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KINETIC STUDIES ON THE BIOSORPTION OF ACID ORANGE 7 ONTO WASTE BIOMASS OF *Phaseolus vulgaris* L.

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Abstract. *The goal of this study was to evaluate the biosorption capacity of biomass of Phaseolus vulgaris L., as an effective material for the biosorption of organic azo dye Acid Orange 7 (AO7). The biosorption properties of the biomass were explored as a function of batch operating conditions including contact time, initial pollutant concentration and biomass dosage. The Phaseolus vulgaris L. hull were characterized using Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDX) analysis. Acid orange 7 was selected as a model pollutant due to its extensive use in textile and cosmetic industry. 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 0.827 mg g-1 for AO7 at 20°C. The removal efficiency of AO7 is increasing with the increase on sorbent dose, in the range of studied concentration. Kinetic analysis of the biosorption process was performed, the experimental results were analyzed using pseudo-I order kinetic model, pseudo-II order kinetic model, Ritchie's second-order, Elovich and intraparticle diffusion equations. Results show that the pseudo II-order kinetic model agrees very well with the dynamic behavior of the biosorption of AO7 onto Phaseolus vulgaris L. hull. The experimental biosorption results indicated that agricultural waste of bean hull can be an alternative and cheaper biosorbent used for dye removal from industrial effluents.*

Keywords: agricultural waste, biosorption, dye, kinetic modelling, low-cost sorbent

1. Introduction

Extensive use of synthetic dyes in many industrial processes such as textile, leather tanning, rubber, plastics, paint, solvent, pulp, paper, printing, photographic, pharmaceutical, food and cosmetic generates large quantities of colored effluents. It is estimated that over 100000 commercially available dyes are used industrially [1] and over 7 x 105 tons of synthetic dyes are produced annually worldwide [2-4]. It is reported that around 2% of the dyes produced annually are discharged in the effluents from manufacturing operation and 10% from the textile and associated industries and persist in the environmental compartments as a result of their complex chemical structure stability and synthetic origin [5-8].

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An important class of synthetic dyes widely used in the textile, pharmaceutical, food and cosmetic industries are azo dyes, which represent almost 60-70% of all organic dyes produced in the world [2, 4] and is estimated that over than 3000 azo dyes are on the market [3, 9]. These compounds are water soluble anionic dyes, containing at least one azo group (—N ==N—) as the molecule chromophore, one or more acidic groups.

Discharging of industrial effluents containing azo dyes in water resources must be avoided, because these compounds can contribute to water toxicity and represent an increasing risk for human beings [10, 11] and aquatic organisms [12-15], because these compounds are known to be toxic [16], carcinogenic, mutagenic [17], teratogenic [9, 18-22]. It has been established that the main cause of its chronic toxicity is the electron-withdrawing character of the azo group, which develops an electron deficiency and becomes reduced to carcinogenic amino compounds. The toxic effects of the azo dyes may result from the direct action of the agent itself or of the aromatic amine derivatives generated from the cleavage of the azo bonds [7, 23], which are more toxic and carcinogenic [3, 4, 16, 24].

Due to the synthetic origin of dyes in industrial effluents, cannot be efficiently decolorized by conventional methods and adequate treatment technologies prior to discharging into receiving water bodies are required. Among various methods, the adsorption occupies an important place in dyes removal.

There is comprehensive literature concerning the adsorption of dyes from industrial effluents onto natural materials (clay minerals, zeolites, other siliceous materials and modified minerals) [25-35]; onto complex materials (eg. chitin, chitosan, cross-linked chitosan) [36-43], and especially using activated carbons (prepared by different materials e.g. coal, coconut husk and shells, wood, rise husks and straw, coir pith, natural minerals, seed of plants, olive stones, corncob, sawdust, jute fiber etc.) as adsorbent [6, 44-48], but their use is sometimes limited due to high costs [49].

In recent years, special attention has been given to low-cost treatment methods and natural materials which are by-products or wastes generated in large quantities from industrial [50, 51] and agricultural activities [52-54]. These kinds of materials have been evaluated as low cost adsorbents, abundantly available, renewable nature and environmental friendly materials [52].

In 2014, Kyzas and Kostoglou [55], introduced a new term to describe such kind of biosorbent which are called “green adsorbents” and the process is named “green adsorption”. It is known that the key-element of each adsorbent material is its adsorption capacity, green adsorbents are generally inferior regarding their adsorption capacity, comparative with other conventional adsorbents, but their low-cost and availability makes them competitive [41, 49].

The basic components of the agricultural waste mainly consist of cellulose, hemicellulose, lignin, lipids, proteins, sugars, water, hydrocarbons, and starch, containing a variety of functional groups [56, 57]. The lignin cellulosic biomass shows a potential adsorption capacity for a wide range of pollutants, holding the functional groups such as hydroxyl, carboxyl, phenols, methoxy etc. that can participate in binding the pollutants [16].

The adsorption of dyes from the aqueous solutions has been studied onto various agricultural solid waste such as: rice husk and straw [58-65], guava seed [66, 67], guava leaves [68], peanut hull [69, 70], coconut shells [71, 72], orange and banana peel [56, 73, 74], grapefruit peel [75], lemon peel [76], garlic peel [77], durian peel [78], tea waste [79-81], coffee husks [82], wood sawdust [83, 84], coniferous pinus bark [85], eucalyptus barks [37, 86, 87], rubber wood sawdust [88], de-oiled soya [89], soybean stalk [90], sunflower seed shells [91], olive pomace [92], maize cobs [93, 94], cotton waste [58], pumpkin seed hull [95], mango seed [96], sugar beet pulp [97, 98], sugarcane bagasse [24, 62, 99, 100], spent brewery grains [1, 101], papaya seeds [102], hazelnut shells [8, 103], grapes stalks [104], corn bark [104], poplar leaf [106], pineapple leaf [107], pistachio hull [108], jackfruit peels [109] etc.

