ASSESSMENT OF *PHASEOLUS VULGARIS L.* BIOMASS AS LOW-COST ADSORBENT FOR THE REMOVAL OF CONGO RED DYE FROM AQUEOUS SOLUTIONS

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Abstract

This research deals with the evaluation of available waste biomass of *Phaseolus vulgaris L.*, as low cost adsorbents, in the removal of organic azo dye Congo red (CR). The effects of operational parameters on the efficiency of dye removal, including contact time, initial pollutant concentration and adsorbent dose have been investigated. The obtained results show that the amount of dye uptake was found to increase with the increase of contact time and initial dye concentration. The maximum sorption capacity was 1.291 mg g^{-1} for CR at 20°C. The removal efficiency of CR is increasing with the increase on sorbent dose, in the range of studied concentration (10 - 30 mg L^{-1}). For evaluating the mechanism involved in the sorption process, the experimental results were analyzed using pseudo-I order kinetic model, pseudo-II order kinetic model, the Ritchie second-order model and intraparticle diffusion model. The pseudo II-order kinetic model agrees very well with the dynamic behavior of the sorption of CR dye onto *Phaseolus vulgaris L.* hull. The experimental sorption results indicated that agricultural waste - bean hull could be applied as an low-cost sorbent alternative used for azo dye removal from industrial effluents, taking into account that no pretreatment on the solid is carried out.

Key words: low-cost adsorbent, Congo red, kinetic model, agricultural waste

In many industrial activities, such as manufacturing of textile, leather, rubber, plastics, pharmaceutical, paper, photographic, cosmetic, waxes, mineral oils, food stuffs etc. dyes are used for coloring. It is estimated that over 10,000 different dyes and pigments are used industrially (Chiou M.S., et al., 2004; Jaikumar V. et al., 2009) and over than 7 x 10^5 tons of synthetic dyes are annually produced worldwide (Crini G., 2006; Chequer F.M.D., et al., 2013). Azo colorants are the most important class of synthetic dyes and pigments, representing 60 - 80% of all organic colorants (Püntener A., Page C., 2004). Industrial effluents containing dyes are difficult to be treat, because the dyes organic molecules are stable to light, heat and oxidizing agents and are resistant to microorganism actions. Adsorption has become the most effective method for the decolorization of textile wastewater. Traditionally, activated carbon was the most commonly used adsorbent (Kyzas G.Z., Kostoglou M., 2014).

The biosorption technique has become more popular in recent years and has been proved to be an effective method for treat industrial dye effluents, offering advantages over conventional techniques (Grassi, M., et al., 2012). The main attractions of biosorption are high selectivity, cost effectiveness, high efficiency and good removal performance (Kyzas G.Z., Kostoglou M., 2014). In the last decade, adsorption of the synthetic dyes from the aqueous solutions, has been studied onto various agricultural biosorbent (McKay G., et al., 1999; Robinson T., et al., 2002; Crini G., 2006; Elizalde-Gonzalez M.P. et al., 2008; Hameed B.H., El-Khaiary M.I., 2008; Hameed B.H., Ahmad A.A., 2009; Sonawane G.H., Shrivastava V.S., 2009; Apostol L.C., Gavrilescu M., 2010; Bhatnagar A, Sillanpää M., 2010; Moussavi G., Khosravi R., 2011; Olivella M. et al., 2012).

The present paper is focused to asses the adsorption potential of waste biomass *Phaseolus vulgaris L.* for anionic dye Congo red in aqueous solution.

Congo red is an example of anionic diazo dyes discharged in wastewater from textiles, printing and dying, paper and plastic industries

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(Purkait M.K., et al., 2007). Also, Congo red is used for microscopic preparations, in biochemistry and histology (Vijayakumar G., et al., 2009).

MATERIAL AND METHOD

Biosorbent

The *Phaseolus vulgaris* L. waste used in this study was obtained from a local farm. Before using as sorbent, the waste was washed several times with distilled water to remove dust particles and other water-soluble impurities. After that, the material was dried at 40ºC for 24h. The dried sample was crushed using a laboratory mill (Retsch GM 200, Germany). Finally, the bean hull were sieved and classified. No other chemical or physical treatments were performed prior to adsorption experiments. The sorbent was stored in plastic boxes for further use. For the experimental study bean hull (BH) fractions with size less than 3 mm were used.

