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Adsorption of Direct Yellow 9 and Acid Orange 7 from Aqueous Solutions by Modified Pumice

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Adsorption is widely used for removal of different pollutants from wastewater. In this study, modification of pumice adsorbent by detergents and use of modified pumice for eliminating the direct yellow 9 and acid orange 7, from aqueous solutions was investigated. In this study, cetrimide-C, sodium dodecyl sulfate, cetylpyridinium chloride and hexadecyl trimethyl ammonium bromide detergents were used for modification of pumice. All experiments were performed at batch system. The effect of important parameters on adsorption including adsorbent dosage, dye initial concentration, pH solution and contact time were investigated. The experimental data were compared with the Freundlich, Temkin and Langmuir isotherm models and pseudo first order, pseudo second order and Elovich kinetic models. The results showed that with increasing contact time and adsorbent dosage and decreasing dye initial concentration, dye removal efficiency increased. Also by increasing pH from 1 to 7, dye removal efficiency increased. The maximum direct yellow 9 and acid orange 7 adsorption was obtained at pH 6 and 7, respectively. The maximum adsorption capacity of direct yellow 9 and acid orange 7 was 1.22 and 1.08 mg/g, respectively. The rate constant of direct yellow 9 and acid orange 7 adsorption by modified pumice was 0.014 and 0.007 mg/g min, respectively. The results of this study revealed that modified pumice adsorbent can be used as a suitable and effective adsorbent for removal of some dyes from coloured wastewater.

Key Words: Mineral adsorbent, Adsorption isotherm, Detergent activation, Decolourization.

INTRODUCTION

In recent years, the use of dyes in industry and its disposal to environment have been created many concerns[1]. Dyed wastewater from the textile industry is one of the important sources of water pollution. Discharging of these wastewaters to water reservoirs can be led to increasing the organic load which is biologically non-degradable[2]. The aesthetics effects and decreasing of light transmission and photosynthesis are other adverse effects of discharge of dye wastewater to water body. Nowadays, more than 10,000 types are commercially available which most of them are synthetic and have an aromatic structure and are classified into toxic and carcinogenic pollutants group[3]. The various technologies have been applied for dye removal such as using chemical precipitation, chemical oxidation, photochemical destruction, membrane processes and aerobic and anaerobic biological degradation[4-7]. None of these methods cannot be successfully removed all dyes from wastewater[7]. Some of these methods have been used by industries for dye removal. Among these methods, the adsorption has been recognized as an appropriate method for dye removal. In the adsorption process, the coloured soluble compounds attached to the adsorbent surface and separated from the aqueous phase[7,8]. The adsorption process can be concurrently used for the removal of several dyes and it can also be used as the selected method for reuse of treated water. The adsorption process has advantages such as simple design, low cost, simple operation and no sensitivity to toxic chemicals[8]. Activated carbon is most conventional adsorbent for dye removal from wastewater which is an expensive adsorbent. Recently, the tendency to using cheap adsorbents increased[9-12]. Pumice has been widely used in many studies for pollutants removal from wastewater. Pumice is a volcanic lava rock that is light and porous with extensive adsorption surface[13,14]. The aim of this study was modification of pumice adsorbent by detergents and use of modified pumice for eliminating the dyes, direct yellow 9 (DY9) and acid orange 7 (AO7) from aqueous solutions.

EXPERIMENTAL

Preparation of adsorbent: In this study, pumice adsorbent was obtained from Anar mines (210 Km from Kerman, Iran). The chemical composition of pumice was determined by XRF, which are listed in Table-1.

TABLE-1
CHEMICAL PROPERTIES OF PUMICE ADSORBENT

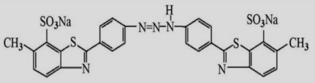
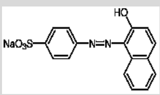
Chemical compound	Per cent (%)
SiO_2	61.53
Al_2O_3	15.49
CaO	5.86
Na_2O	3.60
K_2O	2.75
Fe_2O_3	1.55
MgO	1.21
Loss of ignition	8.01

Pumice was prepared by grinding it in a laboratory type ball-mill prior to use. Then it was sieved through a 40 mesh using ASTM standard sieves. Eventually in order to dust removal, the pumice adsorbent was extensively rinsed with distilled water and was placed in an oven (105 ± 0.5 ºC) for 24 h to remove the water from the pore structure.

