MATERIALS BASED ON ASH FOR ENVIRONMENTAL PROTECTION. II. PRELIMINARY STUDIES ABOUT DYES SORPTION ONTO MATERIALS BASED ON ASH.

Daniela SUTEU[1], Maria HARJA[2]
Gabriela RUSU[1]

[1]"Gh. Asachi" Technical University of Iasi,
Faculty of Chemical Engineering, Department of
Environmental Engineering and Management
e-mail: danasuteu67@yahoo.com

[2]"Gh. Asachi" Technical University of Iasi,
Faculty of Chemical Engineering, Department of
Chemical Engineering

Batch sorption experiments were carried out to remove reactive dye Brilliant Red HE-3B from its aqueous solutions using industrial waste ash and materials based on ash as a low cost sorbent. To establish the most suited type of materials to be used as sorbent for this dye, the effect of various experimental parameters such as solution pH, initial dye concentration, sorbent dose and type of sorbent were investigated. The results of this study show that all of the tested materials have a limited capacity for dye molecules uptake but we also observed that sorbent namely Ads 4 present the best values from the sorption capacity of sorption. The percent of reactive dye Brilliant Red HE-3B sorption has a maximum at pH 2.0 - 5.0 and increases with the increase of sorbent dose, temperature and decreases with increasing initial concentration of solution.

Keywords: *dye, ash, sorbent based on ash, sorption, waste waters.*

By volume and composition of waste waters from dyeing processes, the textile industry has a great polluting impact. In this context, the major tendencies of recent years are elaborations of very strict settlements concerning waste waters disposal, development of new technologies for textile effluents depollution and concluding of syntheses of organic dyes replacing the products of toxicological, allergen and mutagen risk. The wide diversity of dyes chemical structure, their variable content in effluents together with considerable amounts of auxiliary products make impossible the development of a method with general applicability for dyes removal from waste waters of textile dyeing processes. For this purpose, a great variety of methods including coagulation, treatment with oxidizing or reducing agents, ozonization, separation by membranes, floculation, foam flotation and sorption are applicable [1-3]. Dyes removal by **sorption** in batch conditions is a relatively simple method which can be carried out without sophisticated equipments. This method allows the use of a wide variety of sorbtive materials: from active carbon filters, organic waste materials and natural celluloses unconventional materials to conventional ion exchangers based on resins or made by cellulose quaternization [3–9]. The use of sorbtive materials is based on high efficiencies of the sorption process, with lower prices. Being compounds with high molecular weights, the used sorbents must have porosity adequately to sorption of these compounds.

This paper present the results about the evaluation the analytical sorption potential of some sorbents based on ash (industrial waste ash and mixture with ash) in retention by batch sorption of reactive dye Brilliant Red HE-3B from synthetic aqueous solution. Operating variable studied were initial dye concentration, sorbent mass, pH, temperature, type of sorbent. The sorption equilibrium concentrations were determined by UV-vis spectrophotometry analytical method.

MATERIALS AND METHODS

Sorbent materials. The experiments were carried out using ash from CET IASI. Ashe's chemical characterization has been done on the SR EN standard - 450-1:2006 and the specific surface has been determined by the Blaine permeabilimeter. The experimental results are presented in *Table 1* [9]. Some different types of materials with sorptive properties were obtained from ash through zeolitisation during 1hour (zeolite 1h) and 24 hours (zeolite 24h) and by mixed with lime in different proportion (3.75 lime: 6.25 ash) at 70^{0}C and different heating time (1hour – Ads 1h and 4hours- Ads 4h).

Table 1

The characterization of coal ash

Composition, %	Type of ash	
	without carbon (ash-C)	with carbon (ash+C)
SiO_2	51.21	51.83
Al_2O_3	15.08	22.62
Fe_2O_3	6.28	3.44
CaO	5.21	7.52
MgO	1.09	1.075
SO_3	1.1887	2.3121
Ignition loss 700 °C, %	-	7.483
Ignition loss 1200°C - total loss, %	1.3	12.5795
Humidity la 105°C, %	0.446	0.883
Density (kg/m^3)	2518	2155
Specific surface Blaine (cm^2/g)	4126	3298
Oversize 0.04 (mass fraction)	0.1905	0.75

Dye solution. 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. Working solutions (in concentrations of 20-150 mg/L) were prepared by appropriate dilution with bidistilled water of the stock solution (500 mg/L).

