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섬유산업 폐수 처리시 새로운 종이슬러지 흡착제의 제조와 평가

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Preparation and Evaluation of New Adsorbent (Paper Sludge) in the Treatment of Waste Water of Textile Industry

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요약. 수용액에서 Neutral red5 (BR 5)의 흡착을 조사하였다. 250 °C에서 2시간동안 소각한 제지 슬러지로부터 새로운 고형 흡착제를 제조하였다. 제조된 폐수로부터 RB5 염료를 제거하기 위해 배치 시스템으로 실험을 수행한 결과, 상온 pH 5조건에서 80분동안 최대 374.98 mg/g 의 흡착을 보였다. 높은 회귀계수(regression coefficient R^2)와 함께 The Freundlich isotherm이 실험값과 잘 부합하였다.

주제어: 소각 슬러지, 흡착, RB5 염료

ABSTRACT. Neutral red5 (BR 5) adsorption from aqueous solution was investigated. New solid adsorbent was prepared from paper sludge incinerated at 250 °C during 2 hours. Experiments were carried out, in batch system, to remove RB5 dye from the synthetic waste water. Maximum adsorption of 374.98 mg/g at pH 5, at room temperature and contact time of 80 min was obtained. The Langmuir and Freundlich adsorption models were applied to interpret the equilibrium isotherm. The Freundlich isotherm fits quite well with the experimental data (with highly regression coefficient R^2). The incinerated sludge solid samples untreated and treated with BR5 dye were characterized by FT-IR spectrophotometer.

Keywords: Incinerated sludge, Adsorption, RB5 dye

INTRODUCTION

The industry of paper rejects significant amounts of the waste whose setting in discharge was the means the elimination of simplest and cheapest. One distinguishes several dies from valorization of sludge including: the setting as a cover for discharges, the sludge incineration at a prohibitory cost and present a risk related to the pollutant gas impact on the environment such as that of the dioxin[1] (ADEME, 1999/CE), energy valorization (production of biogas like source of heat and of electricity), biological or agricultural valorization (production; manure and of compost) and valorization in the sector of building. The choice of a die must be dependent on the cost of installation, origin of sludge, added-value of the product which results from it and the impact which the die retained on the environment could have. The setting discharges some (also called storage) proves to be a technique little developing and is legally prohibited in many countries[2] (directive 1999/31/CE). In the optics of research on the valorization of the industrial waste, paper sludge appeared candidates potentially which may undergo beneficiation in the treatment of industrial waste water. The methodology followed during this study relates primarily to the preparation (washing, drying and incineration) and valorization in the application of industrial sludge "sludge of purifi-

cation plant of water of rejections of a paper mill GIPEC of Saida (Algeria) in the water treatment charged with dyes, in fact the basic red 5 (RB5).

EXPERIMENTAL

The sludge of purification plant of industrial water "workshop 22" of production unit GIPEC of Rabahia to 10 km from Saida (Algeria) was used in this study. The sludge sample of paper mill was washed, dried with the air during several days and then incinerated at 250 ^{o}C during 2 hours in a muffle furnace. The material resulting from the incineration of sludge was filtered, and it will be indicated by BI.

The cation capacity of exchange CEC and total specific surface TSS of the pure incinerated sludge sample were estimated by the methylene blue BM method.[3] The values of the CEC and TSS obtained are of 23.66 meq/100g and 122.53 m^2/g respectively. *Table* 1 lists experimental results of the physicochemical analyses of incinerated sludge.

Neutral red 5, basic dye 5, NR5 (CI 50040, MW = 319.50 $g.mol^{-1}$, λmax = 520 nm, ε = 25000 cm^{-1} $mole^{-1}dm^{-3}$) from Across product for microbiological analysis and used without any further purification. Structural formula of the dye investigated is shown in *Fig*. 1.

Aqueous dye solution stock was prepared by dissolving accurately weighed neat dye in distilled water to the concentration of 0.1 g/L. Experimental solutions were obtained by successive dilutions. The initial pH of the dye solutions was adjusted by buffer solutions of NaOH/HCl (0.1 M).

The incineration of the paper sludge sample was carried out in a muffle furnace (Nabertherm, ZAH 2002).

The initial pH of the dye aqueous solution was recorded using (WTN: WISSENSCHAFLLICH TECHNISECHE WERKSTÄTTEN; weilehein Allemagne pH-330) digital pH-meter.

X-ray fluorescence was performed on a spectrometer of mark (Oxford). The sample is powder tiny room and prepared (pearl borated) is subjected to a source of X-radiation of fluorescence characteristic of its chemical composition.