In this general context, the present investigation is focused to evaluate the biosorption potential of agricultural waste of *Phaseolus vulgaris* L., in order to uptake Acid Orange 7 from aqueous media. AO7 is an acid monoazo dye, currently used in tanneries, in cosmetic, in paper and textile industries [66] and its presence in effluents causing obvious environmental problems [4]. The results reveal that bean hull could be employed as an effective low-cost and easily available biosorbent for the removal of azo dye – Acid orange 7.

2. Experimental

2.1. Biosorbent

Phaseolus vulgaris L. or common bean is an herbaceous annual plant from the *Fabaceae* family, originated in Central and South America and now is cultivated in many parts of the world. The bean hulls are abundantly available. The *Phaseolus vulgaris* L. waste used in this study was obtained from a local farm. Before using as biosorbent, the waste was washed several times with distilled water to remove dust particles and 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 biosorption experiments. The biosorbent 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 surface morphology and fundamental physical-chemical properties of biosorbent material were characterized using the scanning electron microscope coupled with EDX Analysis (Leica Cambridge S360 Scanning Electron Microscope, SEM), at 20 kV and a 1000×magnification. Prior to analysis, the samples were coated with a thin layer of gold under argon atmosphere.

The functional groups available on the surface of the BH sample were detected using Fourier Transform Infrared (FTIR) analysis. Fourier Transformed Infra Red analysis was performed in a BOMEN MB 104 spectrometer, with a resolution of 4 cm-1 and a speed of 21 scans min-1. The total number of scans was 32. The sample pellets were prepared in KBr. The spectrum was recorded from the range 4000 to 500 cm^{-1}.

Table 1. General characteristics of Acid orange 7

Characteristic	***Information***
CAS	633-96-5
CI	15510
Formula	$C_{16}H_{11}N_2NaO_4S$
Commercial name	Orange II
Molecular weight (g mol^{-1})	350.33
λ_{max} (nm)	485
Molar volume (cm^3 mol^{-1})	280.26
Molecular volume (Å^3 molecule^{-1})	231.95
Molecular surface (Å)	279.02
Molecular dimensions (nm)	1.24 × 0.68 × 0.22
	1.27 × 0.70 × 0.33
	1.36 × 0.73 × 0.23
Natural pH in deionized water	6.1
Polarity	9.6
pKa	pK_1=11.4 pK_2=1.0

2.2 Adsorbate

Acid Orange 7 is an anionic sulfonated monoazo dye, with one azo bonds, chemical name according to EU inventory is sodium 4-[(2-hydroxy-1-naphthyl)azo]benzene sulfonate, synonymous with Orange II. The molecular structure and other general information about the AO7 dye are presented in Table 1 [5, 22, 66, 110].

Acid Orange 7 was provided by Sigma Aldrich. The chemical was used without further purification. Dye was weighed and then dissolved in a proper deionized water volume to prepare the stock solution of 1000 mg L^{-1}. The dye solutions were prepared by dissolving a proper quantity of the dye in deionized water. All reagents used were analytical grade.In aqueous solutions, Acid Orange 7 being a hydroxyazo dye, exists as mixture of azo and hydrazone tautomers being in the equilibrium due to very rapid intramolecular proton transfer [5]. Tautomers are structural isomers of the same chemical substance that spontaneously interconvert with each other and have different chemical properties. In the field of dyes, azo-hydrazone tautomerism is very important. The tautomerism of undissociated and dissociated species and acid–base equilibrium of azo tautomers and hydrazone tautomers for Acid Orange 7 are presented in Fig. 1.

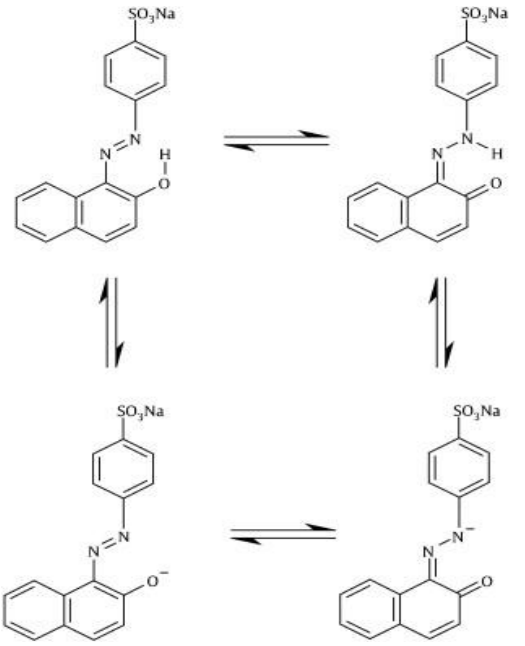

Fig. 1. Azo-hydrazone tautomerism of undissociated and dissociated species and acid–base equilibria of azo tautomers and hydrazone tautomers for Acid Orange 7 – (Greluk and Hubicki, 2011)

In the case of the hydroxyazo dyes, the intramolecular hydrogen-bond dominates the recurring hydroxyazo–hydrazone tautomerism. In the 1-phenylazo-2-naphthol dye (AO7), the hydrazone form predominates [17, 66]. Protonation occurring at the β-nitrogen atom of the azo group gives the positively charged azonium tautomer most likely responsible for the interaction.