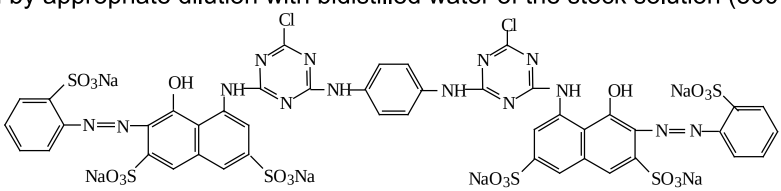

Figure 1. Structure **of reactive dye Brilliant Red HE-3B**

S*orption studies.* The sorption capacity of the tested sorbents was determined by batch method: samples of 0.2g sorbent were contacted with 25mL of solution containing various concentration of dye (20-150 mg/L) into 100mL conical flasks, under an intermittent stirring. The temperature of the aqueous systems was controlled with a thermostatic bath. After 24h, the phases were separated by filtration. The concentrations in the filtrates were analyzed spectrophotometrically with an UV-VIS Digital Spectrophotometer, model S 104D /WPA. The sorption capacity of the sorbents was evaluated by amount of sorbed dye: $q = (C_0\text{-}C)\cdot V\cdot 10^{-3}/G$, (mg of dye/g sorbent) and/or dye removal degree: $R\% = (C_0\text{-}C)\cdot 100/\ C_0$, where: C_0 and C are initial and equilibrium concentration of dye in aqueous system (mg/L), G is amount of sorbent (g), and V is volume of aqueous system (L).

RESULTS AND DISCUSSION

Effect of pH

We worked with an anionic dye and the pH of solution affect the sorption process onto the sorbent based on ash. The effect of pH on sorption was examined at a dye concentration of 60 mg/L at 25 ^{0}C and pH values ranging from 1 to 6 (*Fig. 2*). The pH of aqueous system was adjusted with HCl 1N. *Figure 2* shows that the sorption capacity of the dye depends on the pH of solution and type of sorbent.

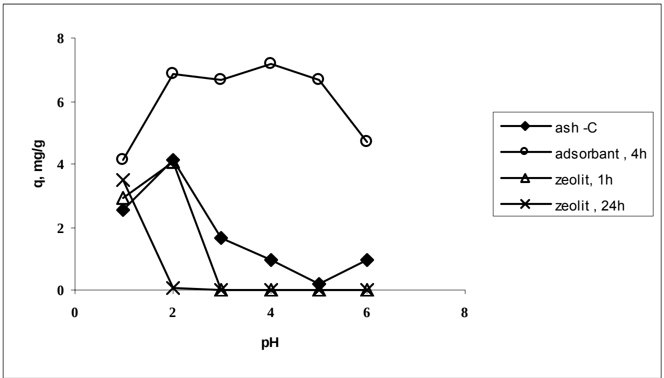

Figure 2**. Effect of pH into reactive dye Brilliant Red HE-3B sorption on different inorganic sorbents.**

Effect of amounts of sorbents

The influence of amount of sorbent (expressed by ratio from dose of sorbent and volume of solution) on the sorption process of reactive dye Brilliant Red HE-3B at pH 4, 30 ^{0}C temperature and 60 mg/L dye concentration in solution is shown in *Figure 3* .The results, presented in *Figure 3,* showed that the for Ads 4h sorbent 0.15g is the amount which assure a higher sorption capacity.

Effect of temperature

The dye sorption onto the inorganic sorbents is dependent of temperature (*Tab. 2*). The data presented in *Table 2* shown that for Ads 1h sorbent the sorption capacity for dye increases with temperature increasing suggesting an endothermic process.

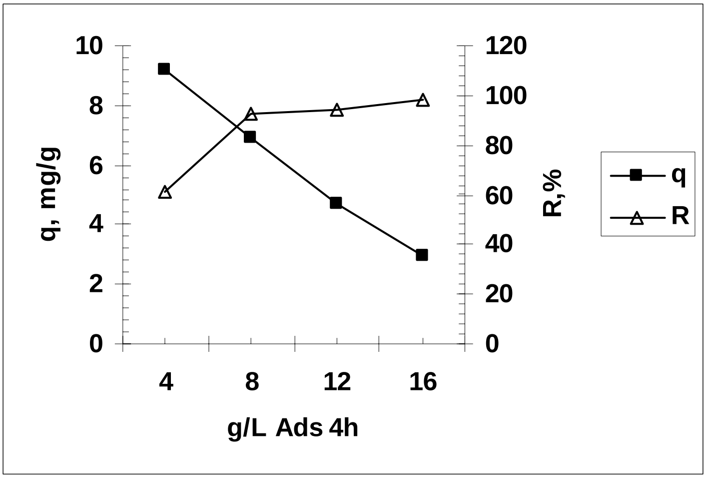

Figure 3. **The influence of amounts of sorbent on the sorption of dye onto Ads 4h sorbent**

