Removal of Dye (Blue 56) From Aqueous Solution via Adsorption onto Pistachio Shell: kinetic and isotherm study of removal process

*A. Ravanpaykar[*1], A. Asfaram[2], M. R. Fathi emadabadi[2]*

[1]Department of Chemistry, Gachsaran Branch, Islamic Azad University, P.O. 75818-63875 Gachsaran, Iran.
[2]Department of Chemistry, Gachsaran Branch, Islamic Azad University, P.O. 75818-63875 Gachsaran, Iran.

Abstract: In the present investigation, shells of pistachio are used as adsorbents and they have been successfully used for the removal of Blue 56, from water samples. The effect of various parameters such as: pH, amounts of adsorbents, size of adsorbent particles and contact time on removal processing were investigated. In this study Freundlich absorption isotherms and Langmuir were investigated. The experimental data were correlated reasonably well by the Freundlich adsorption isotherm and isotherm parameters were calculated. In order to investigate the efficiency of Blue 56 adsorption on the pistachio shell, pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were studied. The model that had good correlation to attract Freundlich was chosen as the model. Its kinetics follows the pseudo second order reaction.

Keywords: Blue 56; Adsorption; Isotherm; Pistachio shell; Kinetics

INTRODUCTION

Approximately 700,000 tones and 10,000 different types of dyes and pigments are produced annually across the world and are extensively used in many industries including textile, leather, pulp, paper, food and plastics (Sadettin and Dönmez, 2006; Kiran *et al*, 2009; Aksakal and Ucun, 2010). Among all the chemical available dye classes, direct azo dyes are water-soluble molecules containing one or more ionic groups (most often sulfonic acid and/or amino groups) and are considered to be recalcitrant, non-biodegradable and persistent (Mohan *et al*, 2008; Akar *et al*, 2009). A significant proportion of these dyes is lost in manufacturing and processing units and entering the environment in wastewater. The colour dye effluents are considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium through reducing photosynthetic activity and primary production due to the coloration of the water in streams (Aksu and Tezer, 2005).

Physico-chemical processes such as electro-coagulation, ozonation, photocatalysis, membrane filtration and adsorption have been employed for the treatment of dye containing wastewater (Patel and Suresh, 2008). Among these technologies the adsorption method is widely used in the removal of synthetic dyes from the industrial effluent (Calvete *et al,* 2009; Liang *et al,* 2010). Through great variety of adsorbents, activated carbon and ion exchange resins have been investigated for removing the dye from wastewater.

Although they have a good adsorption capacity, their high costs limit the commercial application (unit cost of virgin material is about 1 US dollar/kg) as well as activated carbon can not be regenerated easily (thermal regeneration costs are about 1-2 US dollar/kg) (Russo *et al,* 2010).

*Correspoding Author: A. Ravanpaykar, Department of Chemistry, Gachsaran Branch, Islamic Azad University, P.O. Box . 75818-63875. Gachsaran, Iran. Email: rtaleb63@yahoo.com

Therefore, new, low-cost and highly effective sorbents need to be investigated.

Biosorption process employing biopolymers (such as sawdust, wood chips, chitin/chitosan, starch, cyclodextrin and cross linked chitosan/cyclodextrin) and non-viable microbial (fungi, algae and bacteria) biomass has emerged as one of the powerful and attractive options since it is inexpensive.

The adsorption mechanism and the activation parameters were investigated for the adsorption of some dyes such as blue 56 on pistachio shell. The present work aimed to study a convenient and economic method for blue 56 removal from water by adsorption on a low cost and an abundantly available adsorbent, to gain an understanding of the adsorption kinetics, to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption and to calculate the activation energy of system. The effects of initial blue 56 concentrations, solution pH, amount of adsorbent, particle size and temperature on blue 56 adsorption rate have been evaluated.
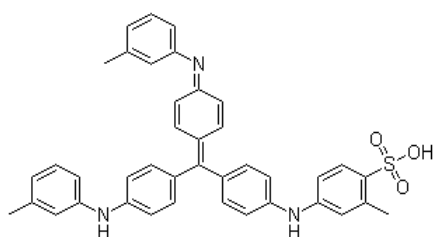

Fig. 1. Structure of Blue 56 (Molecular formula: $C_{40}H_{35}N_3O_3S$ Molecular Weight: 79/637)

MATERIAL AND METHODS

Materials

Absorbent shell pistachio nuts were produced from the waste. Sorbent was prepared with distilled water and washed several times, absorbent was dried for 48 hours in the sun and crushed in a ball mill and sieving samples were manually shaked with stainless steel mesh screens of standard (international ASTM with meshes 40, 60 and 100).

to obtain a particle size between mesh size 0- 177, 210- 297 and 345-500 μm.