2.3. Experimental 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 Acid Orange 7 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 200C, 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. 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 λmax 485 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 bean hull 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 biosorption yield were calculated using the relationships (2):

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

$$Biosorptio\,n - yield\,(\%) = \frac{(C_i - C_e)}{C_i}x100 \qquad (2)$$

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).

The standard deviation was calculated to infer the validity of kinetic models. Standard deviations were calculated with eq. (3):

$$SD = \sqrt{\frac{\sum\left[\left(q_{\exp} - q_{calc}\right)/\,q_{\exp}\right]^2}{(n-1)}} \qquad (3)$$

where, $q_{t,\exp}$ and $q_{t,\mathrm{cal}}$ represent the experimental and predicted q_t values, respectively, and N is the number of data points evaluated.

3. Results and discussions

3.1. Characterization of the biosorbent

The carbohydrate bean hull contains aminoacids (arginine, asparagines, tryptophan, tyrosine, lysine, betaine etc.), vitamin C, salicylic acid, phosphoric acid and minerals. The chemical composition of the *P. vulgaris* L. hull, reported in literature [111-113] is presented in Table 2.

Table 2. Chemical properties 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

Scanning Electron Microscopy (SEM) is widely used to study the morphological features and surface characteristics of the adsorbent materials. It also reveals the surface texture and porosity of adsorbent. Fig. 2 shows the SEM micrograph of BH (bean hull) samples. The SEM image showed a heterogeneous porous structure with large size pores. On the external surface of biosorbent were observed some cavities capable for uptaking dye molecules. This structural feature of the biomass may be important since it increases the total surface area. This kind of biosorbent morphology may suggest that the biosorption process carried out in monolayer.

The results obtained by the EDX Analysis (Energy dispersive X-ray spectroscopy) of bean hull (BH), illustrated in Fig. 3, confirm the presence of organic rich in carbon components as well as the presence of heteroatoms as N, O, Mn and Mg.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was made in order to determine the functional groups involved in the biosorption process. The FTIR spectrum of unloaded biosorbent is shown in Fig. 4. The obtained spectrum is similar with the spectra of other lignocellulosic materials [1, 114, 115].

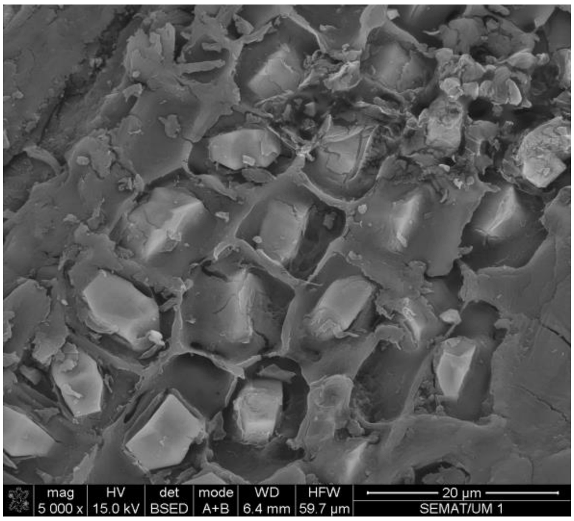

Fig. 2. SEM micrograph of BH before biosorption

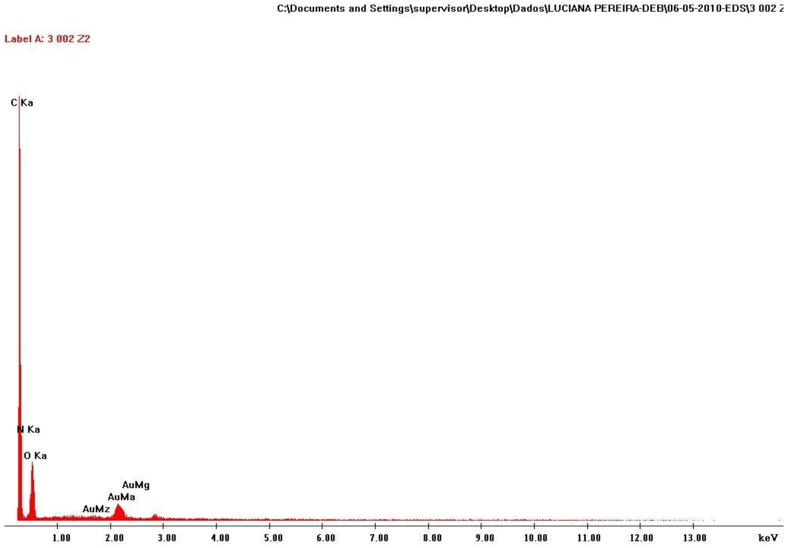

Fig. 3. EDX spectrum of P. vulgaris L. hull before biosorption process

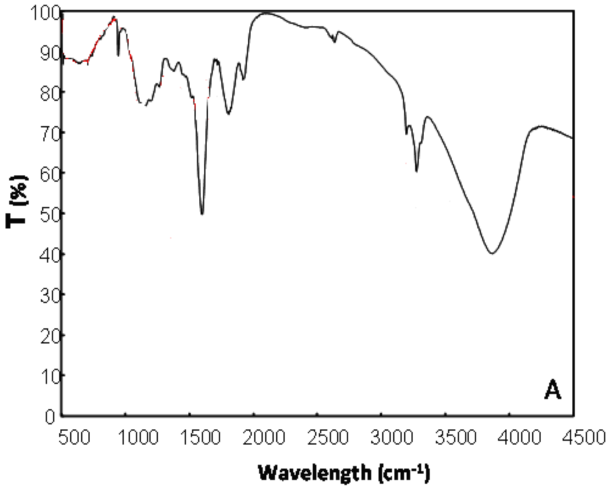

Fig. 4. FTIR spectrum of the biosorbent B.H

The spectrum show the peaks typical for hydroxyl groups at the range 3420 – 3450 cm^{-1}, confirming the presence of the free hydroxyl groups of carboxylic acids, alcohols and phenols on the biosorbent surface. Also, this band corresponds to the O–H stretching vibrations of cellulose, pectin, absorbed water and lignin.