Table 2

The temperature influence into dye sorption on Ads 1h (pH 4, dose of sorbent 8g/L)

Temperature ($^0C \pm 2^0C$)	C_0 (mg/L)	q (mg/g)	Temperature ($^0C \pm 2^0C$)	C_0 (mg/L)	q (mg/g)
5	30	3.62	5	50	5.232
25		3.75	25		6.130
45		4.52	45		6.197

Effect of initial dye concentration

The sorption capacity of some inorganic sorbents for reactive dye Brilliant Red HE-3B was determined at different initial dye concentrations at the fixed initial pH solution and 25^0C temperature. The results plotted in *Figure 4* show that the amount of dye retained increases with increasing of initial concentration.

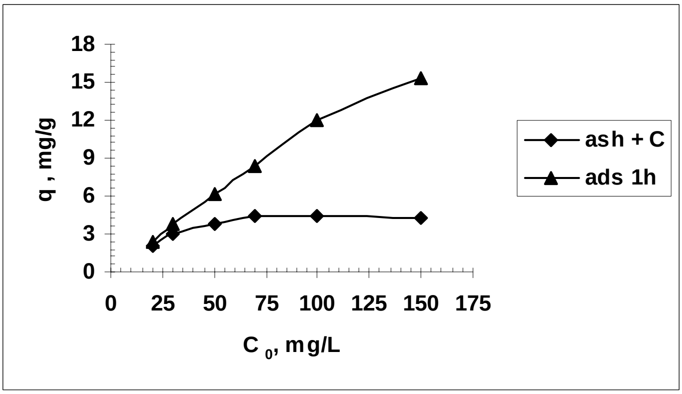

Figure 4. **The influence of initial dye concentration of the sorption process**

Sorption isotherms of the reactive dye Brilliant Red HE-3B onto some types of selected inorganic sorbents at room temperatures are represented in *Figure 5*.The experimental equilibrium sorption data were analyzed using the Langmuir [10] adsorption isotherm models expressed by following equation:

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C} \quad (1)$$

where K_L is the Langmuir constant and is related to energy of the sorption and q_0 is the maximum value of sorption capacity (corresponding to complete monolayer coverage).

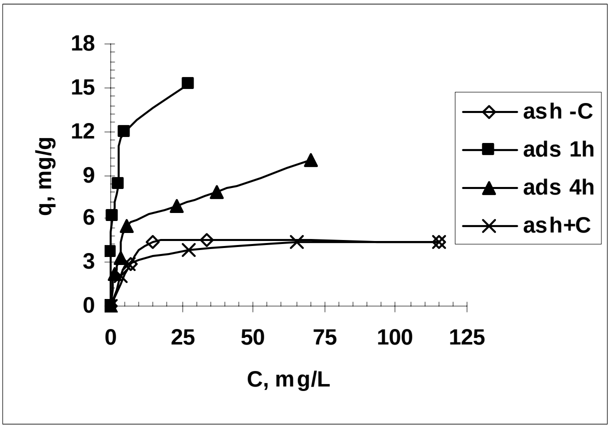

Figure 5. **The sorption isotherms of the reactive dye Brilliant Red HE-3B on inorganic sorbents based on ash at room temperature and pH=4**

The Langmuir sorption parameters were determined by converting the corresponding equation in the linear form. The constants of the sorption isotherms, calculated from the intercepts and slopes of the corresponding linear plots for reactive dye Brilliant Red HE-3B sorption at room temperature, together with their correlation coefficients (R^2), are collected in *Table 3.*

Table 3

The characteristic parameters of reactive dye Brilliant Red HE-3B sorption onto sorbents based on ash

Langmuir parameters	Type of sorbent			
	ash –C	ash +C	**ads 1h**	ads 4h
q_0 (mg/g)	5.136	4.541	**16.00**	9.434
K_L (L/g)	0.1712	0.2572	**0.653**	0.2265
R^2	0.9817	0.9939	**0.9999**	0.9945

CONCLUSIONS

The sorption of reactive dye Brilliant Red HE-3B from aqueous systems onto sorbents based on ash is a function of initial dye concentration, temperature, amount of sorbent and pH of solutions. The results of this study show that the tested sorbents have a limited capacity for dye molecules uptake. Experimental data conclude that **Ads 1h** is the most efficient sorbent (q_0=16.00 mg dye /g sorbent) for sorption process of reactive dye Brilliant Red HE-3B at room temperature, from aqueous systems having moderate acidity (pH =4).

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