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# Kinetic and Equilibrium Studies on the Biosorption of Cl Reactive Orange 16 Dye by Immobilized *Scenedesmus quadricauda*

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The biosorption of commonly used reactive dye, reactive orange 16 (RO 16), from aqueous solutions by live (ILSq) and heat inactivated *Scenedesmus quadricauda* (IHISq) immobilized *Scenedesmus quadricauda* was studied in a batch system with respect to pH, temperature and biosorption time. The ILSq and IHISq exhibited the highest dye uptake capacity at 30 °C, the initial pH value of 2.0 and the initial dye concentration of 300 mg $L^{-1}$. At 300 mg $L^{-1}$ initial dye concentration in the batch system the adsorption capacity was determined as 88.4 mg $g^{-1}$ of dye biosorption for IHISq in 0.5 h. The adsorption capacity of ILSq was observed as 71.2 mg $g^{-1}$ in 0.5 h and 76.4 mg $g^{-1}$ and 82.8 mg $g^{-1}$ of dye biosorption within 1 and 3 h, respectively. The equilibrium concentration and the adsorption capacity at equilibrium were determined using four different sorption models *i.e.*, Langmuir, Temkin, Flory-Huggins and Freundlich isotherm.

**Key Words: Isotherms, kinetics, Biosorption, Immobilized *Scenedesmus quadricauda*, Algae, Reactive orange 16.**

## INTR3ODUCTION

The textile industry uses the dye for the colouration of the fiber. There are over 100,000 commercially available dyes whose amount of production is over $7 \times 10^5$ metric tons per year[1-4]. Dyes are classified into different chemical and application classes according to their variations in application class and chemical nature[5]. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups *e.g.*, vinyl sulfone,

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chlorotriazine, trichloropyrimidine, difluorochloropyrimidine[1,6,7]. They differ from all other classes of dyes in that they are bound to the textile fibers such as cotton to through covalent bonds. They bear such convenient characteristics as bright colour, simple application techniques and low energy consumption and they are extensively used in textile industries[2,8].

Biosorption of azo dyes has been the target of great attention in the last few years[9]. Dyeing industry effluents constitute one of the most problematic waste waters to be treated, not only because of their high chemical and biological oxygen demands, suspended solids and content in toxic compounds but also because of colour, which is the first contaminant to be recognized by human eye. They must also be resilient to both high temperatures and enzyme degradation, resulting from detergent washing[9].

Adsorption has been shown to be the most promising option for non-degradable dyes for the removal from aqueous streams, activated carbon being the most common adsorbent for this process due to its effectiveness and versatility[10]. Adsorption techniques are seen as an economic alternative. Biosorption is the passive uptake of the pollutions from aqueous by the use of non-growing or non living microbial mass. The main attractions of biosorption are high selectivity and efficiency, cost effectiveness and good removal performance. Textile dyes vary greatly in their chemistry and their interactions with microorganisms depend on the chemistry of a particular dye, type of biomass, its preparation and its specific surface properties and environmental conditions (pH, temperature, ionic strength, existence of competing organic or inorganic ligands in solution)[4,11,12]. Micro algae, the primary producers of the aquatic food chains, have been found to be very effective in removing pollutants from waste water. Micro algae have been successfully used as biomass for waste water treatment systems because of their photoautotrophic growth properties[13].

In industrial or technical operations, immobilized microbial cell systems could also provide additional advantages over freely suspended cells[14]. Immobilized cells tend to have higher activity and are more resilient to environmental perturbations such as pH or exposure to toxic chemical concentrations than suspension cells. Natural polymers, such as alginate, chitosan, cellulose and chitin derivatives, have been mostly used as matrix for the immobilization of microbial cells *via* entrapment technique[15].

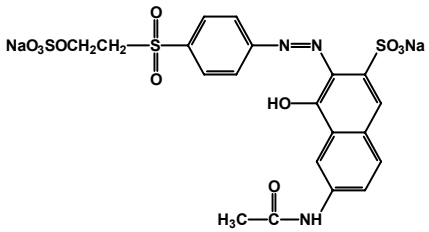
In the present study, Ca-alginate was used as natural polymeric matrix and *Scenedesmus quadricauda* was immobilized in Ca-alginate beads by entrapment. Live *Scenedesmus quadricauda* (ILSq) and heat inactivated *Scenedesmus quadricauda* (IHISq) were used for the sorption of dyes, from aqueous solutions in a batch system. The study investigates the effects of initial dye concentration, initial pH of the solution and time on the dye uptake capacities of ILSq and IHISq were investigated.

