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Effect of heavy metals (Cu^{2+}, Ni^{2+}, Pb^{2+}) on biosorption of basic blue 41 onto dead *Streptomyces Rimosus*

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ABSTRACT

This study explored the feasibility of using dead *Streptomyces Rimosus* as biosorbent for the removal of Basic Blue 41 under different experimental conditions. The effect of various factors, such as, initial substrate concentration, solution pH and co-existing heavy metals (Cu^{2+}, Ni^{2+}, Pb^{2+}), on the biosorption of BB41was investigated. Equilibrium occurred within about 30 min. The Langmuir and Freundlich models were used to describe the isotherm data; of which the Freundlich model described the isotherm data with high correlation coefficient (r^2>0, 98). The maximum monolayer biosorption capacity of biosorbent material was found as 68.02 mg/g. Also, it was observed that the intra-particle diffusion was not the only rate-controlling step. The adsorption mechanism may be partly a result of the ion exchange or complexation between the dye ions and function groups on dead biomass surface. Finally the proposed biosorbent was successfully used for the decolorization of BB41 in presence of Heavy metals. It was determined that dead *Streptomyces Rimosus* show better biosorption performance towards Basic blue 41 in binary adsorption systems at higher pH. The addition of Copper, Lead and Nickel caused a 7.8 %, 4.7% and 1.6% increase in BB41 biosorption, respectively. The effect of the presence of single metal ion concentration on the biosorption of biomass was investigated at an initial pH value of 8.5.

The rate of kinetic processes of single and binary systems onto dead *Streptomyces Rimosus* was described by using three kinetics adsorption models: the pseudo-first order, pseudo-second order and intraparticle diffusion. The pseudo-second-order model was the best choice among the kinetic models to describe the biosorption behaviour of single and binary system onto dead *Streptomyces Rimosus.*

KEYWORDS

Biosorption;
Streptomyces rimosus;
Basic blue 41;
Kinetics and isotherm.

INTRODUCTION

Dyes are extensively used in paper, textile, dyehouses and printing to color the final products[1]. They usually have a synthetic origin and complex aromatic structures making them difficult to degrade[2]. Dyes are classified as anionic, cationic and nonionic dyes[3]. The presence of very small amounts of dyes in water is highly visible and undesirable[4]. Many of these dyes are extremely toxic and even carcinogenic[5], Basic dyes are considered one of the most toxic substances[6], then it is necessary to eliminate them from wastewater before it is discharged. Biosorption is one of the popular and attractive technologies for the removal of colour contaminants from aqueous effluents. Some low cost fungal biomass has been used as biosorbent for the removal of dye and metal ions from wastewater, which included Trametes versicolor[7], Corynebactium glutamicum[8], lentinus sajor caju[9,10], Rhizopus nigricans[11], phanerocheate chrysosporium[10] and aspergillus niger[12]. The main objective of this study is to investigate the effect of heavy metals on the removal efficiency of Basic blue 41 onto bacterial dead *Streptomyces rimosus*. Basic blue 41 is a synthetic azo dye which is used widely in the textile industry. The examining of metal ions effect on the dye adsorption efficiency is more representative of the actual environmental problems. Then, in this paper we report an investigation of Biosorption of basic blue 41 onto an antibiotic waste in the absence and the presence of metal ions (Cu^{2+}, Ni^{2+}, Pb^{2+}).

EXPERIMENTAL PROCEDURES

Dye stuff

The sorbate used in the experiments was Basic Blue 41, (BB41) which is used in textile processing Industry of Bab Ezzouar, Algier, Algeria. This dye is a monoazobasic dye with C.I. no.: 11154 and molecular weight of 483 g/mol. It is particularly suitable for dyeing of acrylic substrates and can also be applied to some polyamide and polyester types, viscose, cotton, and wool. A stock aqueous solution of the dye was prepared in deionised water in the concentration of 1000 mg/l.

Several stock solutions of Ni, Cu and Pb in deionised waters were prepared in the concentration of 5 mg/l from their water-soluble metallic salt ($NiCl_2$-$6H_2O$, $CuCl_2$-$2H_2O$ and Pb $(NO_3)_2 \cdot 6H_2O$ respectively.

Biomass preparation

Dead *S. rimosus* biomass was obtained from oxytetracyclin antibiotic production after fermentation. The collected samples were washed repeatedly with deionised water to remove extraneous materials and salts and dried for 24 h at 50°C in an oven and then screened through a set of sieves to get geometrical size 80–315µm.

Biosorption tests

Batch kinetic biosorption studies were conducted in a temperature- controlled stirrer using 100 mL of adsorbate solution. The samples at different time intervals (5–40 min) were taken and at the end of each agitation period, the mixtures were centrifuged for 20 min at 5000 rpm and then, analyzed using a UV spectrophotometer at λ=605 nm wavelength. The effects of solution pH, initial BB41 concentration and co-existing heavy metals (Cu^{2+}, Ni^{2+}, Pb^{2+}), on the adsorption capacity of 0.6g/L of Dead *S. rimosus* were investigated.

The sorption capacity was calculated by the following expression:

$$q = \frac{(c_i - c_f)}{m} V \tag{1}$$

Where C_i and C_f are the initial and final concentrations of dye (mg/L) in aqueous solution, respectively, V is the volume of the solution and m represents the weight of the biosorbent (g). For the calculation of the basic blue 41removal (R) we used the following expression:

$$R = \frac{(c_i - c_f)}{c_i} \% \tag{2}$$

RESULTS AND DISCUSSION

Biosorption of BB41 in single system

The biosorption of BB41 by natural antibiotic waste was investigated. The effects of contact time, initial concentration and initial pH on the biosorption performance of Dead *S. rimosus* to dye were tested.

(a) Effect of contact time

Contact time is one of the important parameters for successful deployment of the biosorbent for practical application and rapid biosorption[14]. The time of batch mode of dye biosorption onto dead Dead *S. rimosus* (0.6 g/L) was tested at 30 °C Figure 1 indicates that the capacity of dye sorption increased for increasing contact time and become almost constant at 20 min. the results showed that kinetics of biosorption of BB41 consisted of two phases. It was observed that the removal of dye was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium which is dependent on the decrease in the number of vacant sites on the surface of dead biomass.