The band that appeared at 2923 cm^{-1} could be attributed to – CH stretch. The carboxyl ions (COO-) give rise to two bands: a stretching band at 1628 cm^{-1} and a weaker asymmetrical band at 1452 cm^{-1} for the BH. The peaks at 1263 cm^{-1} can be assigned to correspond to bending vibrations of O–C–H, C–C–H and C–O–H groups [116]. The band at 1061 cm^{-1} of the C–O stretching vibrations is evident. The absorption peaks at 1165 and 1053 cm^{-1} are the indicative of P–O stretching vibrations.

3.2. Effect of initial dye concentration on biosorption

The amount of biosorption for dye removal is highly dependent on the initial dye concentration. 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 AO7 onto bean hull. The experiments were performed at 20^0 C and natural pH of solution. The results obtained are shown in Fig. 5. The maximum sorption capacity increased from 0.24 mg g^{-1} to 0.82 mg g^{-1} with the increase of dye concentration from 10 to 30 mg L^{-1}. It is evident that for lower initial concentration, the rate of dye removal is faster, while for higher concentrations the available biosorption sites become fewer and the rate of uptake decrease [110].

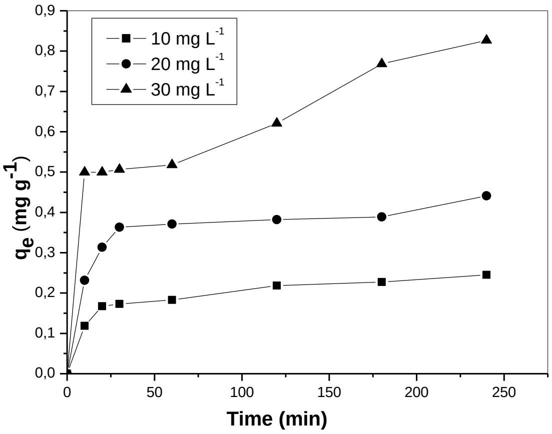

Fig. 5. Effect of initial AO7 concentration on biosorption onto *P. vulgaris* L. waste (biosorbent dose 20 g L^{-1}; C_0 = 10 - 30 mg L^{-1}; T = 20^{0}C)

The biosorption yield of dye is dependent on the initial amount of dye concentration. In Fig. 6 can be observed that the percent of dye biosorbed increased when the dye concentration increased from 10 to 30 mg L^{-1}. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on biosorbent surface. Ashori et al. [90] reported similar effects on the AO7 (25-150 mg L^{-1}) biosorption onto soybean stalk.

3.3. Effect of contact time on dye biosorption

The variation in the AO7 biosorption efficiency of as a function of contact time is presented in Fig. 6. A large quantity of dye molecules has been sorbed onto P. vulgaris hull after a relatively short contact time, where the uptake of more than 65 % of the adsorbed molecules was noticed within the first 30 minutes of the experiments and thereafter it proceeds at a slower rate and finally attains saturation. As it can be observed in the figure the adsorption process could be divided into two stages: the initial stage which was from 0 to 20 min, characterized by rapid adsorption of dye on the biosorbent surface including high dye uptake, and the second stage characterized by the slow dye uptake. It was found that the initial dye concentration did not significantly mark the process time to reach its equilibrium state.

The relatively short contact time, necessary for achieving equilibrium conditions, is an important advantage; this fact can be considered as an initial indication for biosorption of AO7 on P. vulgaris hull is a chemical-reaction controlled, rather than a diffusion controlled process.

The higher rate of removal and biosorption capacity at the beginning of the process can be the effect of a larger number of vacant surface sites available for the sorption of the Acid Orange 7 during the initial stage. After that, the remaining vacant surface sites were gradually occupied by the dye molecules and a decrease in the adsorptive sites for the residual dye molecules in the solution was observed.

The results show that the time profiles of dye uptake were single, smooth and continuous curves leading to saturation, suggesting possible monolayer coverage of AO7 molecules on the surface the biosorbent surface [56, 117, 118]. Comparable results were reported by Hamzeh et al. [119] for AO7 adsorption onto canola stalks.

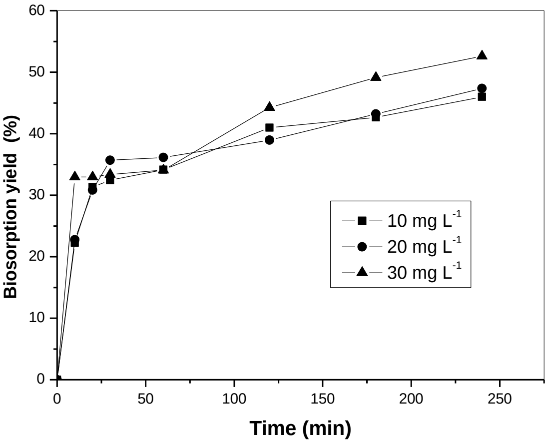

Fig. 6. Effect of the initial concentration on biosorption efficiency of Acid orange 7 onto BH (biosorbent dose 20 g/L, C_0 = 10 - 30 mg L^{-1}; T = 20^0C)

3.4. Effect of biosorbent dose on biosorption efficiency

The effect of biosorbent mass is an important parameter that affects the biosorption process. Study concerning the biosorbent dosage gives an idea of the effectiveness of a biosorbent and the ability of a dye to be sorbed with a minimum dosage. The effect of the bean hull dose used for AO7 biosorption was tested in the range of 5 to 50 g L^{-1}. The sorbent dose influence was studied for 20 mg L^{-1} AO7 concentration, at 200 C and natural pH of solution.

