REMOVAL OF CATIONIC AND ANIONIC DYES FROM SINGLE AND BINARY DYE SYSTEMS WITH PERSIAN CHARRED DOLOMITE USING FIRST-ORDER DERIVATIVE SPECTROPHOTOMETER ANALYSIS METHOD

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Abstract - This research was conducted to study the feasibility of removing cationic and anionic dyes from single- and binary-component systems by a local natural adsorbent of Persian dolomite (treated at about 800 °C). In single system, batch experiments were carried out to examine the effect of contact time, initial dye concentration, temperature, stirring speed and adsorbent dose on the adsorption of dyes. Studies showed that cationic dye was not noticeably adsorbed by charred dolomite; however, charred dolomite has the potential to act as an efficient adsorbent for the removal of the reactive dye from groundwater solution with maximum adsorption capacity of 7.3 mg/g. Rate of dye removal was greatly increased with increasing temperature. Thermodynamic studies showed that the adsorption of RR_{195} on charred dolomite is spontaneous and endothermic. First-order derivative spectrophotometer analysis was used as a method for dye analysis in binary dye system. Study on the effect of two components in binary dye mixture on the adsorption capacity of charred dolomite demonstrated that while RR_{195} enhanced the uptake of the cationic dye (synergism), BV_{16} showed nearly non-interaction effect on the anionic dye removal. In both single and binary dye systems, equilibrium and kinetic data showed that the adsorption process satisfactorily fitted to Langmuir equation and pseudo second order kinetics respectively.

Keywords - Dye adsorption, Charred dolomite, Derivative spectrophotometer, binary dye system

I. INTRODUCTION

Dyes are overwhelmingly taken into consideration as grave source of pollution which stems from their complex aromatic structure leading to resistance to water, light, heat and oxidizing agents. According to the prevailing statistical records, azo dyes account for 60-70% of all synthetic dyes with annual worldwide production estimated at 800,000 tons [1]. Both reactive and cationic dyes are toxic and carcinogenic imperil the aquatic systems and human life [2, 3, 4]. In economic and technical sense, conventional treatment methods have some constraints in dye removal render these systems inefficient [3, 5, 6, 7, 8]. Among all physic-chemical methods, adsorption is of paramount importance in pollutants removal due to its simple design, ease of operation, flexibility and high efficiency [3, 8, 9]. Another advantage worth mentioning is that adsorption is greatly practicable in removal of dyes in low concentrations which obviates the need to use expensive conventional methods [1]. Regardless of wide usage of activated carbon in industries, some emphasized the necessity for finding alternative adsorbents due to the high price of activated carbon, its inefficiency in removal of disperse and vat dyes and difficulty in regeneration. Hence, natural adsorbents have been received significant heed over past few years owing to their abundance, easy acquisition, high efficiency, environmental and economical advantages [10]. Dolomite, a common sedimentary rock-forming mineral, can play a pivotal role as a low-priced and ubiquitous adsorbent. It has the general formula of $AB(CO_3)_2$ and a structure of alternative layers of calcite and Magnesite [11, 12]. With partial calcination of dolomite (dissociation of dolomite to calcium carbonate and magnesium oxide), a solid product consisting of a rigid, porous calcite and the fine powdered magnesium oxide can be produced which are given below:

$$CaMg(CO_3)_2 \longrightarrow CaCO_3 + MgO + CO_2 \quad (1)$$

[11, 13, 14, 15]. Charring process leads to the significant increase in specific surface area and pore volume of raw dolomite which has been proved by previous researchers [16, 17, 18]. Obviously, the modification in the interfacial properties of dolomitic solids improves their adsorption capacity [11]. In multi-component dye mixtures, extensive overlapping of the absorption bands arises from the spectral interferences render the simultaneous analysis of dye complicated. To solve the problem of interfering impact of spectral background, derivative spectrophotometer analysis method can be applied [16, 17, 18, 19]. The aim of this research work was to study the feasibility of cationic and anionic dyes removal by charred dolomite. The effect of different experimental parameters on the adsorption process as well as isotherm and kinetics studies, were examined. Moreover, synergistic, antagonistic and non-

interaction effect of dyes in binary mixture was investigated.