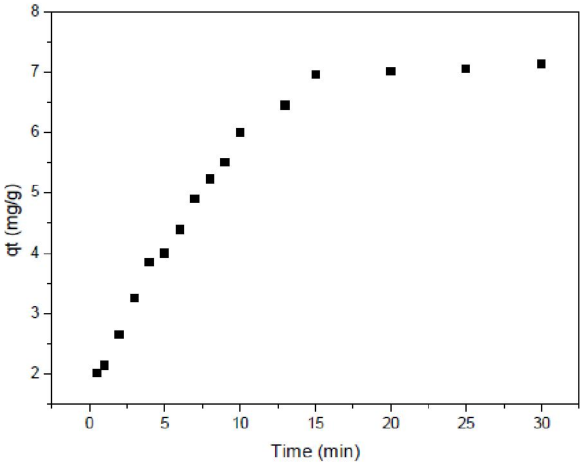

Figure 1 : Effect of contact time on sorption kinetics in single system (T =30°C, pH =8.5, Co =5mg/L, Cs =0.6 g/L).

(b) Effect of initial concentration

In order to study the effect of the initial concentration of BB41 in the solution on the biosorption capacity of dead *S. rimosus* (0.6 g/L), *e*xperiments were performed in the concentration range (5–30 mg/L) at 30 °C. As observed in Figure 2, the higher the initial concentration of dye, the larger was the amount of BB41 biosorbed. It was clear that the removal of dye was dependent on the initial dye concentration. The percentage removal of BB41 biosorbed decreased from 85.8 to 69 % as the initial concentration increases from 5 to 30 mg/L. The lower uptake at higher concentration resulted from an increased ratio of initial number of moles of dye to the available surface area; hence fractional adsorption becomes dependent on initial concentration. Similar results were reported by other researches for princess tree leaf[16] and clay[17]

(c) Effect of initial pH

The pH of dye solution plays an important role in the whole biosorption process and particularly in the adsorption capacity, influencing the surface charge of the biosorbent, the degree of ionization of the dye present in the solution and the dissociation of functional groups on the active sites of biosorbent. These bio macromolecules on the bacterial cell surfaces have several functional groups (such as amino, carboxyl, thiol, sulfydryl and phosphate groups) and biosorption phenomena depends on the protonation or unprotonation of these functional groups on the surface of the cell wall[18].

The pH of the single solution was varied in the range of 3- 10 keeping all other parameters constant. As shown in Figure 3, the percentage of removal increased with an increase in the solution pH. The maximum percentage removal of basic blue 41 was observed as 85.8 % at pH 8.5. High pH has been found to favor adsorption of BB41[19-21].

It is well known that at lower pH, more protons will be available to protonate the adsorbent surface, thereby increasing the repulsion between the positive charged surface of the adsorbent and the cationic dye molecule. Whereas at higher pH the surface becomes anionic and cationic dye adsorption is favoured[22].

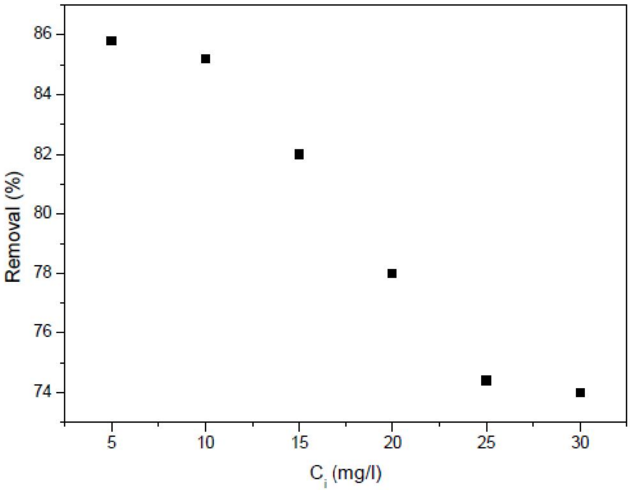

Figure 2 : Effect of initial concentration of dye ions (T =30°C, pH =8.5, Cs =0.6 g/L).

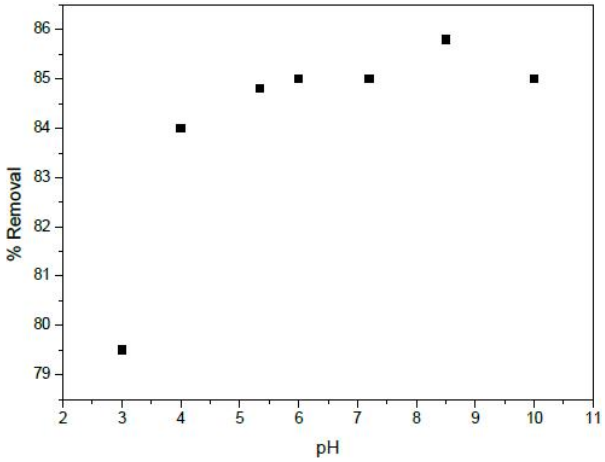

Figure 3 : Effect of solution pH on dye removal (T =30°C, Co =5mg/L, Cs =0.6 g/L).

(d) Isotherm studies in single system

The isotherm data were treated using four of the most commonly used equilibrium models, Langmuir, Freundlich,[25-28]. The mathematical expressions are given by Eqs. (3) - (4), respectively, as follows:

$$\text{Langmuir equation}: \frac{c_e}{q_e} = \frac{1}{q_{max} b} + \frac{c_e}{q_{max}} \quad (3)$$

$$\text{Freundlich equation}: \ln q_e = \ln K_F + \frac{1}{n} C_e \quad (4)$$

Where, K_F, Freundlich constant (l/mg), 1/n, the heterogeneity factor, b, the Langmuir biosorption constant (l/mg) related to the affinity of the binding sites, and q_{max} (mg/g), is the maximum amount of sorbate per unit weight of adsorbent, to form a complete monolayer on the surface bound at high Ce, The best-fit values of the model parameters estimated from Eqs, (3) – (4) by linear regression analyses are listed in TABLE 1 (Figure 4). The higher correlation coefficients indicated that both the Langmiur, and Freundlich models were very suitable for describing the biosorption equilibium of basic blue 41 by dead *S. rimosus* in the studied concentration ranges. The equilibrium data fitted better to the Freundlich isotherm as compared to the other model, also suggested that the surface of antibiotic waste is heterogeneous which is consistent with studies reported before[13]. From TABLE 1, the magnitude of K_F and n, the Freundlich constants, showed easy uptake of the dye from wastewater with high adsorptive capacity of biosorbent. TABLE 1 also indicates that n is greater than unity, indicating that the dye is favourably adsorbed by dead *S. rimosus*.