Procedure

An aliquot of the blue 56 solution, at pH=3.5 and 15±1°C was passed through a mini containing 0.3 gr powder pistachio shells (100 mesh). The absorbance of blue 56 was measured spectrophotometrically at λmax = 603 nm before and after passing of blue 56 through the column. Finally, the percent of removal of blue 56 was calculated by using a calibration curve of blue 56. The concentration of dye in aqueous solution before and after was determined spectrophotometrically. Extraction efficiency of dye is calculated as follows:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where C_o and C_t are the initial concentration and dilute phase concentration of the dye, respectively.

RESULTS AND DISCUSSION

The effect of pH

Textile dyes are complex organic compounds having different aromatic rings and functional groups; the latter have different ionization potentials at different pH and therefore their interaction with microbial biomass depends on the chemistry of a particular dye and the specific chemistry of the bio sorbents. The ionic forms of the dye in solution and the surface electrical charge of the biomass depend on the solution pH. Therefore, pH significantly influences the dye biosorption. The effect of the pH on dye biosorption is presented in Fig. 2.

As seen from the figure, the maximum dye biosorption was observed at pH 2-4 and as the pH increased, the biosorption decreased. Since its chemical structure is hidden, the pKa values of the functional groups of dye molecule cannot be

known. Therefore, it's estimated that at lower pH values there may be an electrostatic attractions between charged dye molecules and charged cell surface. The optimum pH was used to remove the blue color of 56 (3.5).
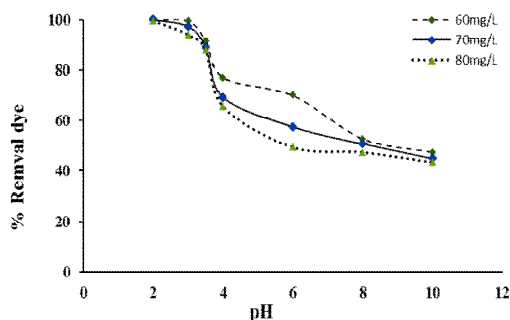

Fig. 2. Effect of pH on adsorption of blue 56 (60, 70 and 80 mg/L) onto PS (0.3 g/25 mL)

The effect of adsorbent amount

The amount of adsorbent, the effect of adsorbent dosage on the adsorption efficiency. Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. the adsorption of blue 56 onto pistachio shells was measured at three concentration dye (60,70, 80) mg/l for different adsorbent dosage(0.1-0.4) gr. effect amount of adsorbent on the removal of the blue color of 56 is shown in Figure (3).
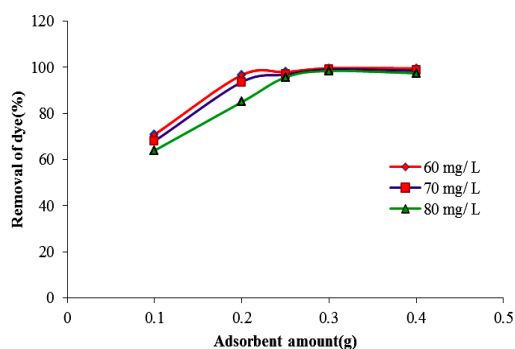

Fig. 3. Effect of amount of Adsorbent on adsorption of blue 56 (60, 70 and 80 mg/L) onto PS

When the adsorbent dose was increased from 0.1to 0.4gr. it can be seen that increase the absorption increases and then remains constant, it was a possible reason for that is the increasing amount of adsorbent concentration to the optimum color for empty and unoccupied absorption sites are more accessible. And the rate of adsorption to remove color and high color, and then remains constant. However, a further increase in the adsorbent mass from 3.0 to 4.0 g, did not yield a significant difference in the efficiency. The optimal value is 0.3 gr.

