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REACTIVE DYE REMOVAL FROM AQUEOUS SOLUTION BY SORPTION ON MODIFIED ASH

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ABSTRACT - Effluents of textile dyeing are characterized by intense colour, chemical oxygen demand, suspended solids and a variety of refractory matter, such as heavy metals and nonionic surfactants. Strong colours may reduce light penetration, thus affecting the growth of plants and having impact on invertebrate and other forms of wildlife. There are a large number of methods for dyes removal, such as membrane separation, flocculation, sonolysis, anaerobic biological treatments, oxidative destruction via UV/ozone treatment, photocatalytic degradation, which have certain efficiency but their initial and operational costs are so great. Sorption is one of the several techniques that have been successfully utilized for dyes removal. A large number of materials have been used as suitable sorbents for decolourization of industrial effluents: activated carbon (the most common but expensive adsorbent), polymeric resins, various low-cost adsorbents (agricultural and industrial by-products, peat, chitin, silica, fly ash, etc.) Our investigation presented the preliminary results of the study on modified ash, which has been tested for its use as material with sorptive properties in the recovery of dyes from waste waters. The batch equilibrium of reactive dye Brilliant Red HE-3B sorption on industrial waste, based on ash was investigated in order to explore its potential use as low cost sorbent for wastewater dye removal. The results indicated that the sorption of tested dye depended on initial dye concentration, sorbent mass, pH, temperature and contact time. The sorption of dyes increased with ash dose, dye concentration and temperature increase. Even if the sorption capacity of ash was relatively small, ash could be used for the removal of dyes from aqueous effluents.

Key words: dye, ash, sorption, wastewater

REZUMAT - Reținerea coloranților reactivi din soluții apoase prin sorbție pe cenuşă modificată. Efluenții textili, având adesea o compoziție complexă, se caracterizează prin: colorație intensă, consum chimic de oxigen, solide în suspensie şi o mare varietate de alte materii, cum ar fi metale grele şi surfactanți neionici. Colorația intensă poate reduce penetrarea

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luminii, afectând astfel creşterea plantelor şi având impact asupra nevertebratelor. Există o mare varietate de metode pentru reţinerea coloranţilor, cum ar fi separarea prin membrane, flocularea, sonoliza, tratamentele anaerobe, destrucţia oxidativă prin tratament cu radiaţii UV sau ozon, degradarea fotocatalitică, precipitarea, care, deşi nu au o eficienţă ridicată, se caracterizează prin costuri operaţionale ridicate. Sorbţia este o tehnică care se utilizează cu succes în reţinerea coloranţilor. Există un număr mare de materiale utilizate ca sorbenţi pentru decolorarea efluenţilor textili: cărbune activ, răşini polimerice, o mare varietate de adsorbenţi ieftini (subproduse agricole si industriale, turbă, chitină, siliciu, cenuşă etc.). Cercetarea noastră prezintă rezultatele preliminare ale studiului privind utilizarea cenuşii de termocentrală modificată ca material cu proprietăţi sorbtive în reţinerea coloranţilor din ape uzate. A fost studiată sorbţia în condiţiile statice ale unui colorant reactiv Roşu Briliant HE-3B, pentru a aprecia potenţialul sorbtiv al cenuşii. Rezultatele au indicat faptul că sorbţia colorantului testat depinde de concentraţia initială a colorantului, doza de sorbent, pH-ul, temperatura, timpul de contact. Sorbţia coloranţilor creşte odată cu creşterea cantităţii de cenuşă, a concentraţiei coloranţilor şi a temperaturii. Chiar dacă capacitatea sorbtivă a cenuşii este relativ redusă, ea poate fi folosită pentru reţinerea coloranţilor din efluenţii din soluţii apoase.

Cuvinte cheie: colorant, cenuşă, sorbţie, ape uzate

INTRODUCTION

Effluents of textile dyeing / finishing processes have often a complex composition, characterized by intense colour, high chemical oxygen demand, suspended solids and a variety of refractory matter such as heavy metals, nonionic surfactants, etc. It has been suggested that strong colours can reduce light penetration, thus affecting the growth of plants and impacting on invertebrates and other forms of wildlife (Crini, 2006).