TABLE 1 : Isotherm constant for biosorption of BB41 onto dead dead *S. rimosus* in single system.

Parameters					
Freundlich			Langmuir		
K_F	n	r^2	q_{max}	b	r^2
9.93	1.54	0.990	57..3	0.205	0.987

(e) Biosorption kinetics in single system

Several kinetic models have been proposed to understand the behaviour of the adsorbent and also to examine the controlling mechanism of the adsorption process and to test the experimental data. In order to analyse the adsorption kinetic, pseudo-first, pseudo-second order, and intraparticle models were applied to the experimental data.

(A) Pseudo-first order model

The rate constant of adsorption is determined from the following first order rate expression given by Langergren[32]:

$$\text{Log} \frac{(q_e - q_t)}{q_e} = \frac{K_1}{2.3} t \quad (5)$$

K_1 is the first-order rate constant (min^{-1}) of biosorption.

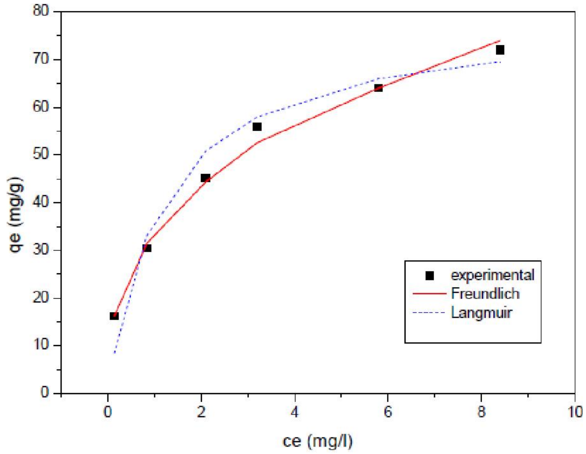

Figure 4 : Adsorption isotherms of BB41 on dead dead *Streptomyces rimosus* in single system.

A straight line of ln $(q_e\text{-}q_t)/q_e$ versus t (Figure 5) would suggest that this kinetic model is applicable to the data tested, and K_1 and q_e were determined from the slope and intercept of the plot, respectively. The kinetic data in TABLE 2 demonstrate that that the biosorption of BB41 onto dead dead *S. rimosus* does not follow pseudo-first order kinetics.

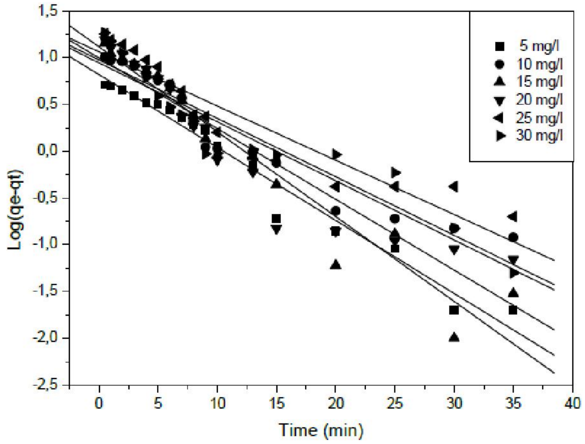

Figure 5 : Effects of initial dye concentration on the on the pseudo-first-order kinetics of BB41 in single system (T =30°C, pH =8.5, Cs =0.6 g/L).

(B) Pseudo-second order model

The kinetic data were further analyzed using a pseudo-second order relation proposed by Ho[33] which is represented by:

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min).

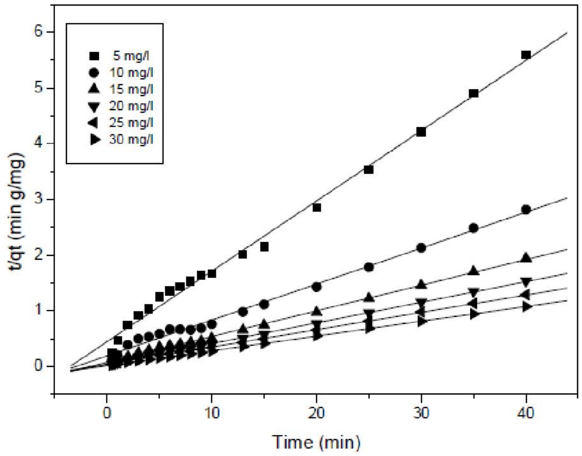

Figure 6 : Effects of initial dye concentration on the pseudo-second order kinetics of BB41 in single system (T =30°C, pH =8.5, Cs =0.6 g/L).

The initial adsorption rate, h, (mg/g.min) is expressed as

$$h = K_2 q_e^2 \qquad (7)$$

The application of the linear form of pseudo-second-order kinetic model on our experimental results is presented in Figure 6. Both constants K_2 and *h* were calculated from the intercept and slope of the line obtained by plotting t/q_t versus *t*. It can be seen from TABLE 2 that the equilibrium biosorption capacity, q_e, increases as the initial dye concentration, C_i, increased from 5 to 30mg/L. For example, the values of qe increased from7.93 m/g at 5mg/L to 38.46 mg/g at 30 mg/L. Also, from TABLE 2, it was noticed that the variations of the initial adsorption rate, *h*, seem to have an increasing trend with increasing initial dye concentration. The diverse effect of the initial concentration on *h* was also observed with other sorption systems reported[34,35]. The best fit model was selected based on the linear regression correlation coefficients, R^2 values and equal or close values of qe from the experiments and the predict model as well. The experimental data showed a good compliance with the pseudo-second order equation and the regression coefficients for the linear plots were also higher than 0.99 in single system.

The pseudo-first order and the second order kinetic models could not identify the diffusion mechanism and the kinetic results were then analysed by using the intraparticle model.