The effect of particle size

Removal is directly related with surface area of adsorbent; therefore, the effect of particle size (figure 4) was studied. It was found that percent removal of reactive dye was decreased with increasing particle size of adsorbent. The size of the adsorbent has a greater influence on the rate of adsorption. The influence of particle size (mesh size) was studied with 40, 60 and 100 mesh sizes in three concentration (60, 70, 80) mg/l. it is observed that the reduction in size results in increased efficiency of adsorption with maximum reduction of 99.5% in mesh (100).

The effect of concentration of dyes

The effect of dye concentration on its adsorption was studied by pistachio shells. The concentration ranges of dyes were 50 mg/L to 100 mg/L. The concentrations at which Blue 56 and fast Blue dyes show maximum adsorption were 50 mg/L and 70 mg/L, respectively. (Fig. 5)
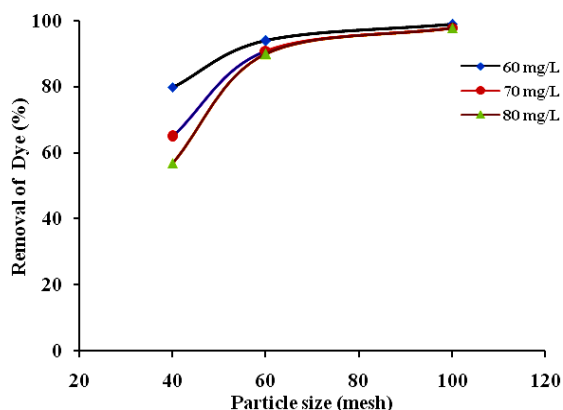
Fig. 4. Effect of particle size on adsorption of blue 56 (60, 70 and 80 0.3 gr/25 ml) onto PS
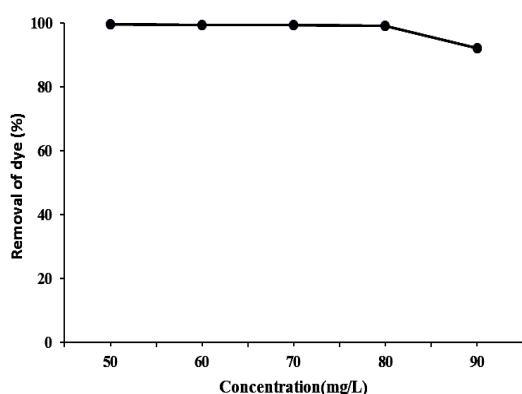

Fig. 5. Effect of concentration on adsorption of blue 56 (50, 60, 70, 80 and 90 mg/L 0.3 gr/25 ml) onto PS

The effect of contact time on the adsorption efficiency

The batch experimental data obtained from the adsorption of blue 56 in pH=3.5 onto the pistachio shells showed that a contact time of 11 min was generally sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. (Fig.6)
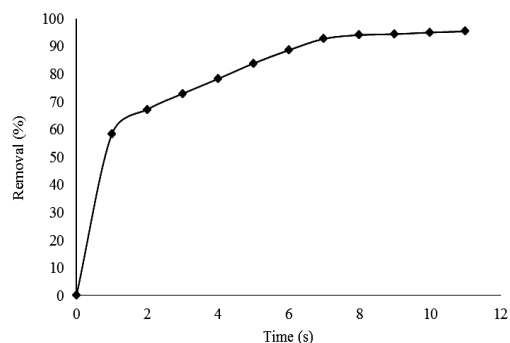

Fig. 6. Effect of contact time on adsorption of blue 56 (80 mg/L .0.3 gr 25 ml) onto PS

In some cases, equilibrium was almost attained in 5 or 8 min, depending on the values of operating variables. These results indicate that the adsorption process can be considered very fast. To summarize, take into account the cost of energy consumed in agitation, longer contact times (>12 min) unnecessarily prolonged the process to obtain similar result.

KINETIC EXPERIMENTS

Kinetic experiments were performed using flasks containing 25 mL of Blue 56 solutions at concentrations of 80 mg/L. The procedure used in kinetic tests was similar to those conducted in the first part of the study. In each test, 25 mL of Blue 56 solution with the desired concentration was added to each flask and the pH was adjusted to 3.5. After the adjustments, 0.3 g of PHP was added and the resultant suspension was stirred at 2000 rpm for 1–11 min at 25 ∘C. The results were analyzed for fitness with pseudo-first and -second order models.