Figure 7 shows that the removal efficiency of the AO7, increased with increase in the biosorbent dose. This effect may be due to the availability of surface activities combined with a larger surface area at higher concentration of the biomass. Usually the removal capacity, increases with increasing of the biosorbent doses, since the amount of pollutant adsorbed per mass unit decreases with the increasing of adsorbent dose in the liquid-solid system [120]. When the BH dose increase from 5 to 50 g L^{-1}, the biosorption capacity decrease from 0.92 mg g^{-1} to 0.13 mg g^{-1}. The increase in the extent of removal of AO7 is found to be relatively low after a dose of 20 g L^{-1}, which has been considered as optimum dose of BH for further experiments.

The decrease in amount of AO7 adsorbed with increasing BH mass may be considered the effect of overlapping or partial aggregation of biosorption sites on the biosorbent surface, resulting in a decrease in total adsorbent surface area available for dye molecules [92, 119].

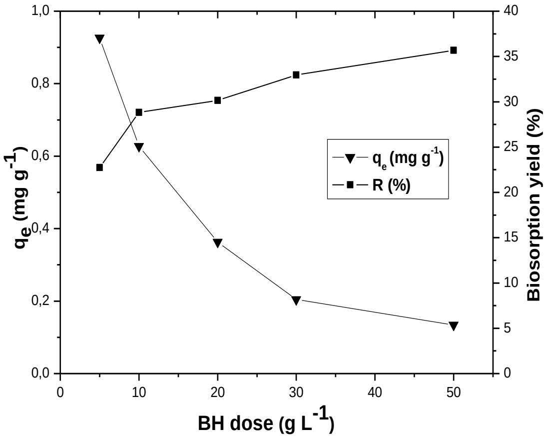

Fig. 7. Effect of biosorbent dose on the AO7 biosorption yield (C_0 = 20 mg L^{-1}; biosorbent dose 5-50 g L^{-1}; contact time 24 hours)

3.5. Kinetic modeling

The determination of the biosorption kinetics is an important stage for designing batch biosorption systems. In order to select the optimum operating conditions for full scale batch systems, information on the kinetics of solute uptake are necessary. The nature of the biosorption process is depending on physical or chemical characteristics of the adsorbent system and also on the process conditions. In order to study the mechanism of biosorption and potential rate determining steps, different kinetic models have been used to test experimental data. In this study, Lagergren pseudo-first-order, the Ho pseudo-second-order, the Ritchie second order kinetic model, Elovich equation and the Weber-Morris intraparticle diffusion model were used to describe kinetic biosorption data.

The models equation and values of the predicted dye uptake capacity, rate constants along with correlation coefficients were calculated and tabulated in Table 3 (Eqs. 4-8). The best curve-to-data fitting model was selected by the highest value of linear correlation coefficients (R^2) and standard deviation (SD).

3.5.1 Pseudo-first-order kinetic model

The Langergren equation (4) - a pseudo-first-order equation was applied to the experimental date in order to describe the kinetics of biosorption process.

By applying the pseudo-first order model to the experimental values the slope and the intercept of each linear fit were used to calculate the first order rate constant k_1 (min^{-1}), the predicted dye adsorption capacity at equilibrium q_{e1} (mg g^{-1}) and correlation coefficients and presented in Table 3. The plot of log ($q_e - q_t$) versus t, illustrated in Fig. 8, suggest that first-order rate equation is not valid for the system AO7-BH. The calculated q_{e1} is not equal to experimental q_e, suggesting the insufficiency of pseudo-first order model to fit the kinetic data for the all range of initial concentrations. These results show that the biosorption of AO7 onto BH does not follow a pseudo-first order model, for the whole range of contact time, indicating that AO7 does not adsorb onto material occupying one adsorption site.

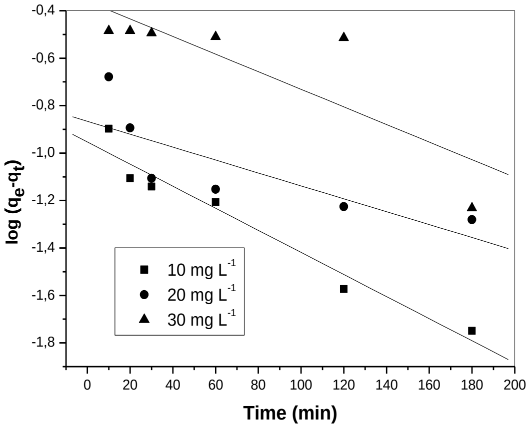

Fig. 8. Pseudo-first-order kinetics of AO7 sorption onto BH biomass

3.5.2. Pseudo-second order kinetics

Kinetic data were analyzed with the pseudo-second order kinetic model (eq. 5). The pseudo-second order model (the Ho model) is based on the sorption capacity on the solid phase. If the pseudo second-order kinetic is applicable, the plot of *t/qt* versus *t* should give a linear relationship.

The equilibrium biosorption capacity q_{e2} (mg g^{-1}) and the second-order constants k_2 (g mg^{-1} min^{-1}) were determined from the plot depicted in Fig. 9 and are listed in Table 3. From Fig. 9 can be observed that the linear plot of *t/qt* versus *t* shows a very good agreement with experimental data. Also, the correlation coefficients (R^2) for the second-order kinetic model (Table 3) are higher than 0.99 and SD values are the lowest, in the range of 10 mg/L - 30 mg/L AO7. These high R^2 values confirm a good fit of the kinetic models to the experimental kinetic data.