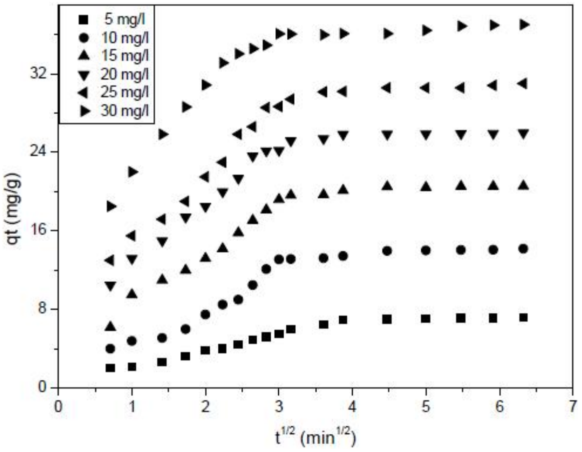

Figure 7 : Plot of intraparticle diffusion of dye onto dead *Streptomyces rimosus* at various initial concentrations in single system

This model is developed by Weber and Morris[36], and McKay and Poots[37], the rate of intra-particle diffusion is calculated by:

$$q_t = K_i t^{1/2} + C \qquad (8)$$

Where K_i is the intra-particle diffusion rate constant (mg /g min$^{1/2}$). According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate controlling step[38-39]. It is generally found that the plot of qt against $t^{1/2}$ may present a multinearity, which indicated that two or more steps occurred in the process. In single system, any plot did not passed through the origin and this deviation from the origin (Figure 7) might be due to the difference in the mass transfer rate in the initial and final stages of biosorption. It can be observed that, the plots had the same general features and there were two different portions, representing the different stages in biosorption. The calculated K_i (Second portion) values for each initial concentration are given in TABLE 2. It was found that the intraparticle rate constant values (Ki), increased with increasing dye concentration. The observed increase in Ki values with increasing initial BB41 concentration can be explained by the growing effect of driving force resulted in reducing the diffusion of BB41 species in the boundary layer and enhancing the diffusion in the solid. The corresponding values of intraparticle diffusion rate constant, Ki, for the various concentrations of BB41 ions (5-30 mg/L) varied from 0.209 to 0.369 mg/g.min$^{1/2}$.

TABLE 2 : Kinetic parameters for the biosorption of BB41 in single system

C0	Experimental	Pseudo-first order			Pseudo-second order				Intraparticle diffusion		
(mg/L)	qe_{xp} (mg/g)	$q_{e,cal}$ mg/g	k_1 1/min	R^2	$q_{e,cal}$ (mg/g)	h mg/g.min	K_2 g/mg.min	R^2	Ki (mg/g.mn$^{1/2}$)	R^2	Di (cm^2/s)
5	7.15	6.62	0.179	0.987	7.93	2.22	0.035	0.997	0.209	0.820	$0.780.10^{-8}$
10	14.2	8.85	0.145	0.958	15.62	5.18	0.021	0.997	0.340	0.932	$0.923.10^{-8}$
15	20.56	13.09	0.208	0.968	21.73	12.5	0.026	0.999	0.298	0.878	$1.613.10^{-8}$
20	26	9.97	0.174	0.939	27.02	22.72	0.031	0.999	0.211	0.825	$2.357.10^{-8}$
25	31	11.63	0.135	0.936	32.25	23.8	0.022	0.999	0.392	0.908	$1.995.10^{-8}$
30	37	9.49	0.143	0.942	38.46	55.55	0.037	0.999	0.369	0.944	$4.002.10^{-8}$

Also, the diffusion coefficients for the intra-particle transport of dye within the pores of dead biomass particles have been calculated by employing Eqs. (9) and (10)[40].

$$D_P = \frac{0.03 r_0^2}{t_{1/2}} \quad (9)$$

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (10)$$

Where D_i is the diffusion coefficient with the unit cm^2/s; $t_{1/2}$ is the time (s) for half-adsorption of dye and r is the average radius of the adsorbent particle in cm. The value of r_0 (average radius) was calculated as 75×10^{-4} cm. In these calculations, it has been assumed that the solid phase consists of spherical particles. This behaviour of concentration dependent diffusivity agrees with literature works[41]. The diffusion coefficient, Di, varied from $0.78.10^{-8}$ to $4.02.10^{-8}$cm^2/s with an increase of initial dye concentration increased from 5 to 30 mg/L. This behaviour of concentration dependent diffusivity agrees with literature works[42]. The values of the internal diffusion coefficient, Di, shown in TABLE 2 fell well within the magnitudes reported in literature[43], specifically for chemisorptions system ($10^{-5} - 10^{-13}$cm^2/s).

Removal of basic blue 41 in binary system

In the application of adsorption for purification of wastewater, the solution will normally be a mixture of many compounds rather than a single one. The interactions of these compounds may mutually enhance or inhibit adsorption capacity[44]. The effects of initial pH (3 - 8.5) and biosorbent concentration (0.05 – 0.7 g/l) on the biosorption of BR46 by *Streptomyces rimosus* biomass were examined in binary system.

(a) Effect of pH

Figures 8 a, b and c present the variation of BB41 biosorption on dead *Streptomyces rimosus* in the presence of metal ions (Ni, Cu or Pb) at different solution pH.

It was observed from Figure 8, that the biosorption of BB41 increased from 11 to 14.54 mg/g at 40 min when pH of the binary solution increased from 3 to 8.5. At pH 3, the percentage removal of BB41 is 79.5 % in the single system which decreased to 63.66 %, 66.2 % and 72 % in the presence of Cu^{2+}, Ni^{2+} and Pb^{2+} respectively. Consequently the binary solution exhibited inhibitory biosorption for the dye, thereby resulting in a lower biosorption yield. Then, at lower pH the presence of ion metal develops a competition for these bio sorption sites on the surface and some sites are occupied by the second component (Ni, Cu or Pb).

Biosorption of BB41 is enhanced at higher pH at higher pH (pH>7), which is probably due to surface precipitation of heavy metal ions on this biomass.

It is well known that heavy metal ions will react with hydroxyl species in basic solution. When pH is increased, more hydroxyl ion will be presented in the solution, resulting in surface precipitation. Species diagram constructed by Mavros et al.[44] showed that Ni (II) are the only ions present in the nickel solution at pH < 6. The precipitation of Ni (II) as $Ni(OH)_2$ precipitate takes place at pH > 7.7. This is also confirmed in the present study and those of other investigators[45,46]. This precipitate represents the adsorption site on the solid surface and thus, biosorption of BB41 is increased. Similar trend was observed with copper and lead.

(b) Effect of adsorbent dose

One of the parameters that strongly affect the sorption capacity is the amount of the biosorbent. The biosorbent concentration was varied between 0.05 and 0.7 g/l at fixed pH (pH=8.5) for binary system studies. The effect of antibiotic waste dosage on BB41 removal was shown in Figure 9. The percentage of BB41 removal with each metal ion increased with adsorbent dosage and then reached a saturation value. Highest sorption (93% removal of basic blue 41with copper, 89.93 % with lead and 87.23 % with nickel) was achieved at C_s =0.3 g/l.