II. MATERIALS AND METHODS

2.1. Characterization of adsorbents and adsorbates

Absorption measurements were conducted in batch mode using HACH DR-5000 UV-Vis Spectrophotometer. The morphology of the adsorbent was characterized with $MIRA_3$, TE-SCAN CO. The X-ray diffractogram of charred dolomite was determined using X' Pert Pro with Cu Kα radiation. The typical chemical compositions of the adsorbent were obtained by XRF test using ED 2000, Oxford CO. Samples of charred dolomite were analyzed for specific surface area using BET nitrogen adsorption (BElSORP Mini Microtrac Bel Corp). All samples were centrifuged with SIGMA 3-18KS Spectrophotometry. Simultaneous analysis of dyes in binary mixture was done with First-order Derivative Spectrophotometry Analysis Method using spectroscopy software (Spectragryph version 1.1.2). Dolomite ore which is from the Khorasan province of Iran was used as adsorbent. Charred dolomite sample (thermally processed product) used in this study was supplied from Iranian Refractory Procurement & Production Co. and sieved to fine powder ($0.074<x<0.149$ mm). The dolomite samples were previously calcinated in muffle furnace at the temperature around 800 °C for about 4 hours. Basic Violet 16 (BV_{16}, $C_{23}H_{29}ClN_2$) and Reactive Red 195 (RR_{195}, $C_{31}H_{19}ClN_7Na_5O_{19}S_6$) were provided from Jin-Jiang dyestuff Co. Ltd, China and Atul Co. Ltd, India. All chemicals were supplied by Merck. Dyes stock solutions were prepared by dissolving known amounts of BV_{16} and RR_{195} in groundwater, and different initial concentrations were obtained from the stock solutions by dilution.

2.2. Eexperimental methods

The influence of different parameters such as mass–volume ratio; initial dye concentration; agitation speed and temperature on removal efficiency of dyes has been studied. For variation in mass–volume ratio, the mass of the charred dolomite ranged from 0.3-1.8 g in 0.5 L of solution (constant dye concentration of 20 mgL^{-1}, constant impeller speed 200 rpm at ambient temperature in natural pH of dye solution). For variation in concentration, the initial concentration of dye solution ranged from 10 to 50 $mg\ L^{-1}$ (constant mass volume ratio of 1.5 g/0.5 L of solution, constant impeller speed 200 rpm and at ambient temperature). For variation in agitation rate, a variable speed motor was ranged from 100 to 300 rpm (constant mass volume ratio of 1.5 g/0.5 L of solution, constant dye concentration of 20 mgL^{-1} at ambient temperature). To study the effect of temperature, temperature ranges from 25-45 °C (constant mass volume ratio of 1.5 g/0.5 L of solution, constant dye concentration of 20 mgL^{-1}, constant impeller speed 200 rpm in natural pH). From environmental point of view, pH was considered constant in all tests with natural pH of the solution. The measurements were made at the maximum wavelength 540 for RR_{195}. At the end of adsorption period, the supernatant was centrifuged for 10 min at 8000 min^{-1}.

III. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

Results of the BET nitrogen adsorption analysis on charred dolomite showed that the specific surface area , total pore volume and mean pore volume of charred dolomite are 11.88 m^2/g, 0.096 [$cm^3\ g^{-1}$] and 32.465 nm respectively. The chemical composition of the charred dolomite sample is 28.36% MgO, 0.64% Al_2O_3, 1.24% SiO_2 and 49.08% CaO. The results of chemical analysis on charred dolomite indicated that calcium oxide and magnesium oxide are the principal components of the adsorbent.