Vis-absorption spectra of the dye in aqueous solution and adsorbed on incinerated sludge were obtained by Model: UV – 2401 (PC) SHIMADZU – corporation spectrometer in the range 350 - 800 nm, using 1 cm optical pathway cells.

FTIR spectra were measured in dispersed clay-Na in KBr pellets (1/200 w/w) with Perkin-Elmer spectrometer in the range 4000 - 400 cm^{-1}, with resolution 4^{o}.

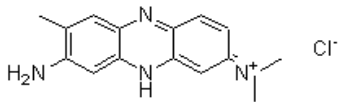

Fig. 1. Molecular structural of neutral red 5 (BR5) cation.

The effect of initial pH on sorption BR5 dye by incinerated sludge was performed on BR5/BI suspension in 50 mg/l BR5 dye (solid /liquid ratio of 1g/L) and over a range of pH values from 2 to 12. The initial pH values of the experimental solutions were adjusted with 0.1 N HCl and 0.1 N NaOH solutions. The suspensions were stirred for 80 mn, and then separated by centrifugation. Dye concentrations in the supernatant solution were estimated by measuring absorbance at maximum wavelength of dye.

The adsorption experiments of the BR5 dye by incinerated sludge were carried out, in batch system at 19 - 22 ^{o}C, with varying the initial concentration of RB5 from 5 to 60 mg/L with solid/liquid ratio of 0,1 g/L. The experiments were established at optimal values of pH (ph = 5) and contact time (80 min). The residual concentration of RB5 in the supernatant was followed by spectrophotometer.

The amount of BR5 adsorbed on the incinerated sludge and the removal rate P(%) were calculated based on following equations (1) and (2):

$$Q\ (mg/g) = (C_o - C_e)V/C_o \quad (1)$$

$$P\ (\%) = (C_o - C_e)100/C_o \quad (2)$$

Where C_0 and C_e are the initial and equilibrium solution concentrations (mg/L) respectively. V is volume of the solutions (L), and m is the weight of incinerated sludge (g) used.

Adsorption isotherms were applied to evaluate the performance of the adsorption process. Langmuir and Freundlich are used to describe the interactions between the adsorbates and adsorbents. Langmuir isotherm is valid for monolayer adsorption on a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The interaction between adsorbates and adsorbent are negligible. The linearized equation[4] (3) is given as follows:

$$\frac{C_e}{Q_m} = \frac{1}{Q_m K_1} + \frac{C_e}{Q_m} \quad (3)$$

where Q_m (mg/g) is the maximum amount of the dye per unit weight of incinerated sludge to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, and K_L is the Langmuir constant related to the affinity of binding sites (l/g).

A plot of Ce/Q_m *vs* C_e leads to a straight line with the slope of $1/q_m$ and an intercept of $1/K_L$ Freundlich isotherm describes repulsive interactions adsorbed solute particles. This empirical model is based on adsorption on a heterogeneous surface representing that binding sites are not equivalent. The logarithmic form of freundlich equation[5] (4) is expressed as follows:

Table 1.Chemical composition and main properties of the incinerated sludge

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	SiO_2/Al_2O_3	LF
14.12	9.84	2.34	26.5	1.76	0.42	0	3.9	1.43	41.93
pH		CEC (mg/g)			CEC (meq/100g)			SS (m^2/g)	
8.5		75.61			23.66			122.53	

LF: Loss of Fire. CEC: Cation Exchange Capacity. TSS: Total specific Surface

Table 2. Adsorption isotherm parameters of BR5 dye on the incinerated sludge for Co = 5 - 60 mg/L, m/v = 0.1 g/L, pH = 5, T = 19 - 22 °C and contact time of 80 min.

Experimental results	Theoretical results					
BR5/BI system	Langmuir		Freundlich			
Q_{max} (mg/g)	Q_{max} (mg/g)	K_L (L/g)	R^2	K_F (L/g)	1/n	R^2
374.9823	344.8	0.0451	0.19	23.469	1.3	0.95

R: Coefficient of regression

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where Q_e is roughly an indicator of the adsorption capacity and (1/n) of the adsorption intensity. Values n > 1 represent a favorable adsorption condition. 1/n and K_F can be determined from the linear plot of LogCe *vs* Log C_e.