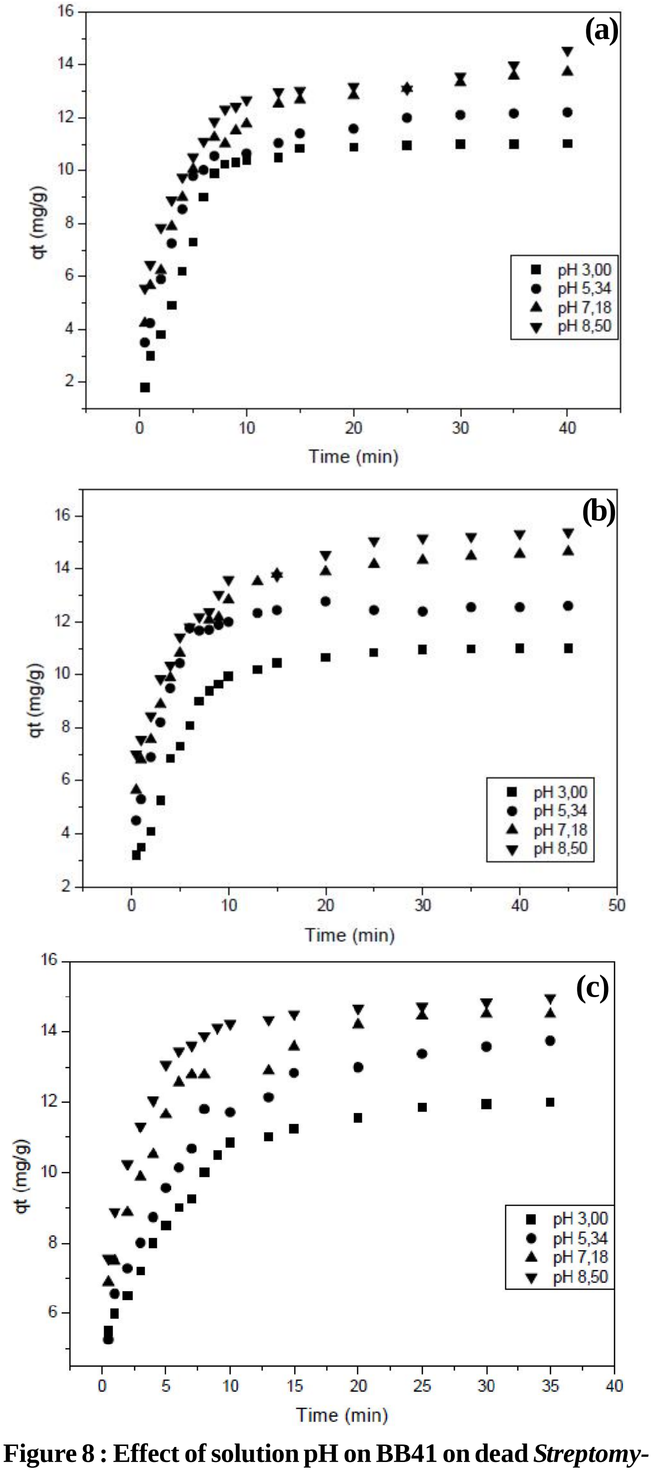

Figure 8 : Effect of solution pH on BB41 on dead *Streptomyces rimosus* in binary system a) with Nickel b) with Copper c) with Lead.

The decrease of percentage removal with increase of biomass (C_S > 0.3 g/l) dose might be due to the formation of aggregates between the biomass particles at high biomass doses, reducing the effective active area

It is clearly seen that the adsorbent dose was seriously affected by the presence of metals ions. Thus, compared with % removal of BB41 in single system, the percentage removal in binary system is higher and with small biosorbent quantity (0.3 g/l). In conclusion, BB41 could still be effectively removed from aqueous solution in the presence of Cu^{2+}, Ni^{2+} and Pb^{2+} ions,

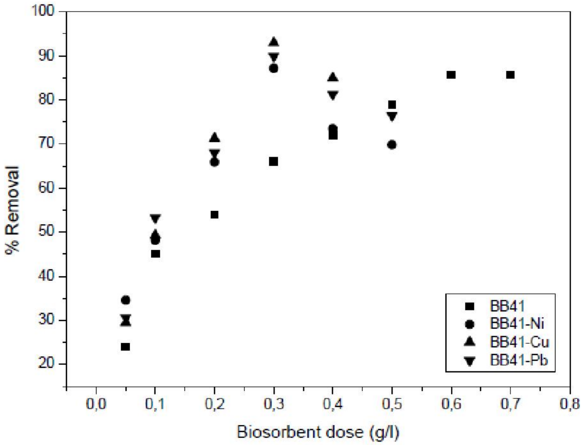

Figure 9 : Dye biosorption on dead *Streptomyces rimosus* at different biosorbent doses in binary system (T =30°C, pH = 8.5).

Biosorption isotherm models in binary system

The data for BB41-Ni, BB41-Cu and BB41-Pb binary system have been analyzed by Freundlich and Langmuir equations models. The results of these analyses, using linear regression procedures, are shown in TABLE 3. This result suggest that dead *Streptomyces rimosus* has a higher affinity to BB41 biosorption in binary system. The *n* values calculated for the adsorption in binary system enhanced with the presence of metal ions, indicating that the biosorption intensity was satisfactory affected by the presence of other component. The value of *n*, which is significantly higher than unity, indicated that both in single and binary BB41 dyes is favourably adsorbed by dead *Streptomyces rimosus*[47]. Also From the table the magnitude of K_F showed a relatively easy uptake of BB41 from aqueous solution with high biosorptive capacity of dead *Streptomyces rimosus*.

Also, TABLE 3 shows the effect of ions metal added on the Langmuir constants. As seen from this table *Streptomyces rimosus* exhibited a higher maximum biosorption capacity (q_{max}) for binary system than that single system. However the addition of metal ion in solution increased the q_{max} value. The presence of copper (II) (5mg/L) enhanced the maximum BB41 uptake capacity of biomass from 57.3 to 68.02 mg/g. A large value of b (0.311<b< 0.668) in biosorption of BB41 in the presence of metal ions than those in single system indicates the high affinity of the biosorbent for the sorbate.