The chemical composition of carbohydrate of bean hull, reported in literature (Kay D.E., 1979; Aremu M.O. et al., 2006; McGoodwin M., 2008; Câmara C.R.S. et al., 2013), contains aminoacids (arginine, asparagines, tryptophan, tyrosine, lysine, betaine, etc.), vitamin C, salicylic acid, phosphoric acid, minerals and is presented in *table 1*.

Table 1

Chemical composition of carbohydrate of bean hull

Compound	***Amount of compound***
Water	58.30
Proteine (%)	7.40
Carbohydrates (%)	29.80
Fates (%)	1.00
Fibers (%)	1.91
Ash (%)	1.63
Calcium (mg/100g)	50
Phosphorus (mg/100g)	160
Iron (mg/100g)	2.60
Thiamine (mg/100g)	0.34
Riboflavin (mg/100g)	0.19
Ascorbic acid (mg/100g)	27
Carotene (mg/100g)	0.057

The surface morphology and fundamental physical properties of biosorbent were determined by Scanning Electron Microscope (SEM) which is equipped with energy dispersive X-ray Spectrometer (SEM-EDX) (Leica Cambridge S360).

Adsorbate

Congo red (CR) is an anionic sulfonate diazo dye, water soluble; yielding a red colloidal solution, with high solubility in organic solvents, chemical name according to EU inventory is benzidinediazo-bis-1-naphthylamine-4-sulfonic acid. The molecular formula of CR (C.I. 22120) is $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight 696.66 g mol^{-1}. The dye was purchased from Sigma Aldrich and used as received. The molecular structure of the dye molecule is shown in *figure 1*.

Dye was weighed and than dissolved in a proper deionized water volume to prepare the stock solution of 1000 mg L^{-1}. The experimental dye solutions with different concentration were obtained by diluting the stock solution.

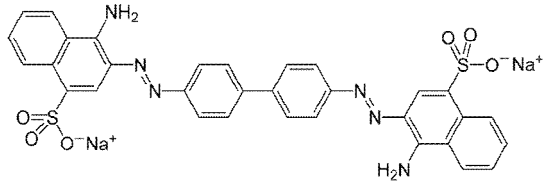

Figure 1 **Molecular structure of Congo red**

Adsorption procedure

The sorption experiments were carried out in batch mode. The effect of contact time and initial dye concentration were studied by shaking the series of flasks containing ten milliliters of CR solution with known initial concentration, in the range of 10 to 30 mg L^{-1} were added to an accurately weighted mass of biosorbent. The samples were agitated in a thermostatic shaker (IKA KS 4000 IC Control, Germany) at 150 rpm and 20^{0}C, at natural pH of solution.

The samples were withdrawn at predetermined intervals of time (10, 20, 30, 60, 120, 180 and 240 min) in order to determine the residual concentration and the equilibrium point. Blank samples, with only the biosorbent and identical volume of distilled water, were conducted simultaneously at similar conditions.

After the experiments, the dye solution was separated from the biosorbent by centrifugation at 6000 rpm for 20 minutes (Hettich EBA 20 Centrifuge, Germany). The supernatant was filtered through quantitative filter papers (0.45 µm - OlimPeak) and the dye concentration in the residual solution was analyzed spectrophotometrically at λ_{max} 497.5 nm (UV-VIS PG Instruments).

The effect of adsorbent dose on the equilibrium uptake of AO7 was investigated with different BH concentrations (5 to 50 g L^{-1}), at fixed initial concentrations of dye. The experiments were carried out for 24 hours to ensure that equilibrium was obtained.

The amount of dye adsorbed onto BH adsorbent at time t, q_t (mg g^{-1}) and at equilibrium, q_e (mg g^{-1}), were obtained by mass balance, according to equations (1) and efficiency of dye removed (*R*) were calculated using the relationships (2):

$$q = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$R\% = \frac{(C_i - C_e)}{C_i} x100 \quad (2)$$

where, C_i and C_e are the initial and equilibrium liquid phase concentrations of dye (mg L^{-1}), *V* is the solution volume (L) and *m* is the mass of biosorbent (g).

Kinetic modeling

The dynamics of sorption describes the rate of CR uptake on bean hull and this rate controls the equilibrium time. In order to study the mechanism of sorption and potential rate determining steps, different kinetic models have been used to test experimental data. The sorption dynamics of Congo red in BH were tested with the Lagergren pseudo-

first-order, the Ho pseudo-second-order, the Ritchie second order kinetic model and the intraparticle diffusion model.