There are various methods for dyes removal, such as membrane separation, flocculation, sonolysis, anaerobic biological treatments, oxidative destruction via UV/ozone treatment, photocatalytic degradation, which have certain efficiency but their initial and operational costs are too high (Crini, 2006; Ramesh *et al.,* 2007; Zaharia *et al.,* 2006; Surpateanu and Zaharia, 2004). These methods are characterized by incomplete removal of dyes, limited tolerance to pH change, moderate or no selectivity for dyes, requirement of high consumption of reagents and energy, very high or low concentration levels of dyes and production of toxic sludge or other waste products that also need treatment before disposal (Şuteu *et al.*, 2007).

Sorption is one of the several techniques that have been successfully used for dyes removal. A large number of materials have been used as suitable sorbents for decolourization of industrial effluents: activated carbon (the most common but expensive adsorbent), polymeric resins, various low-cost adsorbents (agricultural and industrial by-products, peat, chitin, silica, fly ash, etc.) (Ozer *et al.,* 2007; Demirbas, 2009; Sreelatha and Padmaja, 2008; Kaushik and Malik, 2009; Akar *et al.,* 2009; Şuteu *et al.,* 2008; Şuteu *et al.,* 2007; Suteu and Bilba, 2005).

In this scientific paper, we have shown the preliminary results of the studies on modified ash, which has been tested for its use as material with sorptive properties in the recovery of dyes from waste waters. The batch equilibrium of the sorption of reactive dye Brilliant Red HE-3B on industrial waste based on ash was investigated in order to explore its potential use as low cost sorbent for wastewater dye removal. Results have shown that the sorption of tested dye depended on initial dye concentration, sorbent mass, pH, temperature and contact time. The sorption equilibrium concentrations were determined by UV-Vis spectrophotometry analytical method.

MATERIALS AND METHODS

Sorbent materials

The experiments were carried out using coal ash from CET IASI- Romania Company, which was modified by the treatment with different chemical agents. Samples of 5 g ash and 10 g NaOH were treated at 873 K in electric furnace by mixing ash with solid NaOH in platinum ball, cooled during 11 hours, diluted with 150 cm^3 distilled water and boiled for 3 hours at T=373 K for crystallization.

Reactive dye

The reactive dye bifunctional monochlortriazine Brilliant Red HE-3B from BEZEMA (*Figure 1*, MW =1463, adsorption maximum, λ_{max} = 530 nm) was used as commercial salt. The solutions (at concentrations of 20-300 mg/L) were prepared by proper dilution with bidistilled water of the stock solution (500 mg/L).

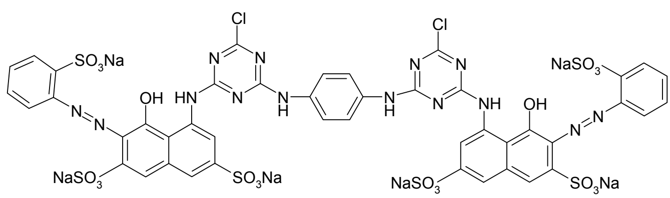

Figure 1- **Bis (monochloro-*s*-triazine) reactive dye (Brilliant Red HE-3B, C.I. Reactive Red 120)**

Sorption studies

Batch sorption experiments were performed by equilibrating 0.15 g of ash with 25 mL solution at different initial concentrations of dye, pH and temperature, under intermittent stirring. After a prefixed time (usually 24 h), the dye content in solutions was determined spectrophotometrically. The sorption efficiency was calculated as percent of dye removal, $R=\frac{c_0-c}{c_0}.100$ (%) or as amount of sorbed dye (retained on ash), $q=\frac{c_0-c}{g}.V$ (mg/g), where c_0 and c are reactive dye concentrations (mg/L) in the aqueous phase, before and after equilibration, respectively, V is the volume of aqueous solution (L) used for equilibration and g is the weight of ash sample (g).

RESULTS AND DISCUSSION

Effect of pH. In our experiments, the initial pH of solutions was adjusted. The pH of aqueous solutions was adjusted to the desired value by adding HCl or NaOH solutions and measured with an RADELKIS OP-271 pH/Ion analyzer. The sorption efficiency of Brilliant Red HE-3B dye on ash as a function of solution pH is shown in *Figure 2*.