TABLE 3 : Parameters for adsorption isotherm of basic red 46 on antibiotic waste in single and binary component system

System	Freundlich			Langmuir		
	K_F	n	R^2	q_{max} mg/g	b L/mg	R^2
BB41	9.93	1.54	0.990	57.3	0.205	0.987
BB41-Pb	18.9	2.40	0.996	66.36	0.311	0.978
BB41-Cu	25.9	2.56	0.982	68.02	0.668	0.994
BB41-Ni	18.4	1.75	0.998	61.73	0.320	0.962

Based on the isotherm profiles of basic blue 41 biosorption in single and binary system (Figures 10 a-c), It is clear that the experimental results are represented by Freundlich isotherm.

Biosorption kinetics models in binary system

In order to analyze the dye sorption kinetics in binary system, the double exponential equation, pseudo-first order, pseudo-second order kinetic and intraparticle diffusion models were applied to the data. The application of the linear form of the three kinetic models on our experimental results are presented in Figures (11-13). The rate constants and the regression coefficient (R^2) values are shown in TABLE 4 and TABLE 5. The experimental data showed a good compliance with the pseudo-second order equation and the regression coefficients for the linear plots were also higher than 0.99 in single and binary system. Also, it can be concluded from TABLE 4 that in binary component system, the values of h is larger than in single component system for basic blue 41 biosorption on dead *Streptomyces rimosus*. Thus the kinetic rates are faster in binary component system than in single component system. A possible explanation for the phenomena is that at binary pollutants mixtures, the driving force is greater, forcing the biosorption of BB41 to get quickly.

In conclusion, as shown in TABLE 4 and TABLE 5, the values of correlation coefficients of pseudo-first-order are less than $R^2 < 0.980$. As a result, the models which provided the best correlation with experimental data were the pseudo-second-order mode and this suggests that the overall rate of the basic blue 41 process appeared to be controlled by chemical process in single and binary system.

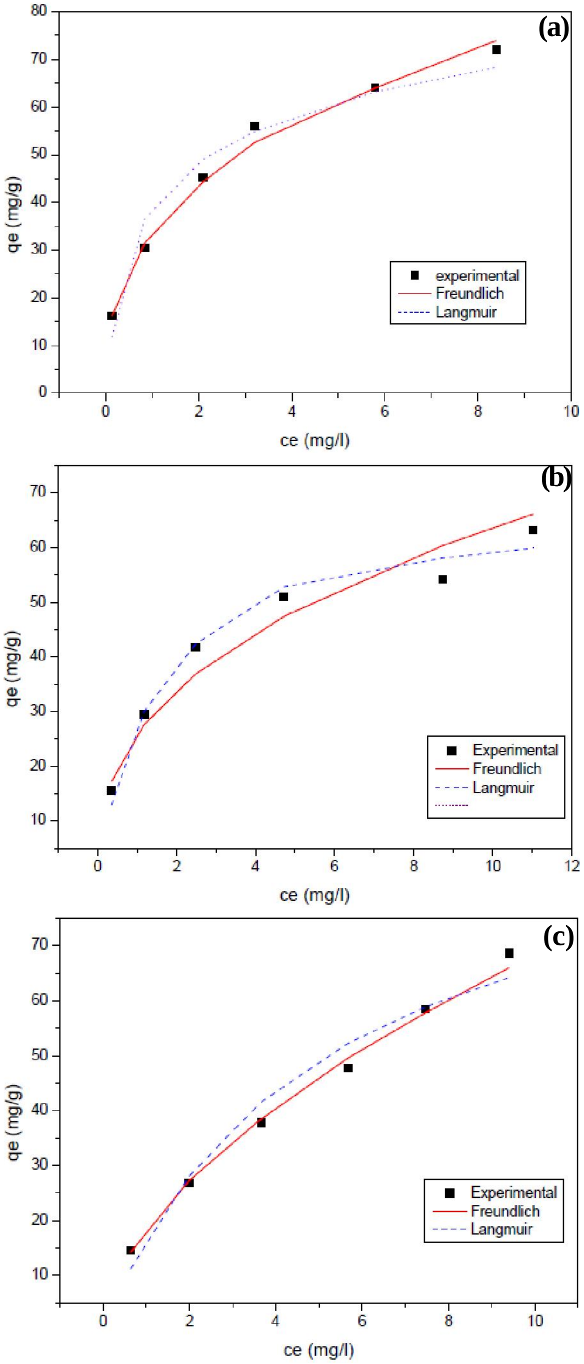

Figure 10 : Adsorption isotherms of BB41on dead *Streptomyces rimosus* in binary system a) with Lead b) with Copper c) with nickel.

Figure 13 shows the intraparticle diffusion results of BB41 on antibiotic waste in binary system. From the figure it can be observed that there are two stages biosorption occurs. The calculated Ki values for each system are given in TABLE 5. BB41 has higher intraparticle rate constant values in binary system than in single. Hence In binary component, BB41 is easily diffused into inner pores of dead *Streptomyces rimosus* and surface precipitation of heavy metal ions, occupying active sites than in single system

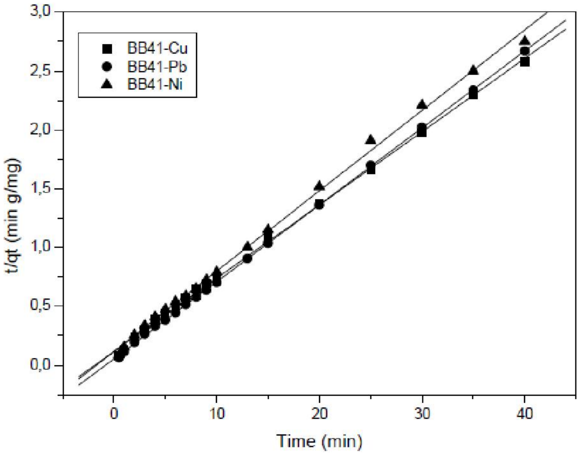

Figure 11 : Pseudo-second- order kinetic for biosorption of BB41 in binary system at pH 8.5.

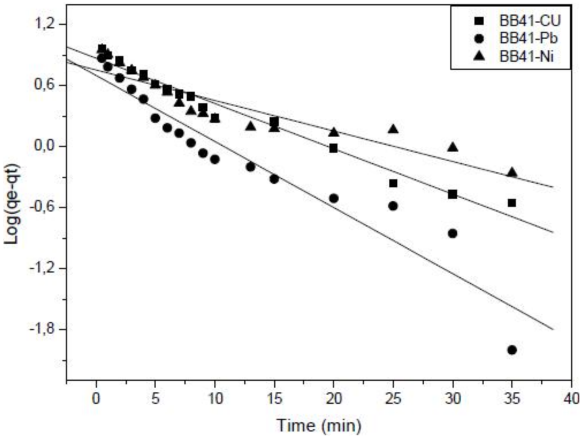

Figure 12 : Pseudo- first- order kinetic for biosorption of BB41 in binary system at pH 8.5.