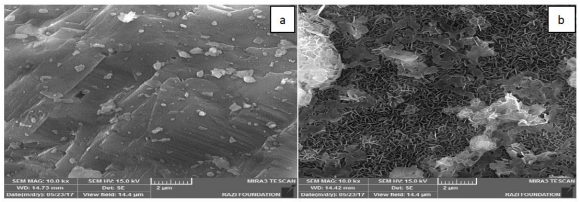

Fig 1. Scanning electron microscopic images of charred dolomite (a: before RR_{195} adsorption) and (b: after RR_{195} adsorption)

According to Fig 1 (a), the structure of Calcite-magnesium oxide is stratified, apparent and compact with some sharp edges. Dolomite sample has some amounts of calcite ($CaCO_3$) impurities, with the light grey areas being identified as calcite and dolomite [20]. A large number of new pores and voids are formed on the surface of charred dolomite after adsorption of RR_{195} on the adsorbent. Furthermore, apparent alteration in surface structure of the sample proves the adsorption of the dye on the surface of the dolomite as well (Fig 1 (b)).

3.2. Effect of experimental parameters on dye removal efficiency

The results showed that with increasing the mass of the adsorbent, the percentage of dye removal efficiency increases. This rise in dye uptake stems from the increase in specific surface area and corresponding more available adsorption sites [9]. In addition, with increasing the speed of agitation, removal efficiency of RR_{195} increases proving that the agitation speed influences the distribution of the dye molecules in the solutions. Fig 2 a shows the effect of varying initial dye concentrations ranges (10–50 $mg.L^{-1}$) on the removal of RR_{195} using charred dolomite. Dye adsorption followed the general pattern of increasing percent sorption with rising

reactive dye concentration. The data also states that the removal rate is rapid between 5 and 99.9% removal, depending on initial dye concentration, occurring within the initial stage of the experiment. After 30 min, as the experiment proceeds, a gradual decrease in the rate of dye removal has been observed. To study the effect of temperature on the adsorption of the dye (RR_{195}) on charred dolomite, experiments were carried out with varying temperature (25, 35, 45 C°) at a constant natural pH of the solution, stirring speed of 200 rpm and initial dye concentration of 20 mg/L. With reference to figure 2 b, while the adsorption of RR_{195} on charred dolomite at 45 C° reached equilibrium quickly in the first 10 min, the time required to reach adsorption equilibrium raised to 30 min at 35 C° and it increased largely to 80 min at 25 C°. Increasing temperature has significant effect on the rate of dye removal and the removal efficiency remains the same in all temperatures. At 25 °C, for contact times of up to 80 min (equilibrium time), the amounts of reactive dye adsorbed increase by 5–96%. For 45 °C, adsorption first followed a linear rising illustrating fast uptake, and then the trend reached the plateau highlighting equilibrium. The rapid dye removal arises from the view that increasing temperature has immense influence on the activation of the adsorption sites. Furthermore, RR_{195} molecules become more reactive at higher temperatures [13].

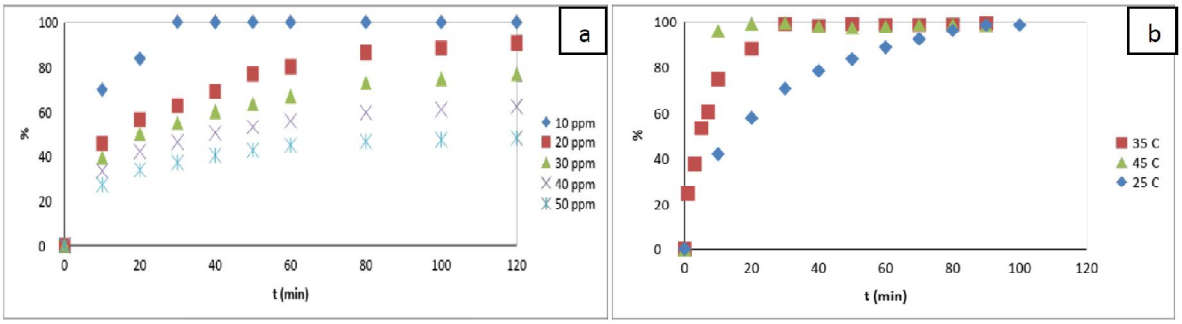

Fig 2. The variation of dye removal efficiency with initial dye concentration at constant adsorbent dose 3 g.L^{-1}, stirring speed 200 rpm, natural pH and ambient T 25 °C (a) and variation of dye removal efficiency with temperature at constant 20 mg.L^{-1} adsorbent dose 3 g.L^{-1}, stirring speed 200 rpm, natural pH (b)