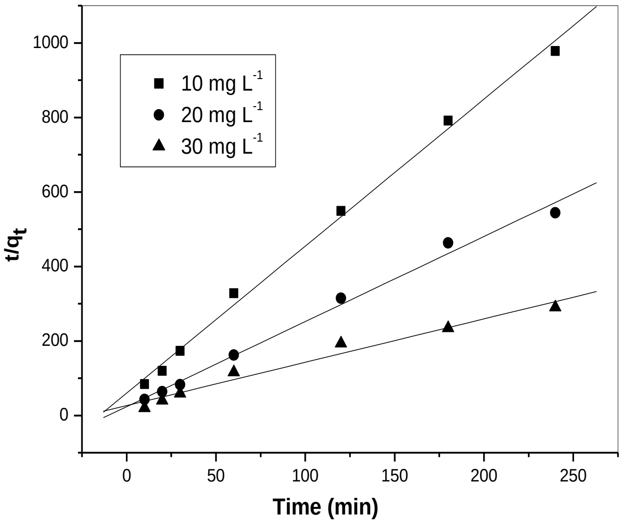

Fig. 9. Pseudo-second-order kinetic plots for the biosorption of AO7 onto BH

The values of q_{e2} predicted by the pseudo-second equation have been also in good agreement with the experimental data, as shown in Table 3. In relation to the pseudo-second order model, it was found that the increases in initial pollutant concentration caused an increase in the q_2 values from 0.2603 to 1.0022 (Table 3). It was also observed in Table 3, that the pseudo-second order rate constant k_2 is decreasing to increase in the initial concentration of the dye from 10 mg L^{-1} to 30 mg L^{-1}, indicating that biosorption has been faster at low concentration. These results indicate that the biosorption of AO7 onto BH follows the pseudo-second-order kinetic model, predicting that chemisorption mechanism being the rate controlling step of the process [121].

Similar phenomena have been reported by Tunali et al. [122] on biosorption of Acid red 57 onto *P. vulgaris* L. residual biomass, by Ashori et al. [90] on biosorption of AO7 onto soybean stalks, canola stalks [119], sugarcane bagasse [24] and in adsorption onto magneticgraphene/chitosan [123].

3.5.3. The Ritchie equation

Ritchie proposed a kinetic model which assumed that one adsorbent molecule was adsorbed onto two surface sites. The plot of $1/q_t$ versus $1/t$ for Ritchie-second-order model is shown in Fig.10.

The parameters of the Ritchie second-order equation (eq. 6), biosorption capacity qe and rate constant k, applied to the removal of AO7 by *Phaseolus vulgaris* L. are presented in Table 3. The Ritchie second order model provided better fitting curves to the experimental data comparing with pseudo-first–order equation. This is evident from de high R^2 (10-20 mg L^{-1}) and lower SD values obtained.

The theoretical values of q_e calculated from the second order plots were found to be closer to the experimental values (Table 3). The Ritchie second order rate constants k_{2R}, decrease with the initial AO7 concentration. This effect may be considered to decrease in the readily available vacant sites as the pollutant concentration is increased. After the easily available sites are occupied the excess dye molecules from aqueous solution find remote sites inside the pores of BH more difficult, which makes the rate of biosorption to decrease with the dye concentration increasing. Similar effect was previously reported by Inbaraj and Sulochana [123] on the adsorption of Rhodamine-B onto jackfruit peel carbon.

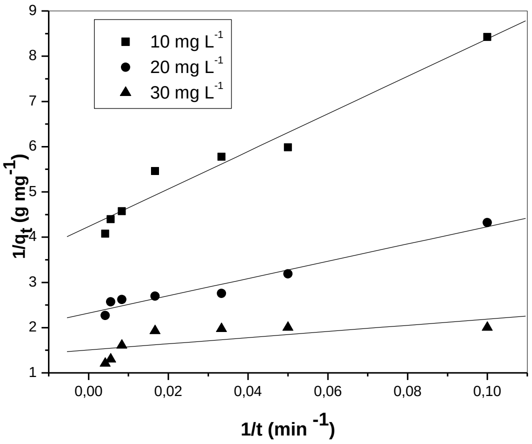

Fig. 10. Ritchie's second-order plots for AO7 biosorption onto BH

3.5.4. The Elovich kinetic equation

Other useful kinetic models suitable to describe adsorption behavior that concurs with the nature of chemical adsorption [124] is the Elovich equation (eq. 7), presented in Table 3. The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. If the biosorption process fits the Elovich model, the plot of qt versus ln *t* should yield a linear relationship with a slope of $1/\beta$ and the intercept $1/\beta$ ln (β). The constant α (mg $g^{-1}min^{-1}$) is the initial sorption rate constant and parameter β (g mg^{-1}) is related to the extent of the surface coverage and to the activation energy of chemisorption. The Elovich equation is recommended to be used to describe the sorption behaviour of systems with a rapid rate in the early period, while it slows down to the equilibrium phase and may be applied for investigated process.

The obtained plots are presented in Fig. 11, and the resulted values of the constants α and β are also listed in Table 3. It was observed that increasing the pollutant initial concentration increase the rate of chemisorption α, from 0.13 to 0.65 which is in accord with the model assumptions. For the Elovich model, parameter β is correlated also with to the extent of surface coverage, it decreased upon increasing the initial concentration. Table 3 shows β values ranging between 28.57 and 9.73, when the AO7 condition is increase from 10 to 30 mg L^{-1}.The fitting to Elovich model presents relative high values (0.96-0.87). A good fit with the Elovich equation suggests the diffusion as the main mechanism involved in the biosorption kinetic of AO7 onto BH, at least for the second stage of the process.