Figure 2 showed that the sorption of tested dye by ash samples decreased with pH increasing, from 4.715 mg/L at pH =1.5 to 0.951 mg/L at pH= 6-7; maximum sorption of Brilliant Red HE-3B dye takes place at pH = 1.5. This behaviour could be attributed to the predominant positive charges of ash surface at low pH that facilitate in this case the electrostatic interactions with the anionic dye.

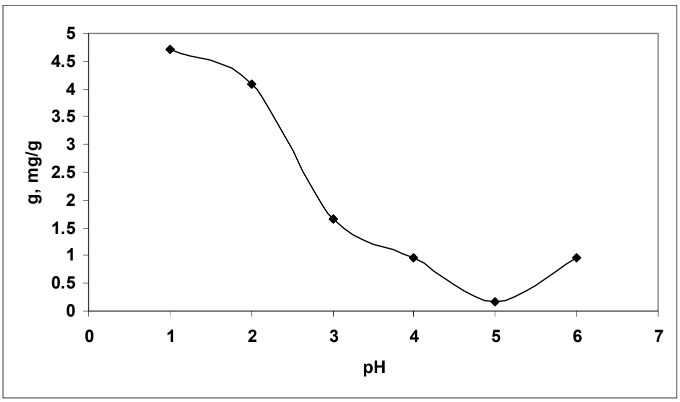

Figure 2 - Effect of pH on the sorption of dye on modified ash: C=80 mg/L; T=20^{0}C

Effect of sorbent dosage. To establish the favourable sorbent dose, different amounts (0.05 – 0.6 g) of modified ash were contacted with aqueous solutions with 80 mg/L dye concentration, at the initial pH= 1.5, for 24 hours at temperature of 20^{0}C. The results of *Figure 3* showed that the percent of dyes removal increased with the increase of ash doses, due to higher number of available sorption sites. In case of more voluminous molecules of reactive dye Brilliant Red HE-3B, the ash dose, which assures a suitable removal percent, is higher than 10 g/L.

Effect of temperature. The dye sorption on modified ash sorbent depends on temperature (*Figure 4*). Data presented in Figure 4 show that the sorption capacities of lignin increased with increasing temperatures, which suggested an endothermic process. This behaviour could be explained by dye molecule diffusion in the internal porous structure of sorbent by high temperatures. The effect is more important at higher concentrations.

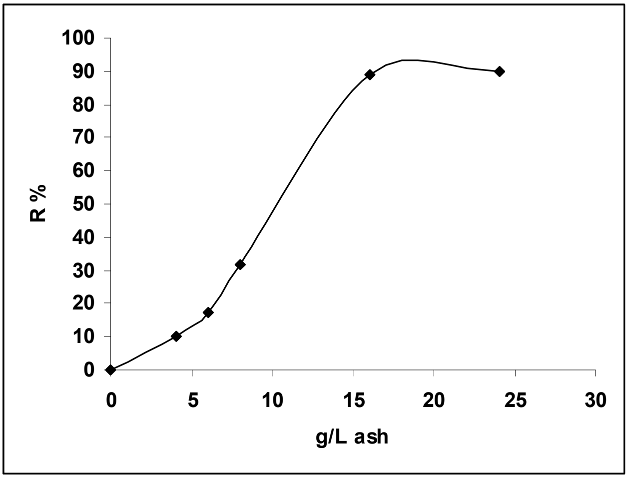

Figure 3 - **The influence of sorbent amount on the sorption of dye on ash: C=80 mg/L; pH 1.5; T=20^{0}C**

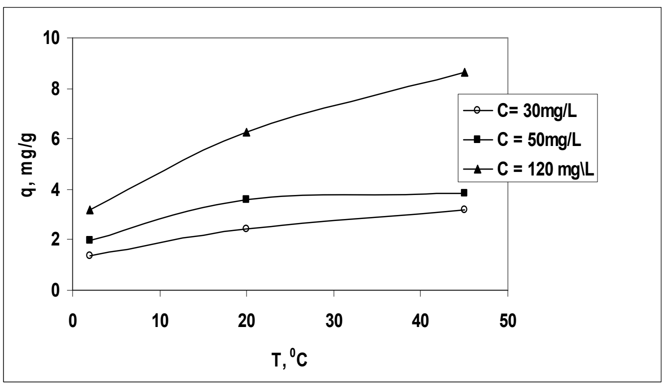

Figure 4 - **The influence of temperature on the sorption of dye on ash: pH 1.5; 6g/L ash; T=20^{0}C**

Effect of initial dye concentration. The capacity of modified ash to remove anionic dyes at the favourable corresponding pH was determined from solutions of various initial concentrations. The results presented in *Figure 5* showed that the removal percent of reactive dye BR has decreased slowly with dye concentration increasing. At the same time, the sorption capacity has increased with dye concentration increase in solution.