In order to modification of the pumice adsorbent, cetrimide-C (CC), sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC) and hexadecyl trimethyl ammonium bromide (HDTM-Br) detergents were used. The detergent activation of pumice was performed in glass reactor. The samples were loaded into the glass reactor and the ratio of liquid to solid was 15 mL/g. The effect of detergent concentration on activation was tested by modified pumice with a specified amount of known concentration (0.1, 0.2, 0.3 mmol/L of each of above detergents) at constant temperature and 24 h contact time. Finally in order to eliminate the extra detergent from the surface of the adsorbent, pumice was washed with distilled water and was dried for 24 h in the oven.

Apparatus and chemicals: Stock solutions of acid orange 7 and direct yellow 9 dyes with the concentration of 1000 mg/L and other necessary concentrations were prepared by dissolving an accurate quantity of them in deionized water. Other concentrations prepared from stock solution. All the chemicals used were in the analytical grade. Acid orange 7 and direct yellow 9 dyes concentrations of the solutions were determined by using a spectrophotometer device (Hitachi model 100-40). The adjusted wavelengths to have the highest absorption were 400 and 485 nm. The instrument response was periodically checked by using standard solutions. The characteristics and chemical structure of the dyes used are shown in Table-2.

TABLE-2
CHARACTERISTICS AND CHEMICAL STRUCTURE OF THE DYES USED

Parameter	Direct yellow 9 (DY9)	Acid orange 7 (AO7)
m.w.	695 g/mol	350.32 g/mol
λ_{max}	400 nm	458 nm
Molecular structure		

Batch adsorption experiments: All adsorption experiments were conducted with 200 mL flasks containing 100 mL of the sample at 20 ± 0.5 ºC and by Jar apparatus. The mixing was done at 150 rpm to ensure approximate equilibrium. The removal efficiency and adsorption capacity were calculated by the following equations 1 and 2:

$$R = [(C_0 - C_e)/C_0] \times 100 \quad (1)$$

$$q_e m = (C_0 - C_e)V \quad (2)$$

Effect of contact time on the adsorption: In order to study the effect of contact time on dye removal efficiency by modified pumice, dye solutions with the initial concentration of 50 mg/L were prepared and the pH of these solutions were maintained at a definite value (7 ± 0.2) by manually adding 0.1 N of HCl or NaOH. Then 40 g/L of modified pumice was added to each flask. The solutions were stirred from 10 to 400 min and at intervals of every 10 min were sampled. In order to prevention of unbalancing adsorbent to solution ratio, each contact time was studied in a separate flask. Finally, the suspension was filtered through a 0.45 μm paper filter and then analyzed for dyes.

Effect of pH solution on adsorption: In order to evaluate the effect of solution pH on adsorption, solutions with the dye initial concentration of 50 mg/L were prepared and the pH of these solutions were adjusted between 1 to 10 by using HCl and NaOH (0.1 N). To each of these solutions the amount of 70 g/L modified pumice was added and it was stirred for 240 minutes. Eventually, the suspension was filtered through a 0.45 μm paper filter and the amount of residual dye was determined by spectrophotometers.

Effect of dye initial concentration and adsorbent dosage: In order to evaluating the adsorption process in different dye initial concentrations and adsorbent dosages, different dye initial concentrations of adsorbate in the range of 10 to 100 mg/L (*i.e.,* 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/L) and different adsorbent dosages in the range of 10 to 100 g/L were studied. The pH of solutions was maintained at 7 by using NaOH and HCl (0.1 N) and they were stirred for 240 min.

RESULTS AND DISCUSSION

Modification of pumice by detergent: The results of different stages of pumice activation by using detergents are shown in Fig. 1. According to the results, modification of pumice by the cationic detergent HDTM-Br has the maximum effect (q_e = 1.4 mg/g) and as the detergent concentration in the solution increases, the activation rate increases, too. The detergent HDTM-Br is stable in different pH and high or low ions concentrations. Thus, pumice destruction or desorption of detergent from pumice surface is very low[15,16].

Effect of contact time on dye adsorption: According to Fig. 2, with increasing the contact time in the adsorption process, efficiency of dye removal increased. So that by increase in contact time from 10 to 400 min, the removal efficiency for direct yellow 9 increased from 22.22 % to 79.54 % and for acid orange 7 increased from 23.46 % to 74.96 %.