## EXPERIMENTAL

Micro alga *Scenedesmus quadricauda* used in this research was isolated from fresh water samples obtained from Lake Mogan in Ankara, Turkey. The cell culture was grown in BG11 medium adjusted to pH 7.0 and maintained at 21 °C with a 16:8 h light dark cycle using 2400 lx light intensity. The resulting biomass was washed with sterile distillated water for several times.

**Dye:** The general characteristics of RO 16 are summarized in Table-1. Reactive orange16 dye (CI 17757) was obtained from Sigma-Aldrich Company Ltd. The range of concentration of prepared dye solutions changed between 10 and 300 mg $L^{-1}$ for Orange 16 (RO16).

TABLE-1
CHARACTERISTICS OF REACTIVE ORANGE 16 (RO16)




m.f.: $C_{20}H_{17}N_3O_{11}S_3Na_2$; m.w.: 617.54; Colour index no. 17757; $\lambda_{max}$ (nm): 388

**Immobilization of *Scenedesmus quadricauda*:** The immobilization of *Scenedesmus quadricauda via* entrapment was carried out as follows: Na-alginate (% 2 g; from *Macrosytia pyrifera*, high viscosity, Sigma Chem. Co., USA) was dissolved in distilled water and mixed with the *Scenedesmus quadricauda*. The mixture was introduced into a solution containing (0.1 M $CaCl_2$) with a burette and stirred to prevent aggregation of the Ca-alginate beads. The beads (*ca.* 4 mm) were cured in this solution for 1 h and then washed twice with 200 mL sterile distilled water. The cured beads were stored in 5 mM $CaCl_2$ solution at 4 ºC until they were used. The heat-inactivated preparation was obtained through boiling the live algae in water for 10 min.

**Scanning electron microscopy:** Samples of algal immobilized beads were coated with a thin layer of gold under vacuum and their structure was examined under a Jeol, JSM-5600 scanning electron microscope at an accelerating voltage of 20 kV.

**Batch experimental procedure:** In order to obtain isotherm and kinetic data, batch biosorption experiments were performed in 500 mL Erlenmeyer flasks containing 100 mL dye synthetic solutions. The flasks were agitated

on a shaker at 150 rpm for 24 h to ensure that equilibrium was reached. The effect of initial solution pH on decolourization of active and heat-inactivated immobilized algal preparations was investigated in the pH range of 2.0-8.0 (which was adjusted with HCl or NaOH solution at the beginning of the experiment) at 30 ºC. The effect of temperature and initial dye concentration between 10 and 300 mg/L on the decolourization capacities of the beads was studied.

The amount of biosorbed dye per unit immobilized algae (mg dye/g biomass) was determined by using the following equation:

$$q_e = (C_o - C_e)V/m \quad (1)$$

where $q_e$ is the adsorption capacity (mg $g^{-1}$), $C_o$ and $C_e$ are the concentration of the dye in initial solution (mg $L^{-1}$) and after biosorption, respectively. V is the volume in aqueous solution (L) and m is the amount of the biomass (g).

The concentration of unadsorbed RO16 dye in the biosorption medium was measured using a double beam UV/Vis spectrophotometer (Spectro RS) at 388 nm.

**Biosorption isotherms in a batch system:** Four biosorption isotherm models were used to fit the experimental data are, as follows: The liberalized Langmuir[16-18], Freundlich[19], Temkin and Flory-Huggins[20-22] isotherm models: (eqn. 1-4, respectively).

$$C_e/q_e = 1/q_m K_L + C_e/q \quad (1)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (2)$$

$$q_e = (RT/b_T) \ln K_T + (RT/b_T) \ln C_e \quad (3)$$

$$\ln (\theta/C_o) = \ln K_{KF} + n \ln (1-\theta) \quad (4)$$

where, $K_L$ = Langmuir isotherm constant related to the measure of affinity of the adsorbate for adsorbent, $q_m$, Langmuir monolayer sorption capacity (mg $g^{-1}$); $K_F$ = biosorption capacity ( L $g^{-1}$); n = biosorption intensity (affinity of the adsorbate for adsorbent); $b_T$ = adsorption potential of the adsorbent; $K_T$ = equilibrium constant corresponding to maximum binding energy (L $g^{-1}$); $\theta = \theta = (1-C_e/C_o)$ is the degree of surface coverage, n = number of dye occupying sorption sites; $K_{FH}$ = equilibrium constant (L $mol^{-1}$); $C_o$ = initial concentration of dye.