Pseudo-first-order model

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows (Lagergren, 1898)**:**

$$\frac{dq}{dt} = k_{1,ad}(q_e - q) \qquad (2)$$

Where, qe is the amount of dye blue 56 adsorbed at equilibrium (mg/g), q is the amount adsorbed at time t (mg/g), $k1, ad$ is the rate constant of first order adsorption (L/min). After integration and applying boundary conditions, $t = 0$ to t and $q = 0$ to qe; the integrated form of equation (2) becomes:

$$\log(q_e - q) = \log(q_e) - \frac{k_{1,ad}}{2.303} t \qquad (3)$$

Values of adsorption rate constant ($k1, ad$) for the dye blue56 adsorption onto pistachio shells were determined from the straight line plot of $\log(qe - q)$ against t. The data were fitted with a poor correlation coefficient (Table 1), indicating that the rate of removal of dye blue 56 onto pistachio shell does not follow the pseudo-first-order equation.

Table 1. Adsorption kinetic parameters for the adsorption of Blue 56 at temperature 25 ± 0.5 ^{o}C on condition optimum: PS amount 0.3 g/25 mL, contact time 11 min and pH=3.5.

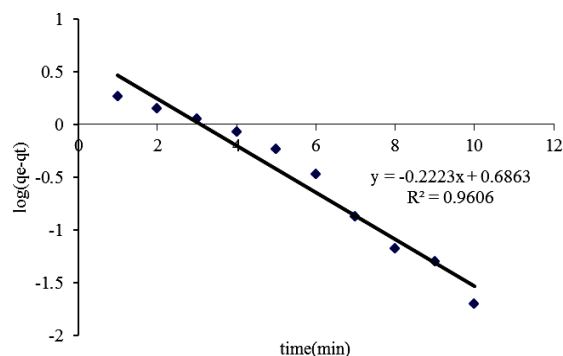| Model		Concentration (60 mg/L)
	q_e(calc) (mg/g)	4.85
Pseudo first-order kinetic model	K_1(min^{-1})	0.511
	R^2	0.960
	q_e(calc) (mg/g)	5.291
Pseudo second-order kinetic model	K_2(g mg^{-1} min^{-1})	0.1641
	R^2	0.997
	h	4.593
	K_{dif} (mg g^{-1} min^{-1})	0.844
Intraparticle diffusion model	C (mg g^{-1})	2.203
	R^2	0.957
q_e(exp) (mg/g)		4.77

Fig. 7. Pseudo-first-order kinetic model plot for the adsorption of DR12B with concentrations 80 mg/L, at temperature 25 ± 0.5 °C on optimum condition: PS amount 0.3 g/25 mL, contact time 11 min and pH=3.5.

Pseudo-second-order model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. Furthermore, it is in agreement with chemisorption being the rate controlling step and is expressed as (Ho *et al*, 2000):

$$\frac{dq}{dt} = k_{2,ad} (q_e - q)^2 \qquad (4)$$

Where $K_{2,ad}$ is the rate constant of second order-adsorption (g/mg. min). For the same boundary conditions the integrated form of equation (4) becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

The initial sorption rate, h (mg/ g. min), at $t = 0$ is defined as:

$$h = k_{2,ad} q_e^2 \qquad (6)$$

Where k_2, ad and h values were determined from the slope and intercept of the plots of t/q against t (Fig. 8).
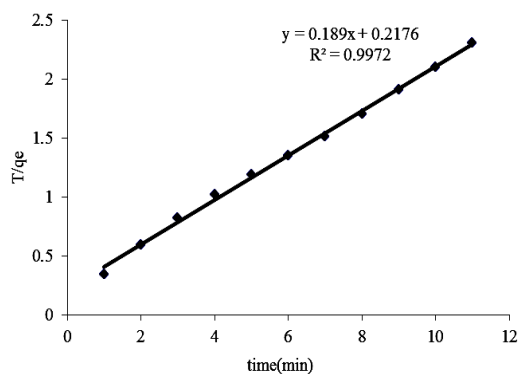
Fig. 8. Pseudo-Second-order kinetic model plot for the adsorption of DR12B with concentrations 80 mg/L, at temperature 25 ± 0.5 °C on optimum condition: PS amount 0.3 g/25 mL, contact time 11 min and pH=3.5.