TABLE 4 : Parameters of kinetic models in binary adsorption system.

system	Experimental	Pseudo-first order			Pseudo-second order			
	qexp (mg/g)	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	H	K_2	R^2
BB41	7.15	6.62	0.179	0.987	7.93	2.22	0.035	0.997
BB41-Pb	14.98	10.8	0.138	0.817	15.29	18.3	0.0782	0.999
BB41-Cu	15.5	9.993	0.0138	0.964	16.08	8.55	0.0331	0.999
BB41-Ni	14.54	9.78	0.069	0.916	14.16	8.51	0.039	0.998

TABLE 5 : Parameters of kinetic models in binary adsorption system.

System	Intraparticle diffusion	
	Ki	R^2
BB41	0.209	0.820
BB41-Pb	0.484	0.947
BB41-Cu	0.664	0.959
BB41-Ni	0.535	0.959

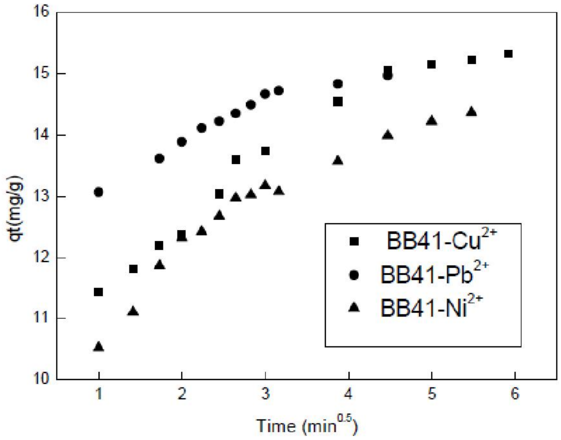

Figure 13 : Intraparticle diffusion for biosorption of BB41 dye onto dead *Streptomyces rimosus* in binary system at pH 8.5.

CONCLUSION

The results of this study suggest that dead *Streptomyces rimosus* offers interesting capacities to absorb of basic blue 41 in binary biosorption system as well as in the single ones. The presence of metals in the wastewater during binary biosorption can have significant consequences. Batch tests have shown that the best experimental condition to adsorb basic blue 41 onto sorbent surface has been achieved by working at pH 8.5. From the kinetic tests, a short equilibrium time around 30min was obtained, indicating that the dead *Streptomyces rimosus* biomass could be used in a biosorption-based continuous.

Biosorption data in binary system showed that the adsorbed amount of dye increase as the presence of metal present in solution. This effect was substantial for presence of copper. We found that the biosorption capacity of biomass increased from 7.15 to 15.5 mg/g in single system and with presence of copper respectively.

The adsorption kinetics in either single or binary system will follow the pseudo-second order kinetics and it is found that the Freundlich isotherm fit the experimental data better than the others. It also suggests the heterogeneous nature of the biosorption of basic blue 41. Sorption on binary system is more effectives that this on single system. Finally, it may be concluded that *Streptomyces rimosus*. may be used for the individual and simultaneous removal of BB41 from effluents.

REFERENCES

[1] Z.Aksu; Application of biosorption for the removal of organic pollutants, A review. Process Biochem., **40**, 997–1026 **(2005)**.

[2] Z.Aksu, Z.Tezer; Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. Process Biochem., **40**, 1347–1361 **(2005)**.

[3] Y.Fu, T.Viraraghavan; Fungal decolorization of dyewastewaters, A review. Biores.Technol., **79**, 251–262 **(2001)**.

[4] T.Robinson, G.McMullan, R.Marchant, P.Nigam; Remediation of dyes in textile effluents: A critical review on current treatment technology with a proposed alternative. Biores.Technol., **77**, 247-255 **(2001)**.

[5] O.Hamdaoui; Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. J.Hazard.Mater., **B135**, 264–273 **(2006)**.

[6] T.Robinson, B.Chandran, P.Nigam; Effect of pretreatments of three waste residues, wheatstraw, corncobs and barley husks on dye adsorption. Bioresour.Tcchnol., **85**, 119-124 **(2002)**.

[7] G.Bayramoglu, S.Bektas, M.Arica; Biosorption of heavy metal ions on immobilized white-rot fungus trametes versicolor, J.Hazard.Mater., **101**, 285 **(2003)**.

[8] S.W.Won, S.B.Choi, B.W.Chung, D.Park, J.M.Park, Y.-S.Yun; Biosorptive decolorization of reactive orange 16 using the waste biomass of corynebacterium glutamicum, Ind.Eng.Chem.Res., **43**, 7865 **(2004)**.

[9] M.Y.Arica, G.Bayramoglu; Cr (IV) biosorption from aqueous solutions using free and immobilized biomass of lentinus sajor-caju: Preparation and kinetic characterization, Coll.Surf.A., **253**, 203 **(2005)**.

[10] K.V.Radha, A.Regupathi, T.Arunagiri, T.Murugesan; Decolorization studies of synthetic dyes using phanerochaete chrysosporium and their kinetics, Process Biochem., **40**, 3377 **(2005)**.

[11] A.Kogei, A.Pavk; Comparison of rhizopus nigricans in a pelleted growth from with some other types of waste microbial biomass as biosorbents for metal ions, World.J.Microb.Biotechnol., **17**, 677 **(2001)**.

[12] G¨ulay Bayramo˘glu, C.G¨okce, M.Elik, Yakup Arica; Biosorption of reactive blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: Batch and continuous flow system studies, J.Hazard.Mater., **B37**, 1689-1697 **(2006)**.

[13] Y.Fu, T.Viraraghavan; Dye biosorption sites in aspergillus niger, Bioresour.Technol., **82**, 139 **(2002)**.

[14] N.Yeddou-Mezenner; Kinetics and mechanism of dye biosorption onto anununtreated antibiotic waste, Desalination, **262**, 251-259 **(2010)**.

[15] T.Akar, S.Tunali; Biosorption performance of botrytis cinerea fungal by product for removal of Cd (II) and Cu (II) ions from aqueous solutions, Miner.Engin., **18**, 1099-1109 **(2005)**.