**Kinetic models for the biosorption:** To determine dye biosorption kinetics, two different kinds of kinetic models were used. Lagergren pseudo-first order and pseudo-second order kinetic models are shown below[7,18, 23-25].

*The pseudo-first order model:*

$$dqt/dt = k_{1,ad} (q_e - q_t) \quad (5)$$

where, $q_e$ is the adsorption capacity, t is the contact time (min), $k_1$ is the pseudo first-order bisorption rate constant ($min^{-1}$), $q_e$ and $q_t$ are the amount of dye biosorbed on the algae at equilibrium (mg $g^{-1}$) and at any time,

respectively. The integration of eqn. 6 with the initial condition, $q_t = 0$ at $t = 0$ leads to

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

The values of the adsorption rate constant ($k_1$) were determined from of the $\ln (q_e - q_t)$ *vs.* t.

*Pseudo- second order model:* The pseudo-second model is defined as

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (7)$$

Integrating and rearranging eqn. 7 with the initial condition $q_t = 0$ at $t = 0$, the following equation is obtained:

$$t/q_t = 1/k_{2,ad}q_e^2 + (1/q_e)t \quad (8)$$

where, $q_t$ is the initial sorption rate (mg $g^{-1}$ $min^{-1}$), at $t \rightarrow 0$ is defined as $h = k_2 q_e^2$ and $k_2$ is the pseudo-second order biosorption rate constant (g $mg^{-1}$ $min^{-1}$). The $q_e$ is determined from the slope of $t/q_t$ *vs.* t and h is determined from the intercept.

## RESULTS AND DISCUSSION

**Characteristics of alginate-based biosorbent systems:** Ca-alginate beads containing *Scenedesmus quadricauda* were used for the removal of dyes from aqueous solution. Alginate is a water-soluble natural polymer, which can be converted into hydrogels *via* cross-linking with divalent calcium ions. Beside the advantages, such as biodegradability and hydrophilicity, the presence of carboxylic groups in the alginate structure enhances the adsorption of dyes[14]. The scanning electron micrograph of immobilized *Scenedesmus quadricauda* bead is depicted in Fig. 1. The micrographs did not indicate any change in the morphology of *Scenedesmus quadricauda*.

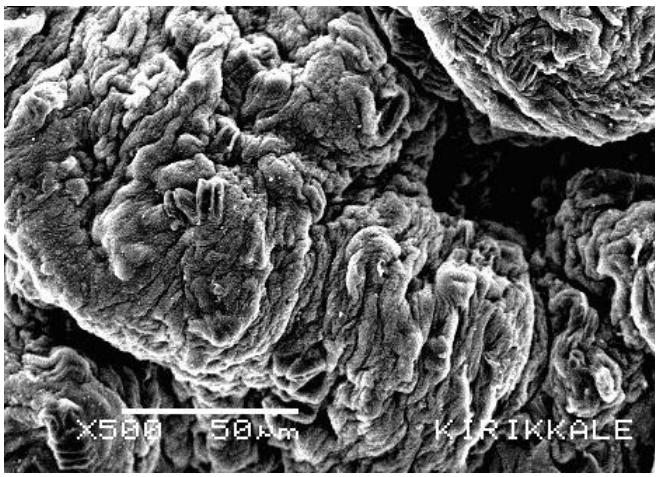



Fig. 1. Scanning electron micrographs of *Scenedesmus quadricauda* immobilized alginate beads

**Effects of initial dye concentration on dye biosorption:** As shown in Fig. 2, the amount of biosorbed Orange 16 onto the ILSq and IHISq preparations at equilibrium were studied and plotted as a function of the initial concentration of RO 16 the biosorption medium. The biosorption capacity, $q_e$ (mg $g^{-1}$), of the ILSq and IHISq increased with increasing concentration of RO 16 at equilibrium ($C_e$, mg $L^{-1}$).