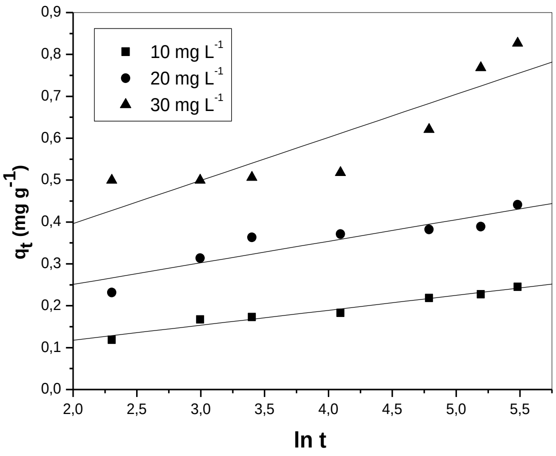

Fig. 11. Plots of Elovich equation for biosorption of AO7 onto BH

3.6. Mechanistic analysis of biosorption process

One of the essential requirements for the proper interpretation of the experimental data obtained during kinetic studies is to identify the steps involved during adsorption process described by external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

Table 3. Kinetic parameters for biosorption of Acid Orange 7 onto bean hull

Kinetic model	***Equation***	***Eq. no.***	***Parameter***	***C_{AO7} = 10 mg L^{-1}***	***C_{AO7} = 20 mg L^{-1}***	***C_{AO7} = 30 mg L^{-1}***
Experimental			***q_e.exp***	***0.2436***	***0.4412***	***0.827***
Pseudo first order kinetic model	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	*(4)*	***q_{e1} (mg g^{-1})***	0.0991	0.1270	0.4215
			k_1 (min^{-1})	15 10^{-3}	9.21 10^{-3}	14.04 10^{-3}
			R^2	**0.9125**	**0.7985**	**0.8239**
			SD	0,0753	0,1535	0,1887
Pseudo second order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	*(5)*	***q_{e2} (mg g^{-1})***	***0.2603***	***0.4309***	***1.0022***
			k_2 (g mg^{-1} min^{-1})	2.9386	0.3051	0.1139
			R^2	***0.9940***	***0.9927***	***0.9920***
			SD	0.0024	0.0018	0.0019
Second order kinetic model Ritchie	$\frac{q_\infty}{q_\infty - q} = \alpha t + 1$	*(6)*	***q_e (mg g^{-1})***	0.236	0.4306	0.5186
			k_2 (g mg^{-1} min^{-1})	0.1025	0.2824	0.2432
			R^2	**0.9792**	**0,9782**	**0.708**
			SD	0,3266	0,1537	0,2757
Elovich equation	$q_t = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln(t)$	*(7)*	***α (mg g^{-1} min^{-1})***	0.1308	0.9111	0.6593
			β (mg g^{-1})	28.572	19.455	9.737
			R^2	**0.9614**	**0.9199**	**0.8797**
			SD	0,0093	0,0285	0,0723
Intra-particle diffusion model (first stage)	$q_t = k_{id} t^{1/2} + C$	*(8)*	***k_{id1} (g mg^{-1} min $^{0.5}$)***	0.0243	0.0572	0.0028
			C_1 (mg g^{-1})	0.0471	0.0528	0.4892
			R^2	**0.9409**	**0.9905**	**0.8248**
			SD	0.0142	0.0061	0.0032
Intra-particle diffusion model (second stage)			***k_{id2} (g mg^{-1} min $^{0.5}$)***	0.0077	0.0080	0.0416
			C_2 (mg g^{-1})	0.1270	0.2996	0.1876
			R^2	**0.9818**	**0.8614**	**0.9810**
			SD	0.0060	0.0194	0.0235

Considering that pseudo-first order and second models cannot identify the adsorption mechanisms, the intraparticle diffusion model and the Elovich equation are further tested in this work.

Several consecutive mass transport steps are involved in the adsorption of solute from solution onto porous material [18, 28, 125, 126]:

- molecule transport in the aqueous solution;
- molecular diffusion through the liquid film surrounding the biosorbent particle;

- diffusion within the liquid included in the pore by internal diffusion or intraparticle diffusion;
- and finally, adsorption into the active sites at the internal surface of the adsorbent particle.

First, the adsorbate migrates through the solution to the exterior surface of the adsorbent particles by, i.e., film diffusion, and then followed by solute movement from particle surface into interior site by pore diffusion; adsorbate is adsorbed. According to the Weber - Morris model (eq. 8), if the rate limiting step is intraparticle diffusion, the plot of solute adsorbed against the square root of the contact time should give a straight line passing trough the origin.

In the present study there were obtained two domains of the line for all the AO7 concentrations (Fig. 12) and the lines do not pass through the origin. This is an indicative of some degree of boundary layer control, which indicate that the intraparticle diffusion is not the only rate controlling step and also other processes may control the rate of biosorption [119].

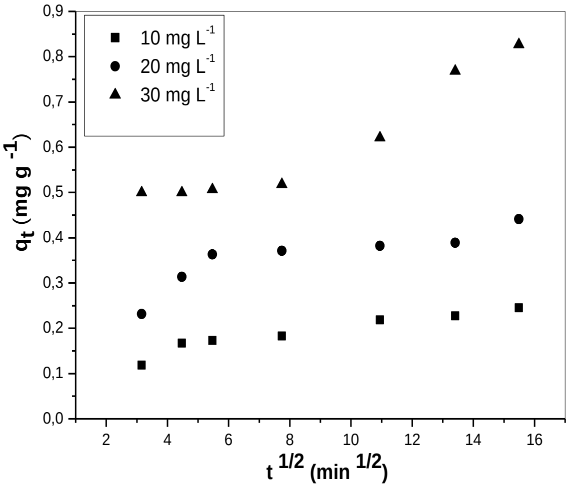

Fig. 12. Plots of Weber – Morris model for biosorption of AO7 onto BH

The first stage of the plot is attributed to boundary layer diffusion, while the second linear portion corresponds to the gradual adsorption process in which the intraparticle or pore diffusion is the limiting rate. These two stages suggest that the biosorption process of AO7 onto proceeds by surface biosorption and intraparticle diffusion.