Effect of solution pH on dye adsorption: The pH is clearly an important parameter that controlled the adsorption process. The adsorption of dye chemical agents on the adsorbent surface, initially is effected by the surface electricity of the adsorbent, which is effected by the solution pH[6]. The experimental results of this stage are shown in Fig. 3. The results showed that with increasing the solution pH from the acidic range to the neutral range, the dye removal efficiency for direct yellow 9 increased from 86.96 to 97.98 % and for acid orange 7 increased from 85.96 to 95.94 %. As the solution pH increased to more than 7 (alkaline range), the dye removal efficiency decreased. The appropriate pH for direct yellow 9 and acid orange 7 removal by using modified pumice was 7 and 6, respectively. The pH of coloured solutions has an important role in the adsorption process and especially on the adsorption capacity. This is likely attributed to the fact that pH causes the electric charge on the adsorbent surface, the ionization rate of substances in the solution and also the disintegration of the chemical agents at the adsorbing sites on the adsorbent surface. The lower adsorption of dye at lower pH values resulted from interference of the H^+ ions for adsorbed on the adsorption sites and in higher pH resulted from an increased electrostatic repulsion between the more negatively charged adsorbate and negatively charged surface sites.

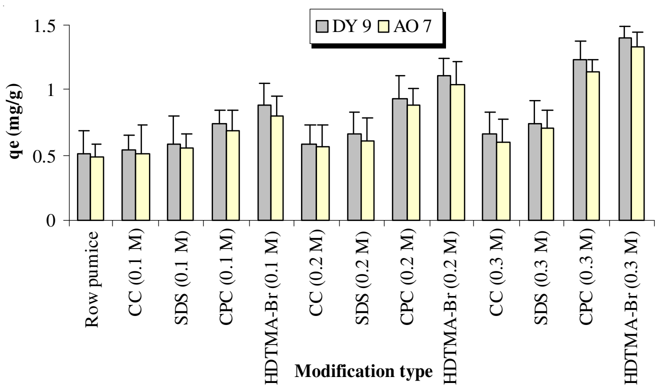


Fig. 1. Effect of activation different methods on pumice (dye initial concentration: 100 mg/L, adsorbent dosage: 50 g/L, pH: 7 and contact time: 180 min)

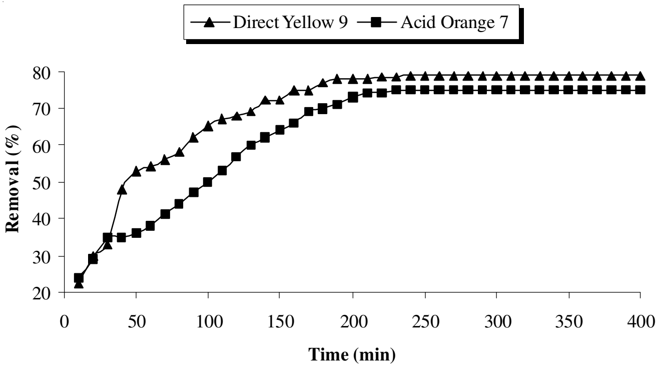


Fig. 2. Effect of contact time on adsorption efficiency (dye initial concentration: 50 mg/L, adsorbent dosage: 40 g/L, pH: 7)

Effect of adsorbent dosage on dye adsorption: The adsorbent dose is one of the important parameter due to its role in determining the absorbent capacity for adsorbing on its surface[17]. Fig. 4 shows the results of studying the dosage of modified pumice on dye removal. The results showed that with increasing the dosage of the adsorbent, dye removal efficiency increased, but the adsorption capacity (q_e) decreased. By increasing the adsorbent dosage from 10 to 100 g/L, the efficiency of direct yellow 9 removal increased from 39.78 to 97.88 % and for acid orange 7 dye increased from 41.79 to 94.76 %. Also with increasing the dosage of adsorbent, q_e for the direct yellow 9 dye decreased from 1.99 to 0.49 mg/g and for the acid orange 7 dye decreased from 2.09 to 0.47 mg/g. By increasing the amount of the adsorbent used, the removal rate increased, which is due to increased in the number of adsorption sites available to a specific amount of dye. Increased in the amount of adsorbent is attributed to a probable increased in interaction between the adsorbed particles, decrease in its surface and increased in the thickness of the penetration route and eventually decrease in adsorption density[18].