**Effects of initial pH on dye biosorption:** The effects of initial pH on dye sorption of ILSq and IHISq were studied in the pH range from 2.0 to 8.0 at 300 mg $L^{-1}$ initial dye concentration and the results are shown in Fig. 3. The biosorption of RO 16 with ILSq and IHISq was determined at pH 2.0 as 80.9 mg $g^{-1}$ and 89.9 mg $g^{-1}$, respectively and declined with further increase in pH.

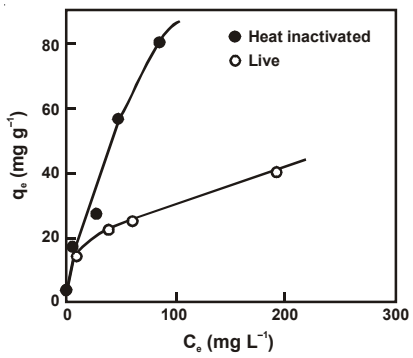



Fig. 2. Adsorption capacity of *S. quadricauda* of the dye concentration at equilibrium for RO16 (pH = 2.0, t = 30 °C, agitation rate =150 rpm)

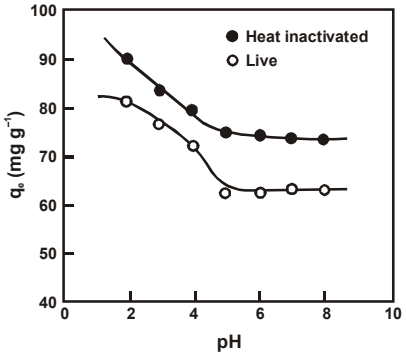



Fig. 3. Effect of initial pH on the equilibrium RO16 sorption capacity of *S. quadricauda* ($C_o$ = 300 mg $L^{-1}$, t = 30 °C, agitation rate = 150 rpm)

The pH of dye solution plays an important role in the whole biosorption process. Dye sorption is highly pH dependent. The azo dyes release coloured dye anions in solution. The cell wall matrix of green algae contains different functional groups such as carboxyl, hydroxyl, sulphate and other charged groups which are created by their complex heteropolysaccharides and lipid components. At lower pH values, the biomass will have a net positive charge. It is expected that nitrogen containing functional groups such as amines or imadazoles in the biomass will also be protonated at acidic pH values. Higher uptakes, obtained at lower pH values may be due to electrostatic attraction between these negatively charged dye anions and positively charged cell surface[17].

**Effects of temperature on dye biosorption:** The effects of temperature on the equilibrium sorption capacity of ILSq and IHISq for RO 16 was investigated in the temperature range of 20-45 °C at the initial dye concentration of 300 mg $L^{-1}$. The biosorption capacity of RO 16 with ILSq and IHISq was obtained at 30 °C as 84.6 mg $g^{-1}$ and 86.9 mg $g^{-1}$, respectively. As shown in Fig. 4 the biosorption of RO 16 dye increased by increasing temperature up to 30 °C. This temperature is suitable to binding with dye and cell wall matrix of *Scenedesmus quadricauda*. Adsorption decreased once the temperature increased due to the decreased surface activity. Because of the decreasing surface activity the adsorption decrease with further increasing temperature.

**Biosorption isotherm:** Langmuir biosorption isotherm was preferred for the estimation of monomolecular adsorption capacity, $q_m$ corresponding to complete monolayer coverage on the biomass surface ($C_e/q_e$) *vs.* $C_e$ plots for ILSq and IHISq were shown in Fig. 5 and linear isotherm parameters, $q_m$, $K_L$ and the coefficient of determination are given in Table-2. The monomolecular adsorption capacity, $q_m$, showed that the immobilized algae had more a mass capacity for IHISq (107.2 mg/g) than ILSq (45.8 mg/g).