The values of the parameters and correlation coefficients are also presented in Table 1. The correlation coefficients of all examined data were found very high ($R^2 > 0.99$). This shows that the model can be applied for the entire adsorption process and confirmed that the sorption of blue 56 onto PHP follows the pseudo-second-order kinetic model.

ISOTHERM DATA ANALYSIS

The parameters obtained from the different models provide important information on the adsorption mechanisms, the surface properties, and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir and Freundlich, isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir isotherm

The Langmuir adsorption isotherm is based on the assumption that all sites possess equal affinity for the adsorbate. It may be represented in the linear form as follows (Langmuir, 1916):

$$\frac{c_e}{q_e} = \frac{1}{K_l Q_m} + \frac{C_e}{Q_m} \qquad (7)$$

Where Q_m is the maximum dye blue 56 uptake, mg/g, K_L the Langmuir adsorption constant, L/mg. The model provides the maximum values where they could not be reached in the experiments. The values of K_L were increased with increasing the dose of adsorbent for PHP, respectively. High K_L values indicate high adsorption affinity. The monolayer saturation capacity, Q_m, were 19.46 mg/L for PHP, respectively.

Freundlich isotherm

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of Freundlich isotherm may be represented as follows (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \qquad (8)$$

Where K_F (L/g) and $1/n_F$ are the Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. The magnitude of K_F shows a high dye blue 56 adsorptive capacity of PHP from studied aqueous solution. Table 3 also indicates that $0 < 1/n_F < 1$, which indicating that the dye blue 56 is favorably adsorbed by PHP at all studied parameters.
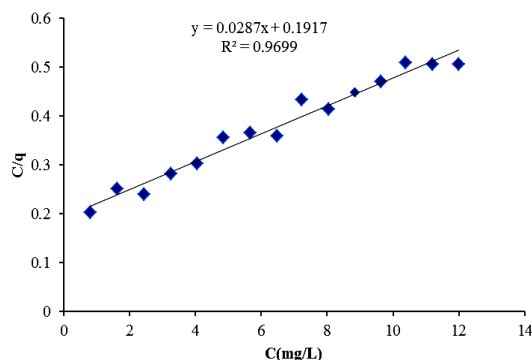
y = 0.0287x + 0.1917
R² = 0.9699

Fig. 9. Langmuier isotherm models plot for the adsorption of BLUE 56 with concentrations 10-130 mg/L, at temperature 25 ± 0.5 °C on optimum condition: PHP amount 0.3 g/25 mL, contact time 11 min and pH=3.5

Table 2: Comparison of the coefficients isotherm parameters for BLUE 56 adsorption onto PHP.

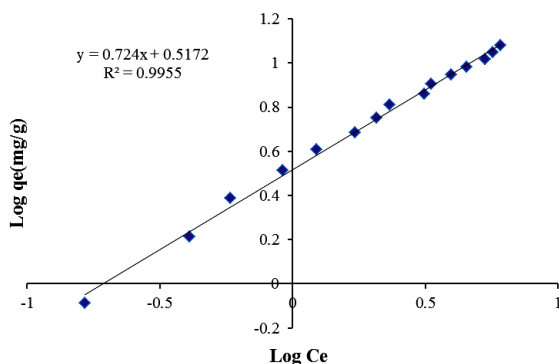| Isotherm Models	Parameters	
	Qe (mg g^{-1})	35.9
Langmuir	K(L mg^{-1})	0.146
	R^2	0.969
	$1/n$	0.724
Freundlich	K_f (L mg^{-1})	1.68
	R^2	0.995

y = 0.724x + 0.5172
R² = 0.9955

Fig. 10. Freundlich isotherm models plot for the adsorption of BLUE 56 with concentrations 10-130 mg/L, at temperature 25 ± 0.5 °C on optimum condition: PHP amount 0.3 g/25 mL, contact time 11 min and pH=3.5

CONCLUSIONS

The results of present investigation show that PHP has considerable potential for the removal of BLUE 56 from aqueous solution over a wide range of concentration. Equilibrium and kinetic studies were conducted for the adsorption of blue 56 from

aqueous solutions onto PHP in the concentration range 10–130 mg/L at pH 3.5 and 298 K. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters have been determined for each isotherm and related correlation coefficients. The Freundlich isotherm was demonstrated to provide the best correlation for the adsorption of blue 56 onto PHP. The adsorbed amounts of blue 56 increased with increase in contact time and reached the equilibrium after 11 min. The equilibrium time is independent of initial blue 56 concentrations. The kinetics of adsorption of blue 56 onto PHP was studied by using pseudo first- and second-order equations. All findings presented in this study suggest that blue 56 /PHP system cannot be described by a first-order reaction model. For the examined system, the pseudo second-order kinetic model provided the best correlation of the experimental data.