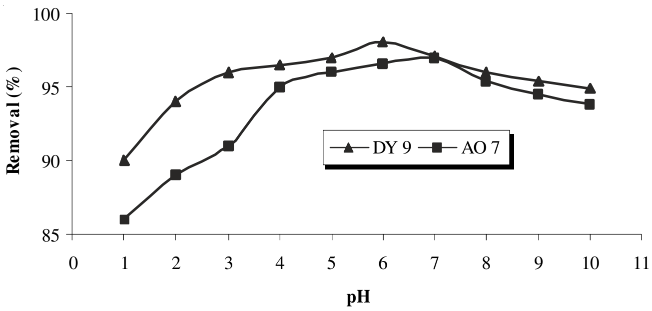


Fig. 3. Effect of initial pH on adsorption efficiency (dye initial concentration: 50 mg/L, adsorbent dosage: 70 g/L and contact time: 240 min)

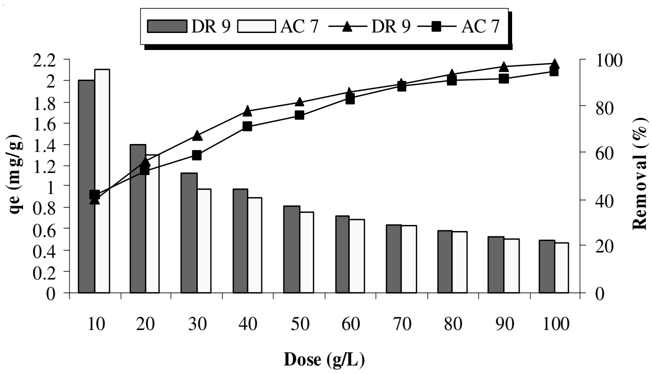


Fig. 4. Effect of the adsorbent dosage on adsorption efficiency (dye initial concentration: 50 mg/L, contact time: 240 min and optimum pH)

Effect of dye initial concentration on dye adsorption: In the batch adsorption process, the dye initial concentration provides an dominant driving force to overcome all mass transfer resistances of the dye between aqueous and solid phase[13]. According to Fig. 5, with increasing the dye initial concentration, the removal efficiency decreases, but the q_e increases. With increased in the dye concentration from 10 to 100 mg/L, the removal efficiency for the direct yellow 9 dye decreased from 99.89 to 78.96 % and for the acid orange 7 dye decreased from 99.85 to 74.87 %. Also by increased in the dye concentration, q_e for direct yellow 9 increased from 0.14 to 1.13 mg/g and for the acid orange 7 dye increased from 0.14 to 1.07 mg/g. Decreasing removal efficiency with increasing dye initial concentration is due to decreased in the available adsorption sites for high concentrations of dye[19-21].

TABLE-3
EQUATIONS, LINEAR FORMS AND THE RESULT FROM THE ISOTHERM CALCULATIONS UNDER STUDY

Isotherm type	Equation	Linear form	Parameter	Direct yellow 9	Acid orange 7
Freundlich [23]	$q_e = K_f C_e^{\frac{1}{n}}$	$q_e = K_f C_e^{\frac{1}{n}}$	N	3.54	3.73
			K_F	0.42	0.37
			R^2	0.94	0.93
Langmuir [24]	$q_e = \frac{Q_m K_L C_e}{1+K_L C_e}$	$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right) C_e$	Q_m	1.22	1.08
			K_L	0.32	0.27
			R^2	0.96	0.97
Temkin [25]	$q_e = \frac{RT}{b_T} Ln(A_T C_e)$	$q_e = B_T \ln A_T + B_T \ln Ce$	A_T	60.95	67.05
			B_T	0.13	0.11
			R^2	0.77	0.76

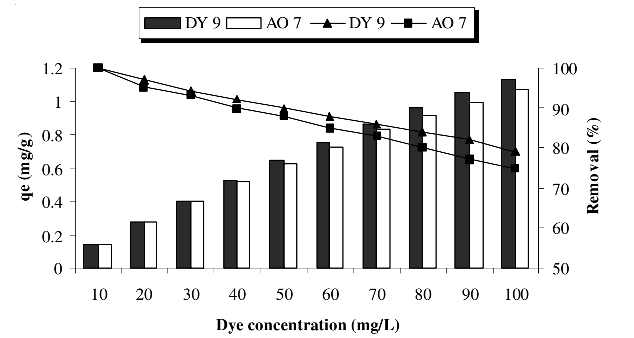


Fig. 5. Effect of initial concentration of dye on adsorption efficiency (adsorbent dose: 70 g/L, contact time: 240 min and optimum pH)

Adsorption isotherm experiments: Analysis of the data obtained from the isotherm is very important to develop an equation which can be applied for proper designing. In addition to, isotherms can be used to describe the interaction between the adsorbent and the adsorbate and also to optimize the amount of adsorbent used[22]. The equations, linear forms and the results from the isotherm calculations are shown in Table-3.