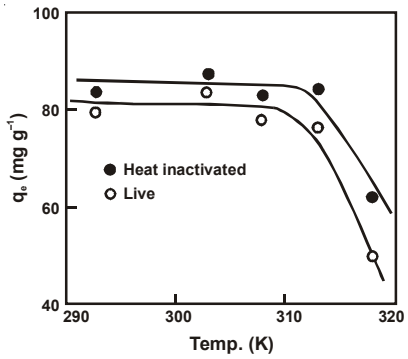



Fig. 4. Effect of temperature on the equilibrium RO16 sorption capacity of *S. quadricauda* ($C_o$: 150 mg $L^{-1}$, pH 2.0, agitation rate: 150 rpm)

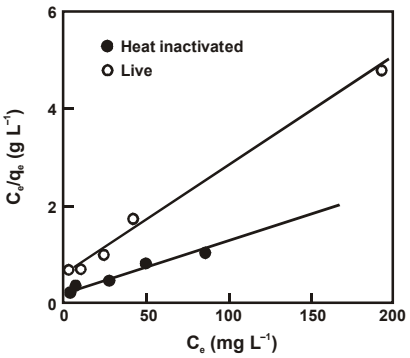



Fig. 5. Linearized Langmuir adsorption isotherms of RO16 (pH 2.0, t = 30 °C, agitation rate = 150 rpm)

Freundlich model was able to determine the biosorption equilibrium of dye on live and physically treated algae biomass preparations. The Freundlich isotherm model was used to fit the experimental data. The Freudlich equation is based on biosorption onto a heterogeneous surface. The plots of ln $q_e$ *vs.* ln $C_e$ for ILSq and IHISq are shown in Fig. 6. $K_F$ and n values of the isotherm model showed easy biosorption of dyes for aqueous medium with a high adsorption capacity of the algae biomass preparations

(Table-2). Values of n > 1 for RO 16 molecule indicates positive binding and a heterogeneous nature of adsorption.

TABLE-2
LANGMUIR, TEMKIN, FLORY-HUGGINS AND FREUNDLICH PARAMETERS FOR THE ADSORPTION ISOTHERMS OF REACTIVE ORANGE 16 (RO16)

| Immobilized *S. quadricauda* | Langmuir | | | Temkin | | |
|---|---|---|---|---|---|---|
| | $K_L$ ($dm^3 g^{-1}$) | $q_m$ (mg $g^{-1}$) | $R^2$ | $K_T$ ($10^2$ L/mol) | $\Delta G^o$ (kJ $mol^{-1}$) | $R^2$ |
| Live | 0.036 | 45.80 | 0.9880 | 0.52 | -9.94 | 0.9771 |
| Inactivated | 0.031 | 107.20 | 0.9741 | 6.79 | -16.40 | 0.9924 |
| | Flory-Huggins | | | Freundlich | | |
| | n | $K_{FH} \times 10^3$ | $R^2$ | $\Delta G^o$ (kJ $mol^{-1}$) | n | $K_F$ (L/g) |
| Live | 3.62 | 4.28 | 0.9995 | -21.1 | 1.751 | 2.43 |
| Inactivated | 3.32 | 29.30 | 0.9788 | -25.9 | 1.290 | 3.93 |

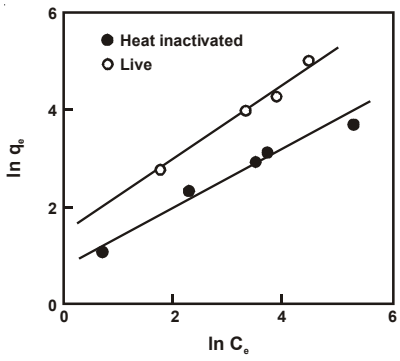



Fig. 6. Linearized Freundlich adsorption isotherms of RO16 (pH 2.0, t = 30 ºC, agitation rate = 150 rpm)

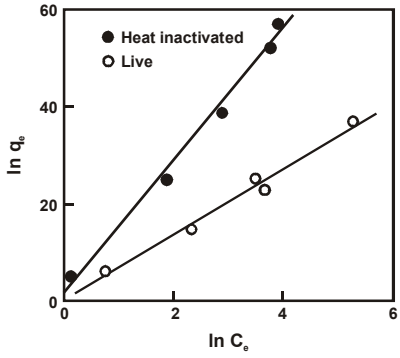



Fig. 7. Linearized Temkin adsorption isotherms of RO 16 (pH 2.0, t = 30 °C, agitation rate = 150 rpm)

