2	(Davila Jimenez M.M., 2009)
Congo Red	hazelnut shells	13.75-1.87	(Carletto R.A., 2008)
Reactive Black 5	sunflower seed shells	0.873	(Osma J.F., 2007)
Rhodamine 6G Methylene Blue	palm shell powder	19.6531 4.2512	(Sreelatha G., 2008)
Methylene Blue	dehydrated peanut hull	108.6	(Ozer D., 2007)
Reactive Red 198	untreated olive pomace	55.84	(Akar T., 2009)
Acid Violet 17	sunflower seed hull	116.27	(Thinakaran N., 2008)
Reactive Orange 16	sunflower seed shells	21.27	(Suteu D., 2010)
Reactive Orange 16	corn cob	25.25	(Suteu D., 2010b)

MATERIAL AND METHOD

The experiments were carried out using wastes resulted from agro-industrial manufacturings:

- **sunflower seed shells –** wasted material obtained from local oil industry and used after air drying at room temperature for two days. The seed shells were grounded and sieved to obtain a particle size range of 0.8 mm and stored in plastic bottle for further use. No other chemical or physical treatments were performed. The major constituents of sunflower seed shells are cellulose, lignin and pentose. We used the fractions with size 800 μm;
- **corncob –** material representing an important by-product from local agro-industrial activities that can be included in the lignocellulosic groups of the adsorptive materials. The crude material was dried at room temperature, granulated and sieved to obtain different fractions. We used the fractions with size < 800 μm.

The cationic phenothiazine dye Methylene Blue (Basic Blue 9) (*fig. 1*, MW = 319.85, adsorption maximum at λ_{max}= 660 nm) was used as commercial salt. Working solutions (in concentration of 19 - 256 mg/L) were prepared by appropriate dilution with bidistilled water of a stock solution (320 mg/L).

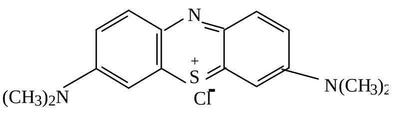

Figure 1 **Structure of Methylene Blue cationic phenothiazine dye**

The experiments were carried out at room temperature in batch condition: samples of 0.1 g sorbent were contacted with 25 mL of aqueous solution containing various concentrations of dye (25.6 - 281.6 mg/L) into 100 mL conical flasks, under an intermittent stirring. The temperature of aqueous systems was controlled with a thermostated assembly.

After 24 h, the phases were separated by filtration. The concentrations in the filtrates were analyzed by absorbance measurements with an SP-830 Plus spectrophotometer, Metertech Inc. Version 1.06, and comparison with the dye calibration curve.

The sorption capacity of the lignin was evaluated by amount of sorbed dye (Eq. 1):

$$q = (C_0-C).V/G \text{ (mg/g)} \qquad (1)$$

and by percentage of dye removal (Eq.2):

$$R = (C_0-C).100/C_0 \text{ (\%)} \qquad (2)$$

where: C_0 and C are the initial and equilibrium concentration of dye in aqueous system (mg/L), G is amount of sorbent (g), and V is volume of aqueous solution (L).

RESULTS AND DISCUSSIONS

Effect of solution pH

In order to establish the behavior of the studied materials in contact with aqueous media containing dyes and the optimal pH range for a high dye sorption efficiency it was determinate the pH_{PZC} value (pH of zero charge) by the method proposed by Nouri and Haghseresht (*fig. 2*) (Nouri S. et al., 2004).

From Figure 2 it can be shown that the value of pH_{PZC} for corncob is 4.8 (Suteu D. et al., 2009c) and for sunflower seed shells is 5 (Suteu D. et al., 2010).

At values of pH < pH_{PZC} the surface charges of the sorbents are positive and susceptible to electrostatic interactions with anionic dye molecule; at pH > pH_{PZC} the sorbent surface is negatively charged and available to bind cationic dye such as Methylene Blue.

Figure 3 presents the influence of pH of the initial dye solution on sorption of Methylene Blue cationic dye onto the tested sorbents (i.e. corncon, sunflower seed shells).