According to Table-3, the adsorption of the direct yellow 9 and acid orange 7 by modified pumice was best fitted to the Langmuir model ($R^2 \geq 0.96$). The amount of Q_m from the Langmuir model shows the necessary amount of adsorbate for producing a monolayer and this amount is higher for direct yellow 9 than acid orange 7 and shows that higher amounts of dye are needed for producing a monolayer. So that, the adsorption capacity for direct yellow 9 is higher than acid orange 7. The amount of "n" in the Freundlich model shows the adsorption intensity and this amount for acid orange 7 is higher than its amount for direct yellow 9 and shows that acid orange 7 is adsorbed by modified pumice more intensively than direct yellow 9. Figs. 6-8 show the dye adsorption isotherm by modified pumice.

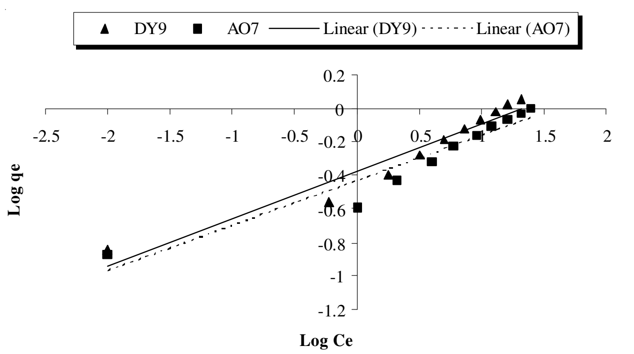


Fig. 6. Plot of Freundlich isotherms acid orange 7 and DY7 adsorption on modified pumice

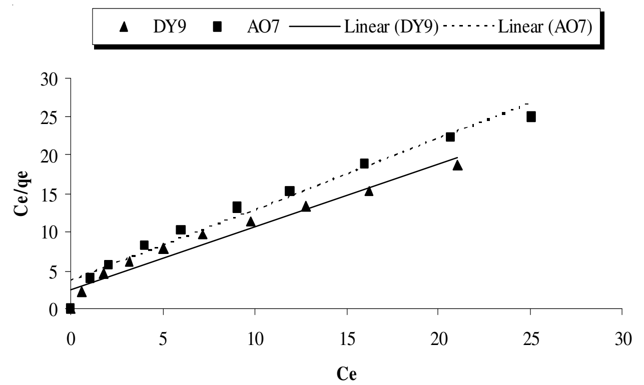


Fig. 7. Plot of Langmuir isotherms acid orange 7 and DY7 adsorption on modified pumice

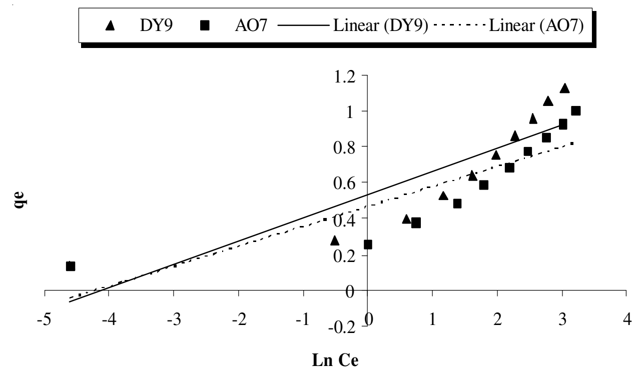


Fig. 8. Plot of Temkin isotherms for acid orange 7 and DY7 adsorption on modified pumice

Adsorption kinetics experiments: The data obtained from kinetics adsorption have been surveyed for understanding the dynamics of adsorption reactions. The kinetics study dye on modified pumice for selecting the optimum operating conditions of the batch processes at full scale is necessary. Thus studying the kinetics of adsorption is beneficial for prediction and interpretation of the adsorption rate that is essential for designing and modeling[16]. Table-4 shows the linear forms and the results obtained of the kinetic calculations of the dye adsorption reaction by modified pumice.