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption sites. The range and distribution of binding energies should depend strongly on the density and distribution of functional groups, both on the dye and on the biosorbent surfaces. Temkin adsorption isotherm model was chosen to determine the adsorption potentials of the adsorbent for adsorbates. $q_e$ *vs.* ln $C_e$ for ILSq and IHISq are presented in Fig. 7 and isotherm parameters are given in Table-2. The Temkin adsorption potential, $K_T$ of algae biomass for immobilized ILSq and IHISq are 52 and 679 (L $mol^{-1}$), respectively. $K_T$ and $\Delta G^o$ as follows:

$$K_T = \exp(-\Delta G^o/RT) \quad (9)$$

where, R is universal gas constant, 8.314 J $mol^{-1}$ $K^{-1}$, T is absolute temperature.

The standard free enthalpy, $\Delta G^o$ values were calculated for ILSq and IHISq in Table-2.

Flory-Huggins model was able to determine the degree of surface coverage characteristics of the adsorbate on the adsorbent. The plots of ln ($\theta$/ $C_o$) *vs.* ln (1-$\theta$) for ILSq and IHISq were showed in Fig. 8 and isotherm parameters are given in Table-2. The biosorption data for Temkin isotherm showed that KFH for ILSq and IHISq are $4.28 \times 10^3$ and $29.3 \times 10^3$ (L $mol^{-1}$), respectively. The values of $\Delta G^o$ were calculated according to eqn. 9. The negative values suggest that the biosorption process is spontaneous in nature and supports an exothermic reaction. The standard free enthalpy values that are obtained by using the Flory-Huggins model is higher than the Temkin isotherm values.

**Biosorption kinetic models:** The effects of time on dye biosorption of both live ILSq and IHISq were investigated in a batch system. The adsorption capacity at equilibrium of the dye *vs.* time is shown in Fig. 9. The adsorption capacity of IHISq was observed to be higher than ILSq.

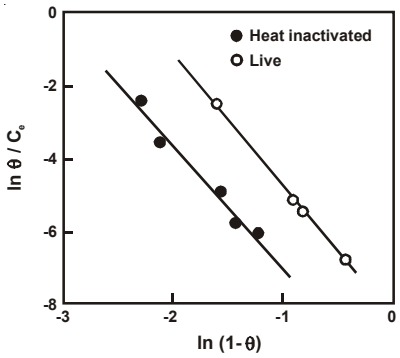



Fig. 8. The linearized Flory-Huggins adsorption isotherms of RO16 (pH 2.0, t = 30 °C, agitation rate = 150 rpm)

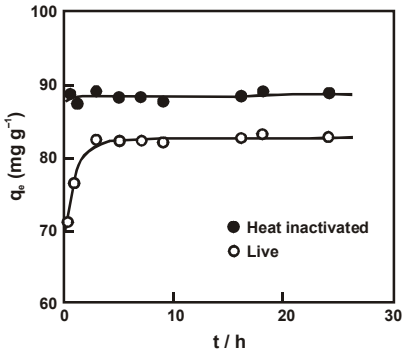



Fig. 9. The equilibrium adsorption time of RO 16 onto *S. quadricauda* ($C_o$:300 mg $L^{-1}$, pH 2.0, t: 30 °C)

The saturation level was reached approximately in 24 h for ILSq and IHISq. At 300 mg $L^{-1}$ initial dye concentration in the batch system the adsorption capacity was determined as 88.4 mg $g^{-1}$ of dye biosorption for IHISq in 0.5 h and after 0.5 h the adsorption capacity was not changed for 24 h. Removal of RO 16 molecules were faster at the initial stage as the driving force was higher, which permitted to overcome all external mass transfer resistances and higher affinity active sites were first occupied. After that, RO 16 concentration in the solution decreased and the remaining

active sites, with lower affinities, were occupied slowly. The adsorption capacity of ILSq was observed as 71.2 mg $g^{-1}$ in 0.5 h and 76.4 mg $g^{-1}$ and 82.8 mg $g^{-1}$ of dye biosorption within 1 and 3 h, respectively and after 3 h the adsorption capacity was not changed although adsorption time had been increased.