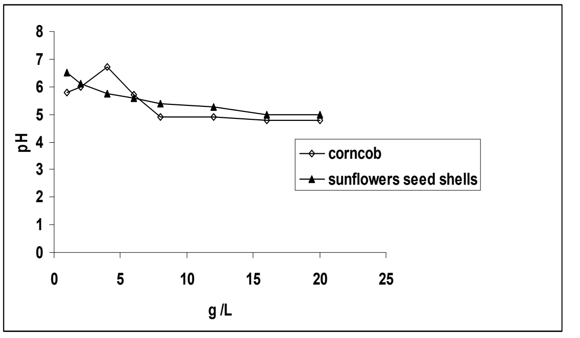

Figure 2 **The values of pH_{PZC} for the studied sorbents: corncob and sunflower seed shells**

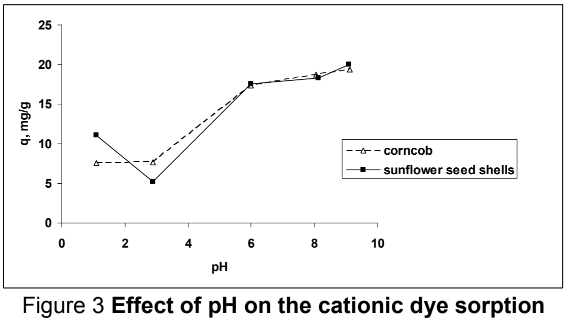

Figure 3 **Effect of pH on the cationic dye sorption onto studied sorbents**

Figure 3 shows that at pH value higher than pH_{PZC} (pH > 5) the surface of lignocellulosic sorbents are susceptible to electrostatic interactions with dye molecule.

Effect of sorbent dose

In order to find the proper amount of sorbent to get a significant sorption retention capacity, we studied the sorption of cationic dye onto the tested sorbents by selecting different amounts of sorbent and maintaining the initial dye concentration (51.2 mg/L) and temperature (20 ± 2^0 C) constant for 24 hours (*Fig. 4* and *5*).

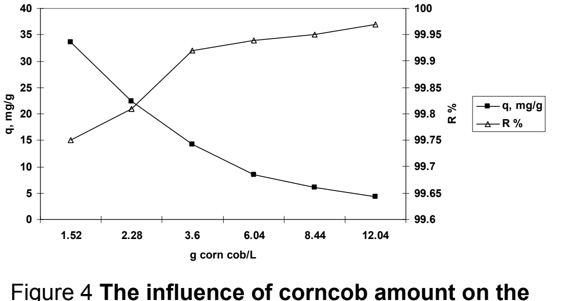

Figure 4 **The influence of corncob amount on the sorption of Methylene Blue dye: 51.2 mg/L, 20^{0}C**

From *Figures 4* and *5* it can be seen that the percent of cationic dye removal increases with the increasing of the sorbent doses.

The percent of dye removal is very good (until 99.97% for both sorbents, sorbent dose higher than 12.08 g/25 mL).

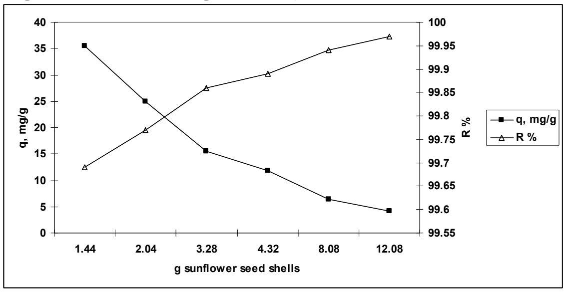

Figure 5 **The influence of amount of sunflower seed shells on the sorption of Methylene Blue dye: 51.2 mg/L, 20^{0}C**

At the same time the amount of cationic dye retained per weight unit of sorbent decreases from 33.6 to 4.25 mg/g (for corncob) and from 35.45 to 4.24 mg/g (for sunflower seed shells). This behavior is due to the increasing of surface area and the number of available sorption sites.

Effect of contact time

In order to establish the optimum conditions of operating in full-scale batch process we studied the effect of contact time on removal of Methylene Blue cationic dye from solutions of initial concentrations of 89.6 mg/L, by sorption onto corncob and sunflower seed shells.

From *figure 6* it can be seen that the amount of sorbed dye increases very fast in time up to 45 min and after increases slowly; nearly 3 hours are required to be attained the sorption equilibrium for the tested cationic dye.