REFERENCES

Akar, S.T., A. Gorgulu, Z. Kaynak, B. Anilan and T. Akar, 2009. biosorption of reactive blue 49 dye under batch and continuous mode using a mixed biosorbent of macro-fungus agaricus bisporus and thuja orientalis cones. chemical engineering journal, vol. 148, No. 1, P. 26-34.

Aksakal, O. and H. Ucun, 2010. equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (reactive red 195) onto pinus sylvestris l. Journal of hazardous materials, vol. 181, No. 1-3, P. 666-672.

Aksu, Z. and S. Tezer, 2005. biosorption of reactive dyes on the green alga chlorella vulgaris. process biochemistry, vol. 40, No. 3-4, P. 1347-1361.

Calvete, T., E.C. Lima, N.F. Cardoso, S.L.P. Dias and F.A. Pavan, 2009. application of carbon

adsorbents prepared from the brazilian pine-fruit-shell for the removal of procion red mx 3b from aqueous solution-kinetic, equilibrium, and thermodynamic studies. Chemical engineering Journal, Vol. 155, No. 3, 2009, P. 627-636.

Freundlich, H.M.F. Uˉber die adsorption in loˉsungen", zeitschrift fuˉr physikalische chemie (1906) **57**: 385–470.

Ho, Y.S., W.T. Chiu and C.C. Wang, "regression analysis for the sorption isotherms of basic dyes on sugarcane dust", bioresource technology. 2005. **96**: 1285– 1291.

Kalavathy, M.H., T. Karthikeyan, S. Rajgopal, L.R. Miranda, 2005. "kinetics and isotherm studies of cu(ii) adsorption onto h3po4- activated rubber wood sawdust", journal of colloid and interface science. **292**: 354-362.

Kiran, I., S. Ilhan, N. Caner, C.F. Iscen and Z. Yildiz, 2009. biosorption properties of dried neurospora crassa for the removal of burazol blue ed dye. desalination, vol. 249, No. 1, P. 273-278.

Lagergren, S., 1898. "zur theorie der sogenannten adsorption geloster stoffe kungliga svenska vetenskapsakademiens", handlingar. **24**, 1–39.

Langmuir, I., 1916. "The constitution and fundamental properties of solids and liquids", J. Am. Chem. Soc. **38**: 2221– 2295.

Liang, S., X. Guo, N. Feng and Q. Tian, 2010. isotherms, kinetics and thermodynamic studies of adsorption of cu^{2+} from aqueous solutions

by mg^{2+}/k^+ type orange peel adsorbents. journal of hazardous materials, Vol. 174, No. 1-3, P. 756-762.

Mohan, S.V., S.V. Ramanaiah and P.N. Sarma, 2008. biosorption of direct azo dye from aqueous phase onto spirogyra sp. i02: evaluation of kinetics and mechanistic aspects. Biochemical Engineering Journal, Vol. 38, No. 1, P. 61-69.

Patel, R. and S. Suresh, 2008. kinetic and equilibrium studies on the biosorption of reactive black 5 dye by aspergillus foetidus. Bioresource Technology, Vol. 99, No. 1, P. 51-58.

Russo, M.E., F. Di Natale, V. Prigione, V. Tigini, A. Marzocchella and G.C. Varese, 2010. adsorption of acid dyes on fungal biomass: equilibrium and kinetics characterization. Chemical Engineering Journal, Vol. 162, No. 2, P. 537-545.

Sadettin, S. and G. Dönmez, 2006. bioaccumulation of reactive dyes by thermophilic cyanobacteria. Process Biochemistry, Vol. 41, No. 4, P. 836-841.

Vijayaraghavan, K., T.V.N. Padmesh, K. Palanivelu and M. Velan, 2006. "biosorption of nickel(ii) ions onto sargassum wightii: application of twoparameter and three-parameter isotherm models", J. of Hazardous Materials; (**B133**): 304- 308.