The experimental kinetic data of biosorption studies were used for the Lagergren first-order and Ritchie second-order kinetic models. The first-order kinetic model indicates that the process of adsorption occurs at a rate proportional to dye concentration, which is suitable especially for low concentration. Ritchie kinetic model is considered to drive from biosorption processes in which the rate-controlling step is an exchange reaction[25,26]. The rate constants, k, for the biosorption of the dye on the algae are presented in Table-3. The data obtained by the first-order kinetic equation were not well-defined biosorption of tested dye on the algae. As seen in Figs. 9 and 10, the experimental value of maximum adsorption capacity, $q_{exp}$, for the ILSq and IHISq are very close to calculated theoretical values, $q_e$, of the Ritchie second-order kinetic models. This process was suitable for description on biosorption kinetic for the removal of RO 16 from aqueous solution onto ILSq and IHISq.

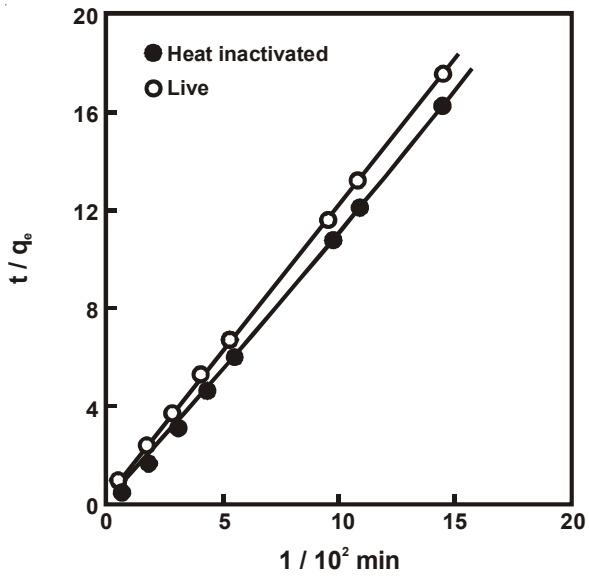



Fig. 10. The second-order kinetic plots for adsorption of RO16 onto *Scenedesmus quadricauda*

TABLE-3
A COMPARISON OF THE FIRST ORDER AND SECOND ORDER RATE CONSTANTS (t = 30 ºC, $C_o$ = 300 mg/L, pH = 2.0)

| Immobilized *S. quadricauda* | Experimental $q_{exp}$ (mg $g^{-1}$) | First order kinetic | | | Second order kinetic | | |
|---|---|---|---|---|---|---|---|
| | | $k_1 \times 10^{-5}$ ($min^{-1}$) | $q_{eq}$ (mg $g^{-1}$) | $R^2$ | $k_2 \times 10^{-3}$ (g $mg^{-1}$ $min^{-1}$) | $q_{eq}$ (mg $g^{-1}$) | $R^2$ |
| Live | 82.8 | 9.0 | 82.8 | 0.9155 | 3.1 | 82.7 | 1.0000 |
| Inactivated | 88.8 | 4.0 | 88.1 | 0.5076 | 22.0 | 88.5 | 0.9999 |

This result indicates that the second-order mechanism is more effective. Sorption can be the rate-limiting step which controls the biosorption process.

## Conclusion

This study examines the capability of ILSq and IHISq for removing RO 16 dye including equilibrium and kinetic studies of biosorption. Experiments were performed as a function of initial pH, temperature and time. The solution pH played a significant role in affecting the capacity of *Scenedesmus quadricauda*. At pH 2.0 ILSq and IHISq have high adsorption yields for dye removal from solutions. The increase in temperature up to 30 °C decreased the biosorption capacity of the biomass. The maximum dye uptake was observed at the initial dye concentration of 300 mg $L^{-1}$. The Freundlich, Langmuir, Temkin and Flory-Huggins adsorption models were used for the mathematical explanations of the biosorption equilibrium of RO 16. The biosorption capacity of ILSq and IHISq preparations for the dye were 82.8 (mg $g^{-1}$) and 88,8 (mg $g^{-1}$), respectively. The present biosorption values are comparable with dye binding by other algal biomass preparations. The biosorption capacity of green algae *Chlorella vulgaris* for Remazol Black B, Remazol Red RR and Remazol Golden Yellow RNL were 555.6, 196.1 and 71.9 mg $g^{-1}$, respectively[4]. The thermopilic cyanobacterial strains (*Synechococcus* sp. and *Phormidium* sp.) for Reactive Red RB, Remazol Blue and Reactive Black B were 14.49 mg $g^{-1}$ for 78.3 mg $L^{-1}$, 16.76 mg $g^{-1}$ for 72.4 mg $L^{-1}$ and 16.95 mg $g^{-1}$ for 61.69 mg $L^{-1}$, respectively[27].