According to Table-4, the pseudo-second order kinetic model is the most appropriate for explaining the results from dye adsorption by modified pumice. The amount of "α" and "k_2" shows the adsorption rate of the adsorbate by the adsorbent materials. The amount of these parameters for direct yellow 9 adsorption by modified pumice is more than acid orange 7 that shows the higher rate of direct yellow 9 adsorption. Figs. 9-11 show the dye adsorption kinetic by modified pumice.

TABLE-4
EQUATIONS AND RESULTS FROM THE KINETICS CALCULATIONS

Kinetic type	Equation	Linear form	Constant	Direct yellow 9	Acid orange 7
First order model [22]	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	k_1	0.021	0.017
			q_e cal	1.61	1.81
			R^2	0.95	0.85
Second order model [26]	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$	k_2	0.014	0.007
			q_e cal	1.58	1.65
			R^2	0.99	0.94
Elovich model [14]	$\frac{dq_t}{dt} = \alpha\exp(-\beta q_t)$	$q_e = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$	α	0.08	0.06
			β	2.97	3.11
			R^2	0.98	0.89

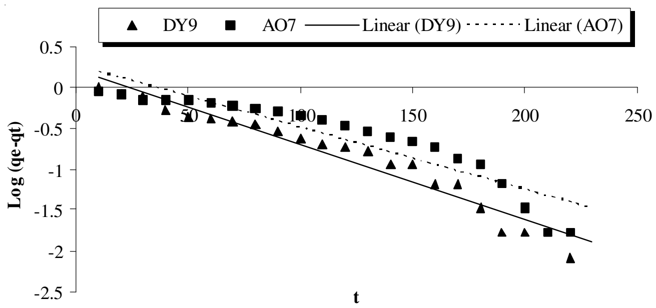


Fig. 9. Pseudo-First order model kinetic for adsorption of dye on modified pumice

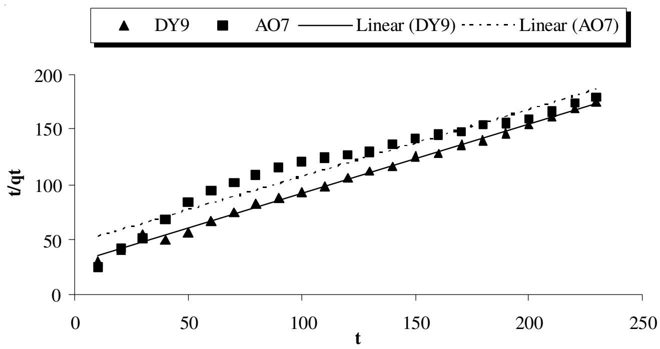


Fig. 10. Pseudo-second order model kinetic for adsorption of dye on modified pumice

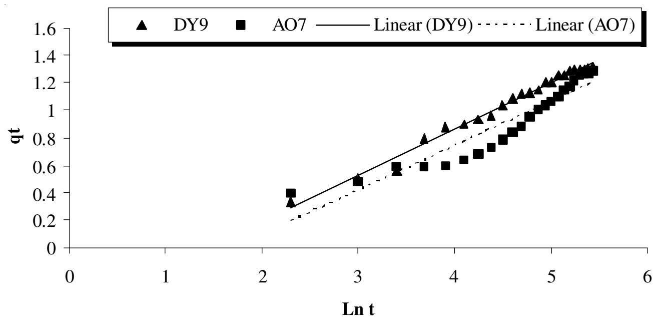


Fig. 11. Elovich model kinetic for adsorption of dye on modified pumice

Conclusion

This study evaluates modification of pumice adsorbent by using cetrimide-C, sodium dodecyl sulfate, cetylpyridinium chloride and hexadecyl trimethyl ammonium bromide detergents and its use for removal of direct yellow 9 and acid orange 7 dyes from aqueous solutions. The study showed that by increasing pH from the acidic range to the neutral range, the removal efficiency increases and on the other hand with increase in the solution pH up to the alkaline range, the removal efficiency decreases. By decreasing the dose of the adsorbent and the dye initial concentration, the removal efficiency decreases and the q_e increases. The isotherms and the kinetics of dye adsorption by modified pumice were also studied. The results showed that the Langmuir and pseudo-second order kinetic model present the adsorption reactions better than the other models.

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