RESULTS AND DISCUSSION

Table 1 lists the results of chemical composition in the incinerated sludge and pH of the BR5/incinerated sludge suspension. The major elements present in BI sample, expressed in terms of oxide, are primarily of silica, alumina, lime and a strong water content with the moderate presence of the elements such as sodium, magnesium, potassium and iron. The loss of fire raised about 41.93%, sign of the important presence of the organic matter and calcite.

The value of pH of the sample BI is estimated at 8.5. This alkalization of the suspension can be attributed to the progressive dissolution of the carbonates (calcite) initially present in incinerated sludge.

Fig. 2 shows that the pH significantly affected the adsorption capacities of the cationic RB5dye onto incinerated sludge. The dye removal increased as the initial pH was increased from 2 to 5, then it decrease considerably to reach a percentage of 7. 65% to pH = 12. However no adsorption is observed with pH = 2. The maximum dye removal of 60.09% of RB5 was achieved with an initial pH of 5.

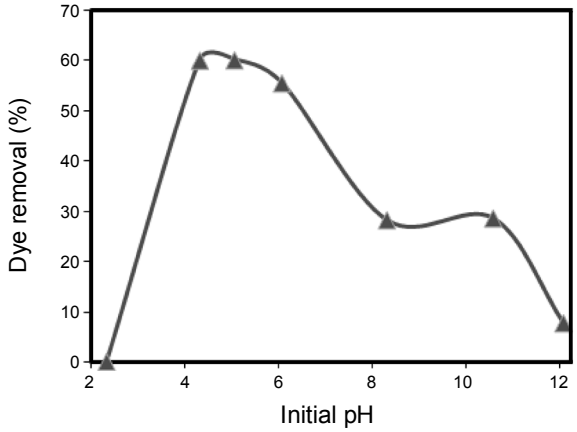

Fig. 2. Effect of pH on *BR5* dye removal by incinerated sludge for C_0 = 50 mg/L, m/v = 0.1 g/L, T = 19 - 22 °C and contact time of 80 min.

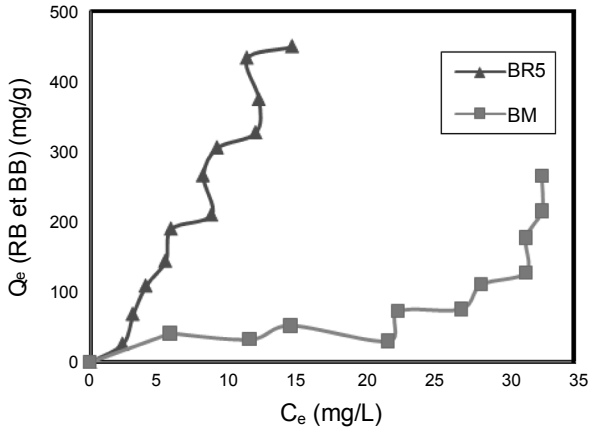

Fig. 3. Adsorption isotherm of BR5 and MB dyes on the incinerated sludge for C_0 = 5 - 60 mg/L, m/v = 0.1 g/L, pH = 5, T = 19 - 22 °C and contact time of 80 mn.

Fig. 3 shows the adsorption isotherms of the dyes using incinerated sludge. The shape of the BR5 isotherm does not show the characteristic plateau of a monolayer in the range of the concentration used. This isotherm can be classified as an (S-shape) isotherm according to Giles classification system.[6] The equilibrium adsorption capacity increases more slowly with the increase in dye concentration. The results of the application of Langmuir and Freundlich linearized models for the obtained experimental data are listed in *Table* 2.

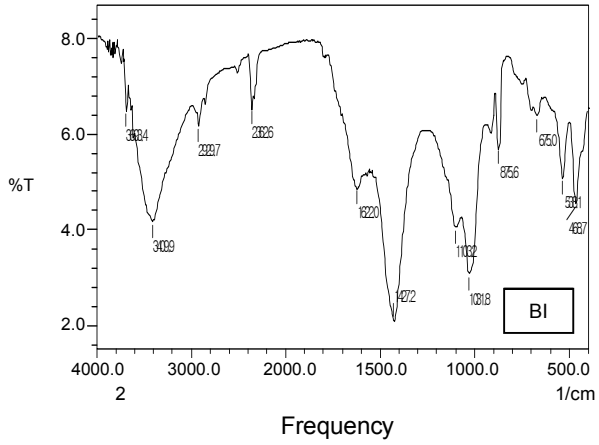

Fig. 4. FT-IR spectrum of the pure incinerated sludge sample.