The first-order and second-order kinetic models were used for the biosorption of the dye on the algae. It was determined that the interactions could be better explained on the basis of second-order kinetic model. The kinetic studies at initial dye concentration showed that the greatest adsorption capacity was completed during the first 0.5 h for IHISq.

In view of the presented data and analysis was considered in this studies, it was concluded that IHISq would be well fitted for biosorption of reactive-azo dye-bearing textile industry wastewater.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. S. Akhtar, A. Khan and Q. Husain, *Chemosphere*, **60**, 291 (2005).
2. Z. Aksu and S. Tezer, *Process Biochem.*, **40**, 997 (2005).
3. H. Zollinger, Colour Chemistry-Synthesis, Properties of Organic Dyes and Pigments, VHC Publishers, New York, pp. 92-100 (1987).
4. T. Robenson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, **77**, 247 (2001).
5. S.V. Mohan, N.C. Rao, K.K. Prasad and J. Karthikeyan, *Waste Manag.*, **22**, 575 (2002).
6. S. Sumathi and B.S. Manju, *Enzyme Microb. Technol.*, **27**, 347 (2000).
7. R. Patel and S. Suresh, *Bioresour. Technol.*, **99**, 51 (2008).
8. Z. Aksu and S. Tezer, *Process Biochem.*, **36**, 431 (2000).
9. T. O'Mahony, E. Guibal and S.M. Tobin, *Enzyme Microbial. Technol.*, **31**, 456 (2002).
10. Y. Al-Degs, M.A. Khraisheh, S.J. Allen and M.N. Ahmad, *Water Res.*, **34**, 927 (2000).
11. Y. Fu and T. Viraraghavan, *Bioresour. Technol.*, **79**, 251 (2001).
12. T.A. Davis, B. Volasky and A.A. Mucci, *Water Res.*, **37**, 4311 (2003).
13. S. Sadettin and G. Dönmez, *Process Biochem.*, **41**, 836 (2006).
14. A. Ergene, S. Tan, H. Katircioglu and Z. Oktem, *Fresenius Environ. Bull.*, **15**, 283 (2006).
15. J.A. Ramsay, W.H.W. Mok, Y.S. Luu and M. Savage, *Chemosphere*, **61**, 956 (2005).
16. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
17. Z. Aksu, I.A. Iisiloglu, *Chem. Eng. J.*, **127**, 177 (2007).
18. K. Vijayaraghavan and Y.S. Yun, *Dyes Pigm*., **76**, 726 (2008).
19. H. Freundlich, *J. Phys. Chem.*, **57**, 385 (1907).
20. M.J. Horsfall and A.I. Spiff, *Acta Chem. Slov.*, **52**, 174 (2005).
21. J.Y. Farah, N. Sh El-Gendy and L.A. Farahat, *J. Hazard. Mater.*, **148**, 402 (2007).
22. V.S. Mane, I.D. Mall and V.C. Srivastava, *J. Environ. Manag.*, **84**, 390 (2007).
23. Z. Al-Qodah, W.K. Lafi, Z. Al-Anber, M. Al-Shannag and A. Harahsheh, *Desalination*, **217**, 212 (2007).
24. Z. Aksu and S.S. Cagatay, *Sep. Purif. Technol.*, **48**, 24 (2006).
25. C.W. Cheung, J.F. Porter and G. McKay, *J. Chem. Technol. Biotechnol.*, **75**, 963 (2000).
26. Z. Aksu, *Process Biochem.*, **38**, 89 (2002).
27. Z. Aksu and G. Dönmez, *Chemosphere*, **50**, 1075 (2003).

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