RESULTS AND DISCUSSIONS

Morphologic characterization of biosorbent

The surface morphology of the wastes particle was analyzed by scanning electron microscopy (SEM). *Figure 2* and *figure 3* show the SEM micrographs and EDX analysis of BH samples. The micrographs showed a heterogeneous porous structure with pores of large size.

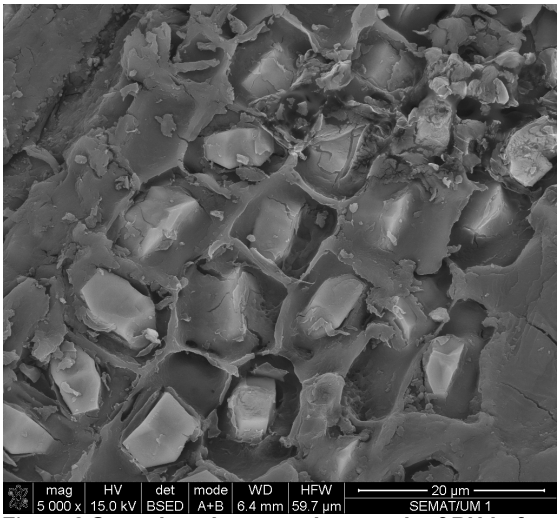

Figure 2 **Scanning electron micrograph of BH before adsorption process**

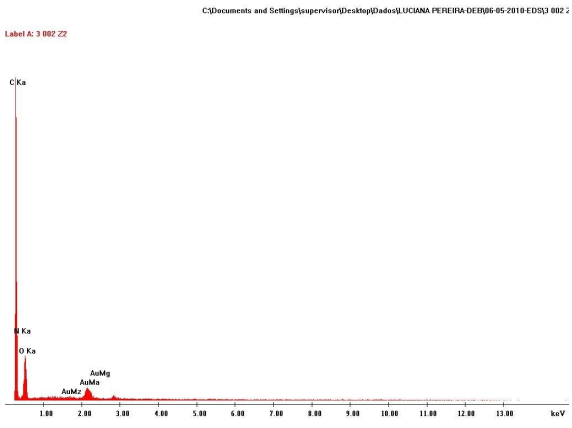

Figure 3 **EDX spectrum of BH before adsorption process**

Effect of initial dye concentration on biosorption

Three different concentrations, respectively 10, 20 and 30 mg L^{-1} were selected to investigate the effect of initial dye concentration (C_0) on the sorption of CR onto bean hull. The experiments were performed at 20^0 C and natural pH of solution.

The results obtained are shown in *figure 4*. The maximum sorption capacity increased from 0.45 mg g^{-1} to 1.29 mg g^{-1} with the increase of CR dye concentration from 10 to 30 mg L^{-1}.

The increase in the concentration of pollutant led to an increase in collision between the molecules and biosorbent particles hence increased the driving force to overcome resistance to mass transfer and thus an increase in uptake capacity (Smaranda C., 2011). This effect may be as a result of a decrease in the total adsorption surface area available for dye molecules to bind due to aggregation or overlapping of active sites.

Also, was observed (see *figure 4*) that rapid adsorption of CR dyes took place within the first minutes, after this initial step of high dye adsorption rate, the adsorption rate became slower and the equilibrium state was reached.

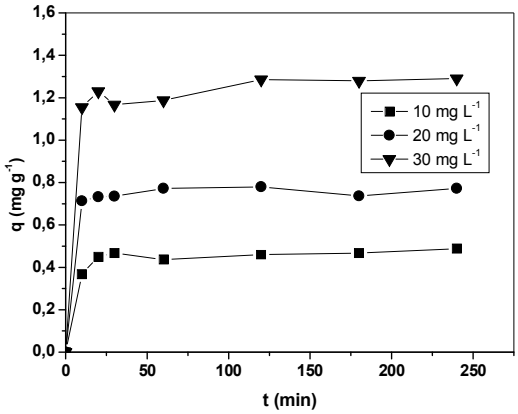

Figure 4 **Effect of initial CR concentration and contact time on sorption onto bean hull (sorbent dose 5 g L^{-1}; initial dye concentration in solution: 10 - 30 mg L^{-1}; temperature 20^0C)**

Effect of contact time

The amount of CR uptake per unit of vegetable biomass (mg g^{-1}) improves with contact time increasing and reached the equilibrium after 20 minutes. As can be seen in the *figure 5* the initial dye concentration did not affect significant the process time to reach its equilibrium state.