3.3. Isotherm studies

Table 1. The Langmuir and Freundlich isotherm constants and correlation coefficients for RR_{195} adsorption onto charred dolomite in single ad binary dye system

Isotherms and parameters	Langmuir isotherm model			Freundlich isotherm model		
	q_{max}	b	R^2	K_F	n	R^2
RR_{195} (Single system)	7.32	0.73	0.999	4.6	0.131	0.982
RR_{195} (Binary system)	7.74	0.14	0.995	1.88	0.473	0.959

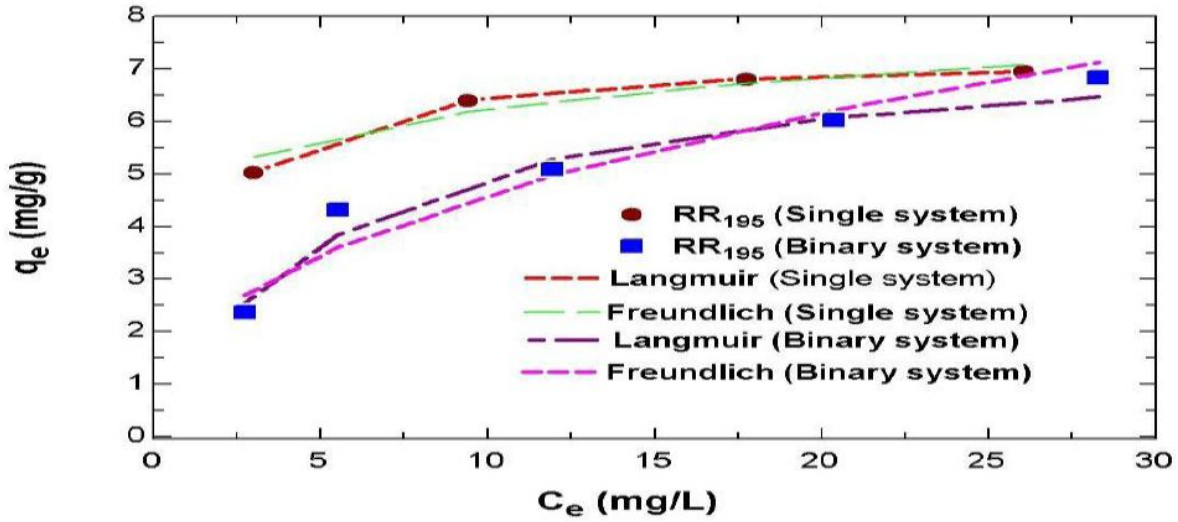

Fig 3. Equilibrium isotherms of RR_{195} adsorption on charred dolomite in single and binary dye system (3 g/L dose, 200 rpm, natural pH, ambient T)

Based on linear correlation coefficient, the Langmuir equation represents the best fit of experimental data than Freundlich isotherm equation in both single and binary dye systems. The adsorption isotherm of the dye exhibits Langmuir behavior emphasizing a monolayer adsorption. The monolayer saturation capacity of charred dolomite, Q_{max}, was found 7.3 mg/g. The Freundlich constant, n, was found to be higher than 1 which reveals that the adsorption of RR_{195} on charred dolomite is favorable. The magnitude of K_F showed a relatively easy uptake of an anionic dye (RR_{195}) by Charred dolomite (Table 1).