The parameters for this kinetic model are given in Table 3. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter kid1 (mg/g min$^{0.5}$). The calculated values for intraparticle diffusion coefficient kid1 (Table 3) were given by 0.007, 0.008 and 0.041 mg/g min$^{0.5}$ for an initial dye concentration of 10, 20, and 30 mg/L. The k_{id2} values increased with the initial AO7 concentration, indicating that the intraparticle diffusion was favored at high initial concentrations. The values of C (Table 3) give information about the thickness of boundary layer. Obtained results show that the thickness of boundary layer is increasing with the increase of the AO7 initial concentration. According to the results presented in Table 3, correlation coefficients were found high for the intraparticle diffusion model in the whole initial dye concentration range and for both stages. Also, the double nature of intraparticle diffusion plot confirms the presence of both film and pore diffusion.

Table 4 presents a comparison with other agricultural biosorbents used for AO7 removal. In present study, the process takes places in short time and at room temperature, which could be considered an important advantage because reduce production costs by using a cheap raw material and eliminating energy costs associated. Also, the obtained results indicate that BH can be successfully used as biosorbent for Acid orange 7 without any previous chemical treatments.

Table 4. The performance of different types of agricultural waste for AO7 removal from aqueous solutions

Type of sorbent	q_{max} *(mg g^{-1})*	*Initial AO7 concentration (mg L^{-1})*	*Temperature (°C)*	*References*
Soybean stalk	1.80-7.80	50-150	25	[90]
Canola stalks (*Brassica napus* L.)	4.78- 14.92	50-200	25	[119]
Spent brewery grains	101.9 - 493.8	30-843	20	[101]
Moringa Oleifera Seeds	0.75 – 4.41	5-25	25	[110]
Mango seed	17	50	25	[96]
Guava seed (*Psidium guajava* L.)	0.67	50	25	[67]
De-oiled soya	8.87	35	30	[9]
Sugarcane bagasse	28.01	40	30	[24]
Bean hull	0.24 - 0.82	10-30	20	*This study*

Abdolali et al. [54] noticed that the main mechanisms known for dye biosorption process on cellulosic material includes a combination of several mechanisms including electrostatic attraction, complexation, ion exchange, covalent binding, Van der Waals attraction, adsorption and microprecipitation. Physical adsorption takes place because of weak Van der Waals' attraction forces, whereas the so-called chemisorption is a result of relatively strong chemical bonding between adsorbates and adsorbent surface functional groups.

A very good conformation to the pseudo-second order model suggests that the rate-determining step may be chemisorptions involving valence forces through sharing or exchange of electrons between biosorbent and sorbate.

The mechanisms of AO7 biosorption onto Phaseolus vulgaris L. may include electrostatic interactions between negatively charged dye SO_3^- group and positively charged BH surfaces; H–bonding between oxygen and nitrogen containing functional groups of AO7 and biosorbent surface; hydrophobic–hydrophobic interactions between hydrophobic parts of the dye and the biosorbent.

Chemical biosorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, acids, phenolic hydroxides, and ethers as chemical bonding agents [54], functional groups which have been highlighted in the case of BH, by FTIR analysis (Fig. 4).

4. Conclusions

The present investigation is dealt with the biosorption of Acid orange 7 dye on agricultural been hull. The main conclusion of the study is that encouraging results were obtained with Phaseolus vulgaris L. hull tested as biosorbent for AO7 dye and demonstrate an adequate potential for being exploited as an economically viable and indigenous material for azo dyes biosorption from aqueous flows.

Also, the utilization of this lignocellulosic wastes and by-products as biosorbent is an eco-friendly technique, which may be a way of agricultural waste minimization.

The results show that dye removal is strongly dependant on biosorbent dose, time contact and initial dye concentration. The removal of Acid Orange 7 was observed to be rapid at the primary stages of biosorption process, which is an important advantage; this fact can be considered as an initial indication for biosorption of AO7 on P. vulgaris hull is a chemical-reaction controlled.

A detailed analysis using five kinetic equations was carried out to investigate the biosorption of AO7 onto BH. Based on the regression coefficient values (R2) and standard deviation (SD), the pseudo-second-order model can be used to predict the biosorption kinetic of AO7 onto bean hull. The values of qe predicted by the pseudo-second equation have been also in good agreement with the experimental data, indicating a chemical interaction between the azo dye and BH. The Weber–Morris analysis demonstrated that external mass transfer and intraparticle diffusion occurred simultaneously during the AO7 biosorption onto Phaseolus vulgaris L. hull.

FTIR, SEM and EDX analysis indicated the presence of functional groups able to interact with the sulphonate group of the dye.

It is important to mention that the obtained results indicates that BH can be successfully used as biosorbent of dye Acid orange 7 in aqueous solution without any previous chemical treatments.

Future investigations should be conducted with a view to selectively separating the present dye contaminant, regenerating of the exhausted biomass, and designing a continuous biosorption system. This work represents a part of a large experimental program elaborated within a National Research Grant, BIOSACC - IDEI PROGRAMME.

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