The experiments relives that biosorption capacity of bean hull is higher at the beginning of the process, due to a larger number of vacant surface sites are available for the adsorption of the CR during the initial stage (0 to 20 minutes). After these sites are progressively occupied by the dye molecules the more difficult the adsorption becomes and the process tends to become unfavorable. Comparable results were obtained for sorption of Congo red on soil (Smaranda C. et al., 2011) and sorption of Erythrosine B onto bean hull (Apostol L.C., Gvrilescu M., 2010).

The results show that the time profiles of dye uptake were single, smooth and continuous curves leading to saturation, which may suggesting

the possible monolayer coverage of CR molecules on the surface of BH particles (Mafra M.R., et al., 2013; Yakout S.M., Hassan S.H., 2014).

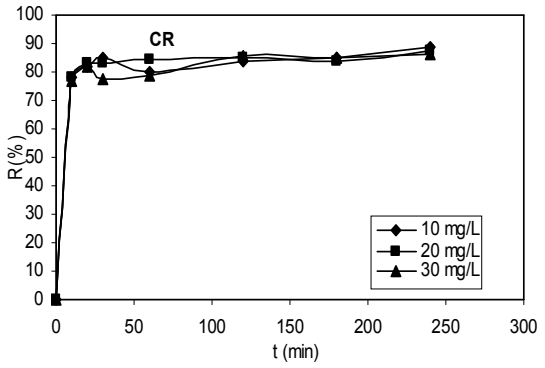

Figure 5 **Effect of the initial concentration on the removal efficiency of Congo red by BH (biosorbent dose 5 g/L, pH 7-7.5)**

Effect of biosorbent mass

The effect of biosorbent mass is an important parameter that may affects the sorption capacity. The study investigate the effect of biosorbent dose by varying the amount of bean hull in the range of 5 to 50 g L^{-1}which was contacted with a fixed concentration of CR. The sorbent dose influence was studied at 20° C for 20 mg L^{-1} CR concentration and natural pH of solution.

Figure 6 shows that the removal efficiency of the CR, decrease very slowly with increase in the biosorbent dose. The increasing the biosorbent dose from 5 to 50 g L^{-1} led to a decrease in the amount of CR molecules adsorbed per unit mass of the adsorbent leading to the decreases in q_e values from 3.29 mg g^{-1} to 0.31 mg g^{-1}.

The maximum of dyes uptake has maximum values when adsorbent dose of 5.0 g L-1 was used, for this reason for further experiments this concentration was used.

The increase of BH dose cause a decrease of the amount of Congo red adsorbed per mass unit at the equilibrium. This effect could be attributed to increase of surface area and the availability of more adsorption sites, but the percent of dyes removed from the aqueous solution is maintained high, over 83%.

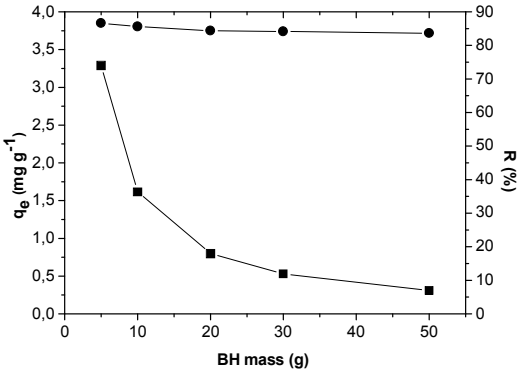

Figure 6 **Effect of BH mass on the CR adsorption efficiency (initial dye concentration 20 mg L^{-1}; bean hull dose 5 - 50 g L^{-1}; contact time 24 hours)**

Kinetic modeling

Mathematical models that can describe the behavior of a batch biosorption process operated under different experimental conditions are very useful for scale up studies or process optimization. A number of models with varying degrees of complexity have been developed to describe the kinetics of pollutants adsorption in batch systems.

The relatively short contact time, necessary for achieving equilibrium conditions, apart from the evident processing advantages, is considered as an initial indication that adsorption of on *P. vulgaris* hull is a chemical-reaction controlled, rather than a diffusion controlled process.