[16] Fatih Deniz, D.Saadet; Saygideger, Removal of a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf, Desalination, **268**, 6-11 **(2011)**.

[17] A.Bennani Karima, B.Mounir, M.Hachkar, M.Bakassec, A.Yaacoubi; Removal of basic red 46 dye from aqueous solution by adsorption onto moroccan clay, Journal of Hazardous Materials **168**, 304–309 **(2009)**.

[18] J.M.Deacon; Fungal biology, 4th Edition. Blackwell Publishing Ltd., **(2006)**.

[19] Asim Olgun, Necip Atar; Equilibrium and kinetic adsorption study of basic yellow 28 and basic red 46 by a boron industry waste, Journal of Hazardous Materials, **161**, 148-156 **(2009)**.

[20] V.Farkas; Biosynthesis of cell wall of fungi. Microbiol.Res., **43**, 117–141 **(1980)**.

[21] Meral Turabik; Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of basic red 46 and basic yellow 28 by first order derivative spectrophotometric analysis method, Journal of Hazardous Materials, **158**, 52–64 **(2008)**.

[22] M.S.Chiou, G.S.Chuang; Competitive adsorption of dye metanil yellow and RB15 in acidic solutions on chemically cross-linked chitosan beads, Chemosphere, **62**, 731–740 **(2006)**.

[23] G.Akkaya, A.Özer; Biosorption of acid red 274 (AR 274) on dicranella varia: Determination of equilibrium and kinetic model parameters, Process Biochem., **40**, 3559–3568 **(2005)**.

[24] R.S.Bai, T.E.Abraham; Biosorption of Cr (VI) from aqueous solution by rhizopus nigricans, Bioresour.Technol., **79**, 73–81 **(2001)**.

[25] I.Langmuir; The adsorption of gases on plane surfaces of glass, mica and platinum. J.Am.Chem.Soc., **40**, 1361-1403 **(1918)**.

[26] H.M.F.Freundlich; Über die adsorption in lösungen. Zeitschrift für Physikalische. Chemie (Leipzig), **57A**, 385-470 **(1906)**.

[27] M.J.Temkin, V.Pyzhev; Kinetic of ammonia synthesis on promoted iron catalysis. S.Acta Physiochim.URSS, **12**, 327-356 **(1940)**.

[28] M.M.Dubinin; The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chem.Rev., **60**, 235 **(1960)**.

[29] S.S.Dubey, R.K.Gupta; Removal behavior of babool bark (Acacia nilotica) for submicro concentrations of Hg2+ from aqueous solutions: a radiotracer study, Sep.Purif.Technol., **41(1)**, 21–28 **(2005)**.

[30] S.Tunali, T.Akar, A.S.Ozcan, I.Koran, A.Ozcan; Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by cephalosporium aphidicola, Sep.Purif.Technol., **47**, 105–112 **(2006)**.

[31] Chih-Huang Weng, Yi-Fong Pan; Adsorption of a cationic dye (methylene blue) onto spent activated clay, Journal of Hazardous Materials, **144**, 355-362 **(2007)**.

[32] S.Lagergren, B.K.Svenska; Zur theorie der sogenannten adsorption geloster stoffe. Vetenskapsakad.Handl, **24**, 1-39 **(1898)**.

[33] Y.S.Ho; Review of second order models for adsorption systems, J.Hazard.Mater, **B136**, 681-689 **(2006)**.

[34] Z.Aksu, I.A.Tatlý, O.Tunc; A comparative adsorption/ biosorption study of acid blue 161: Effect of temperature on equilibrium and kinetic parameters. Chem.Eng.J., **142**, 23–39 **(2008)**.

[35] O.Anjaneya, M.Santoshkumar, S.Nayak Anand, T.B.Karegoudar; Biosorption of acid violet dye from aqueous solutions using native biomass of a new isolate of penicillium sp. International Biodeterioration & Biodegradation, **63**, 782–787 **(2009)**.

[36] W.J.Weber, J.C.Morris; Kinetic of adsorption on carbon from solution, J.Sanit.Eng.Div.Am. Soc.Civ.Eng., **89**, 31-60 **(1963)**.

[37] G.Mckay, V.J.P.Poots; Kinetic and diffusion process in colour removal from effluent using wood as an adsorbent, J.Chem.Technol.Biotechnol., **30**, 279-292 **(1980)**.

[38] N.Kannan, M.M.Sundaram; Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study, Dyes Pigments, **51**, 25–40 **(2001)**.

[39] Necmettin Caner, Ismail Kiran, Semra Ilhan, Cansu Filik Iscen; Isotherm and kinetic studies of burazol blue ED dye biosorption by dried anaerobic sludge. Journal of Hazardous Materials, **165**, 279–284 **(2009)**.

[40] A.K.Bhattacharya, C.Venkobar; Removal of cadmium by low cost adsorbents, J.Environ.Eng., **110(1)**, 110-122 **(1984)**.

[41] G.M.Walker, L.Hansen, J.A.Hanna, S.J.Allen; Kinetics of a reactive dye adsorption onto dolomic sorbents,Water Res., **37(9)**, 2081–2089 **(2003)**.

[42] D.Chatzopoulos, A.Varma, R.L.Irvine; Activated carbon adsorption and desorption of toluene in the aqueous phase, AIChE J., **39**, 2027–2041 **(1993)**.

[43] Y.S.Ho, G.McKay; Competitive sorption of copper and nickel ions from aqueous solution using peat, Adsorption **5**, 409–417 **(1999)**.

[44] P.Mavros, A.I.Zouboulis, N.K.Lazaridis; Removal of metal ions from wastewaters. The case of nickel, J.Environ.Technol., **14**, 83-91 **(1993)**.

[45] Vimal Chandra Srivastava, Indra Deo Mall, Indra Mani Mishra; Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chemical Engineering Journal, **117**, 79–91 **(2006)**.

[46] F.A.A.Al-Rub, M.H.El-Naas, F.Benyahia, I.Ashour; Biosorption of nickel on blank alginate beads, free and immobilized algal cells, Process Biochem., **39**, 1767–1773 **(2004)**.

[47] M.M.Dávila, -Jimenez, M.P.Elizalde-Gonzalez, A.A.Peláez-Cid; Adsorption interaction between natural adsorbents and textile dyes in aqueous solution, J.Colloid Interf.Sci., **A254(1-3)**, 107-114 **(2005)**.