Effect of contact time. The effect of contact time on the adsorption of Brilliant Red HE-3B dye was shown in *Figure 6*. Almost 60 minutes were necessary for the sorption equilibrium of this dye.

Figure 6 showed that sorption was very fast initially and then slowly reached the sorption equilibrium. This can be the consequence of the fact that a large number of free surface sites are available for sorption during the initial stage and, afterwards, the remaining free surface sites are difficult to be occupied, because of repulsive forces between the phases.

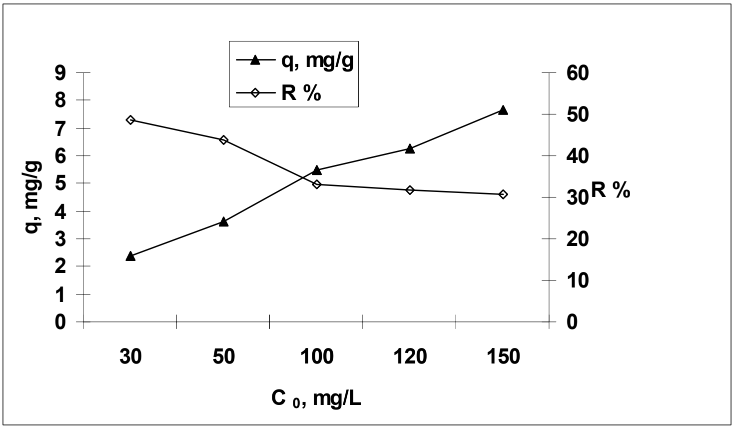

Figure 5 - **The influence of initial dye concentration on the sorption onto ash: pH 1.5; 6 g/L ash; T=20^{0}C**

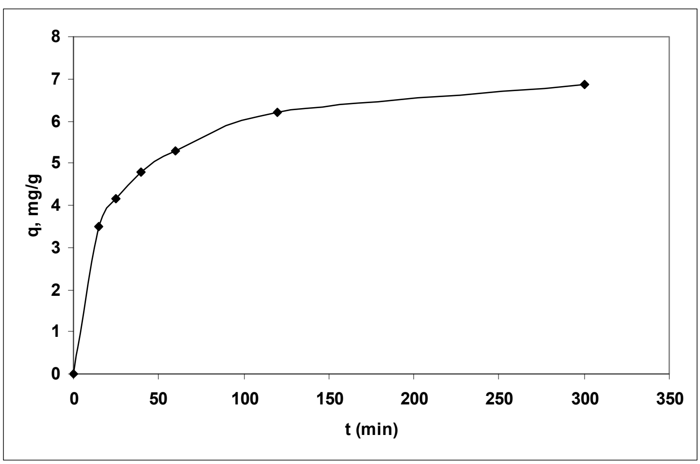

Figure 6 - **Effect of contact time on uptake of Brilliant Red HE-3B dye on ash: pH 1.5; 6 g/L ash; T=20^{0}C; C=70 mg/L**

CONCLUSIONS

The removal of the anionic dye Brilliant Red HE-3B from aqueous solution was investigated by using as sorbent ash modified by its treatment in electric furnace with solid NaOH in platinum ball, cooled during 11 hours, diluted with 150 cm^3 distilled water and boiled for 3 hours at T= 373 K for crystallization.

The sorption of dyes onto ash depends on the initial pH solution, dose of ash, dye concentration and temperature.

The best pH value was 1.5. The sorption of dyes increases with ash dose, dye concentration and temperature increase.

Even if the sorption capacity of ash is relatively small, ash can be used for the removal of dyes from aqueous effluents.

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