The adsorption dynamics of CR onto BH were tested with the Lagergren pseudo-first-order, the Ho pseudo-second-order, the Ritchie second-order model and the intraparticle diffusion model. The models equation and obtained results are presented in *table 2*.

Table 2.

Sorption kinetic parameters for adsorption of Congo red onto BH

Kinetic model	***Equation***	***Parameters***	***10 mg/L***	***20 mg/L***	***30 mg/L***
Experimental		q_e (mg/g)	0.488	0.772	1.291
Pseudo first order kinetic model	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}$	k_1 (min^{-1})	0.089	0.011	0.077
		q_e (mg/g)	0.853	0.055	3.318
		R^2	0.927	0.851	0.942
Pseudo second order kinetic model	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2 (g/mg min)	0.543	2.041	1.900
		q_e (mg/g)	***0.486***	***0.765***	***1.303***
		h (mg/g min)	0.443	0.009	0.049
		R^2	***0.998***	***0.998***	***0.999***
The Ritchie second order kinetic model	$\frac{q_\infty}{q_\infty - q} = \alpha t + 1$	q_e (mg/g)	0.236	0.430	0.518
		α	0.107	0.282	0.243
		R^2	0.974	0.952	0.938
Intra-particle diffusion model	$q_t = k_{id} t^{1/2} + C$	k_{id1} (mg g^{-1} $min^{-0.5}$)	0.443	0.009	0.049
		C	0.238	0.685	0.995
		R^2	0.917	0.886	0.823

The best fit for the experimental series of this study was achieved by the application of pseudo-second order kinetic equation. The values of q_e predicted by the pseudo-second equation are also in very good agreement with the experimental data for all studied concentrations and the initial sorption rate is increasing with the increase of the initial dye concentration from 10 to 30 mg L^{-1} (*tab 2*).

Comparing the values of regression coefficients R^2 of the applied kinetic models, the pseudo-second-order model can be used to predict the adsorption kinetic of Congo red onto BH.

The plots of the linearized form of the pseudo-second order kinetic model for the adsorption of Congo red on bean hull are shown in *figure 7*. Similar results were reported by Purkait M.K., et al., (2007).

Also, the intraparticle diffusion model describe well the kinetics of Congo red on BH, especial for concentration 10 mg L^{-1}, when the regression coefficients for the first line is R^2= 0.917.

The linearity of the plots indicates that intraparticle diffusion might play a significant role in the initial stage of adsorption of CR onto BH, because the intra-particle diffusion equation is valid only for initial kinetic data

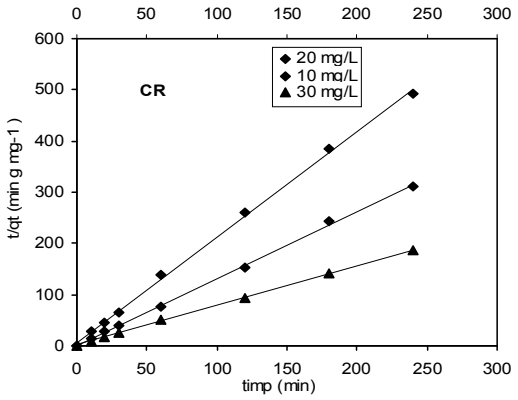

Figure 7 **Pseudo-second-order kinetics of Congo red sorption onto BH biomass**

CONCLUSIONS

The present study shows that the agricultural wastes biomass such *Phaseolus vulgaris L.* hull has significant potential as cheap and effective biosorbent for the removal of anionic dyes from aqueous solution.

The obtained results show that initial dye concentration and sorbent dose affect the uptake capacity of adsorbent.

The relatively short contact time, necessary for achieving equilibrium conditions, is an advantages, considered as an initial indication, that adsorption of CR on BH is probably chemical controlled, rather than a diffusion controlled process.

A detailed analysis using four kinetic models was carried out to investigate the biosorption of CR onto BH. Based on the regression coefficient values, the sorption dynamic of CR onto bean hull agreed very well with the pseudo second-order kinetic model. The results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate-controlling step of the process.

The obtained results revealed that bean hull could be employed as an effective low-cost and easily available biosorbent for the removal of anionic dye - Congo red. This work represents a part of a large experimental program elaborated within National Research Grant BIOSACC - IDEI PROGRAMME.

ACKNOWLEGMENTS

This paper was elaborated with the support of a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0559, Contract 265/2011.

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