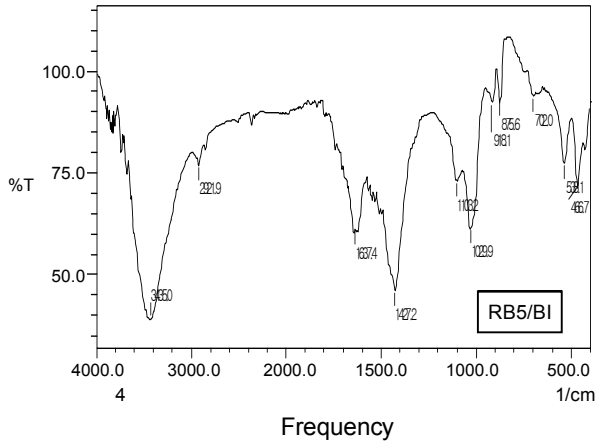

Fig. 5. FT-IR spectrum of the BR5/ incinerated sludge sample.

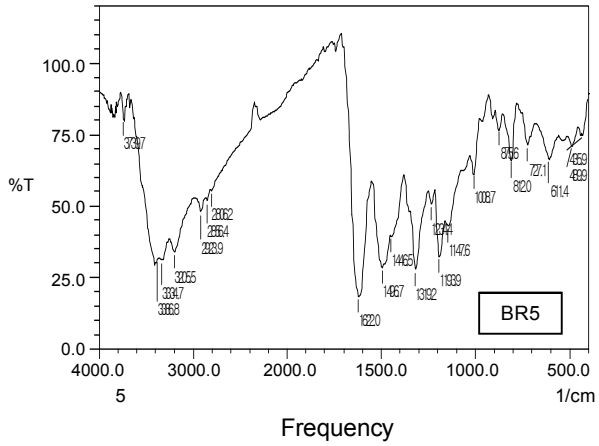

Fig. 6. FT-IR spectrum of the pure BR5 dye sample.

Freundlich model was fitted to the adsorption data with highly significant coefficients of regression ($R^2 > 0.95$). The value of 1/n (1/n > 1) reveals the nature and strength of adsorptive forces involved indicating the existence of strong adsorption forces operating on heterogeneous surface incinerated sludge.

Maximum adsorption capacity of 374.98 mg/g was obtained.

The profile of the BM isotherm is L-3 type, is obtained when the polymoléculaires layers appear only when surface is almost entirely covered with a monomolecular layer.[7]

In order to investigate the interactions between BR5 and incinerated sludge, FTIR analysis was conducted. As shown in *Fig*. 4, the spectrum of the pure incinerated sludge (*Fig*. 4) allows identifying the characteristic absorption band of the acid functional groupings, which are in general oxygenated functions of surface of the incinerated sludge such as cellulose (3409.9, 2929.7, 2500, 1427 and 1103.2 cm^{-1}), kaolinite (3693.4 cm^{-1} (OH^-), 912 cm^{-1} (Al-OH), 700 cm^{-1}, 468.7cm^{-1} (Si-O) and 538.1 cm^{-1} (Si-O-AL)), calcite (2515, 1797, 1427.2, 875.6 and 710 cm^{-1}) and talk (675 cm^{-1}).

The band at 1630 cm^{-1} is also attributed to physical adsorbed water. The FTIR spectra of the incinerated sludge samples untreated and treated with BR5 (*Fig*. 5) show a great similarity of some absorption bands with some differences in the intensity. The assignment and interpretation of the bands are the following: a less intense band at 2855 cm^{-1}, assigned to symmetrical aliphatic carbon ($-CH_2$)[12] and a second weak band near 435 cm^{-1} (no identified) corresponding to the RB5 dye (*Fig*. 6). The obtained results indicate a specific interaction between BR5 dye molecules and the incinerated sludge surface.

CONCLUSION

Adsorption of neutral red 5 (BR 5) from aqueous solution using a new prepared adsorbent was investigated. Results show that the adsorption capacity of the incinerated sludge was significantly affected by the pH. The uptake increased more slowly with increase in initial dye concentration. The incinerated sludge exhibited excellent performance for adsorption of RB5 with a maximum of 374. 98 mg/g.

The adsorption data were well fitted with Freundlich adsorptive model.

The strong interaction forces operating on heterogeneous surface of the incinerated sludge between the dissociation of the oxygenated groupings, which are in general acid functional and dimethylamine goup [$-N^+(CH_3)_2$] of the BR5 dye can be used to explain the high adsorption capacity of cationic dye onto incinerated sludge.[8]

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