3.4. Kinetic studies

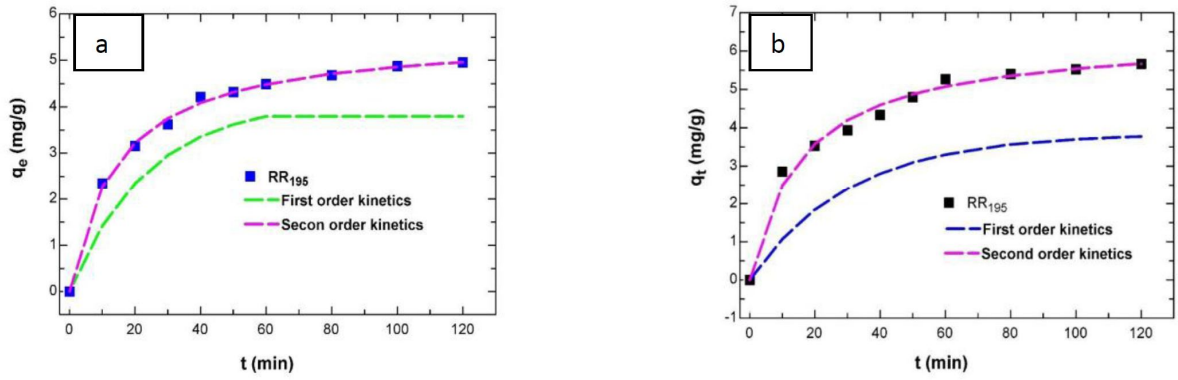

Fig 4. Effect of contact time on the uptake of RR_{195} by the thermally treated dolomite in single system (a) at $C_{0\ RR195}$= 20 mg.L^{-1}, 25 °C, 200 rpm, natural pH. and in binary system (b) at $C_{0\ BV16,\ RR195}$= 20 mg.L^{-1}, 25 °C, 200 rpm, natural pH.

With reference to equilibrium, kinetics and thermodynamic parameters, the adsorption mechanism is concluded chemisorption. It can be seen from figures 4 (a, b), the adsorption rate is almost rapid in the first 10 min in both single and binary dye systems. The rate gradually decreases after this initial step reaching equilibrium at about 80 min. Fast adsorption at the initial contact time originates from the availability of large number of surface sites (13).

3.5. Thermodynamic studies

The values of free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are presented in Table 2. Results are reliable since the coefficient is suitable.

Table 3. Thermodynamic parameters for RR_{195} adsorption onto thermally treated dolomites

Samples	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2
D_{800}	0.267	79.77	0.9225

The ΔG values are negative in the temperature range studied suggesting that the process is spontaneous. The calculated free energies are found to decrease with temperature illustrating that better adsorption is concluded at high temperatures. The positive ΔH values indicate that the RR_{195} adsorption is endothermic. To specify, the process is favored by an increase in temperature through the activation of the adsorption sites. The positive values of ΔS prove an increase in randomness at the solid–solution interface [13].

3.6. Dyes interaction studies

Studies on the effects of the presence of the cationic dye in solution on the adsorption of RR_{195} on charred dolomite were carried out. In single and binary dye**1-** systems, nearly the same adsorption capacities concluded demonstrating that the presence of BV_{16} nearly had no antagonistic effect on the adsorption of RR_{195} on charred dolomite. In contrast, the adsorption capacity of charred dolomite for BV_{16} was increased with the increase of C_{RR195} at fixed concentration of BV_{16} highlighting synergism. This promotion could be associated with the structure of RR_{195} molecule. Some -SO_3- groups present in the structure of the reactive dye would interact with the functional groups on the surface of charred dolomite and negatively charged active sites are created with other free -SO_3- groups results in the adsorption of cationic dye. In other words, RR_{195} can be regarded as a bridge to connect BV_{16} and charred dolomite. Similar results were reported by Wang et al [21].

CONCLUSION

Natural Persian dolomite treated at 800 °C was shown to be effective for removing anionic and

cationic dyes from groundwater aqueous solutions. The maximum adsorption capacity for charred dolomite was concluded 7.3 mg/g. Optimum conditions were found at amount of adsorbent 3 g/L, contact time 80 min and stirring speed 200 rpm. The study illustrated that the quality of the water improved with an increase in the amount of adsorbent and stirring speed. The rate of adsorption in these systems is highly dependent on temperature. Study on multi-component interactions revealed that reactive dye played a crucial role in the removal of cationic dye (synergistic effect). In single dye system, BV_{16} was not removed by charred dolomite due to the similar charges of the dye and the adsorbent. The adsorptive behavior of dolomite was well described by Langmuir isotherm in both single and binary dye systems. It was found that pseudo-second order kinetic model is able to define the experimental data in both single and binary dye systems. Thermodynamic studies showed that the adsorption of RR_{195} on charred dolomite is spontaneous and endothermic.

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