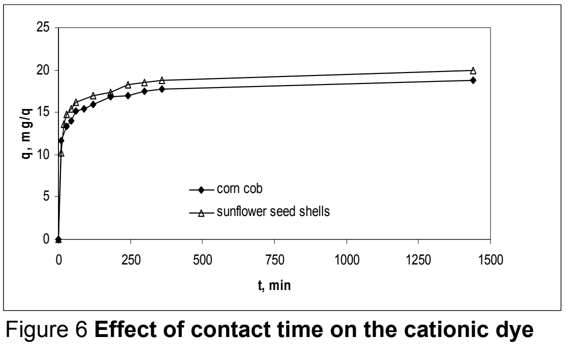

Figure 6 **Effect of contact time on the cationic dye removal by agriculture wasted sorbents: 4 g sorbent/L; 25^{0}C; 89.6 mg/L dye**

The dye sorption capacity reaches the value of 15.373 mg/g at 45 minutes for sunflower seed shells, and 13.94 mg/g at 45 minutes for corncob.

Effect of initial dye concentration

The capacity of studied lignocellulosic sorbent to remove cationic dyes at the favorable specific pH was determined from solutions of various initial concentrations.

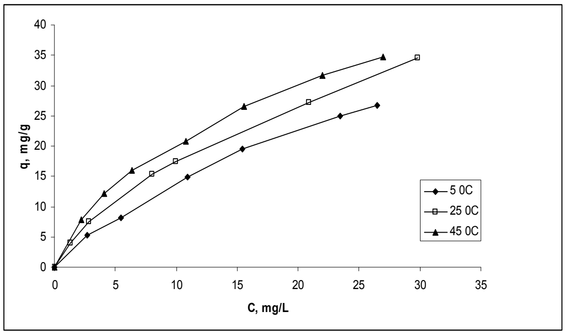

Figure 7 **Effect of dye concentration and temperature on the sorption onto sunflower seed shells: pH= 6; sorbent dose - 4 g/L**

The results presented in *figure 7* show that an increase in initial concentration of cationic dye from 19.2 to 256 mg/L changes the sorption capacity of dye until it reaches the equilibrium.

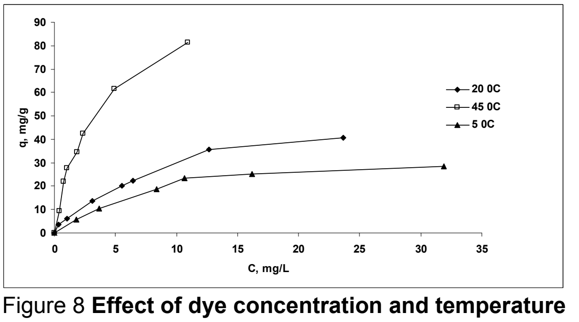

Figure 8 **Effect of dye concentration and temperature on the sorption onto corncob: pH=6; sorbent dose - 4 g/L**

It seems that the maximum sorption capacity of corncob is no higher than 28.44 mg/g at 5°C (Fig. 8), and increases with temperature increasing (i.e. > 81.23 mg/g at 45°C for the same dye concentration, when the initial dye concentration is higher than 150 mg/L).

Effect of temperature

The influence of temperature on the Methylene Blue dye retention by corncob and sunflower seed shells is illustrated also in Figure 7 and 8.

The shape of curves in these figures indicates that the amount of cationic dye onto studied lignocellulosic sorbents increases with an increasing in temperature, suggesting an endothermic process; the effect is more important at high concentrations.

Valorisation of the sorbents loaded with dyes

The dyed sorbents can be reused for several times (i.e. no more than seven sorption cycles) after desorption of dye by treating with HCl solutions. Thus, the treated sorptive material can be usefully reused for textile dye sorption and dyes are recovering and further processing.

Another valorisation directions of sorbents loaded with dyes are neutralization or inertization, and also elimination after drying by using them as energy fuel together with conventional fuels and other potential organic matter. After burning, the ashes can be safely storaged or used as additional raw materials for processing of some composite materials (Rao M. et al., 2002).

CONCLUSIONS

The ability of corncob and sunflower seed shells as sorbents to retain the Methylene Blue dye from aqueous systems was investigated for Methylene Blue cationic dye using batch operational conditions.

The sorption process of cationic dye is studied as a function of sorbent dose, initial dye concentration, temperature and contact time.

The amount of sorbed dye onto corncob and sunflower seed shells is depended on the solution pH and increases with sorbent dose, dye concentration, temperature and contact time increasing. The dye sorption equilibrium was rapidly attained after 3 hours of sorption contact.

Based on these preliminary results of finding the most indicated conditions of Methylene Blue sorption onto corncobs and sunflower seed shells we shall continue our researches with the dye sorption modeling, with the help of sorption isotherms and their characteristic quantitative measures, thermodynamic, and also kinetic parameters.

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