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Research Article

Optimization, isotherm and kinetics studies of the adsorption of azo dyes on eggshell membrane

Ayşe DİNÇER*, Mervecan SEVİLDİK, Tülin AYDEMİR

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Chemistry Department, Faculty of Science and Arts, Manisa Celal Bayar University, Yunusemre, Manisa, Turkey

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*Corresponding author e-mail: ayse.dincer@cbu.edu.tr

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ABSTRACT

Eggshell membrane (ESM) was used as an adsorbent for adsorption of reactive red 195 (RR195) and reactive black 5 (RB5) dyes from aqueous solutions. The experimental conditions were optimized via batch system experiments for maximum azo dyes removal. Adsorption of the dyes was pH dependent highly, and the maximum adsorption of RR195 and RB5 occurred at pH 3.0 and 2.0, respectively. For both dyes, the adsorption process was seen to be obeyed pseudo-second order kinetic and the Langmuir isotherm models. Maximum adsorption capacities (Q_{max}) of ESM for RR195 dye and RB5 were found as 76.9 and 333.33 mg g^{-1}, respectively. The thermodynamic parameters were calculated and the adsorption of the dyes was found to be as exothermic and spontaneous. Moreover, the structural characterization of the ESM was performed by FTIR and SEM analysis.

Keywords: Eggshell membrane, reactive red 195, reactive black 5, adsorption.

Yumurta kabuğu zarı üzerine azo boyaların adsorpsiyonunun optimizasyon, izoterm ve kinetik incelemeleri

ÖZ

Yumurta kabuğu zarı (ESM), reaktif kırmızı 195 (RR195) ve reaktif siyah 5 (RB5) boyalarının sulu çözeltilerden adsorpsiyonunda bir adsorban olarak kullanıldı. Maksimum azo boya giderimi için deneysel koşullar kesikli sistem deneyleri ile optimize edildi. Boyaların adsorpsiyonları pH'a oldukça bağımlıydy ve RR195 ve RB5'in maksimum adsorpsiyonları sırasıyla pH 3.0 ve 2.0'de gerçekleşti. Her iki boya için adsorpsiyon işleminin yalancı ikinci mertebeden kinetik ve Langmuir izoterm modellerine uyduğu görüldü. ESM'nin RR195 ve RB5 için maksimum adsorpsiyon kapasiteleri (Q_{max}) sırasıyla 76,9 ve 333,33 mg g^{-1} olarak bulundu. Termodinamik parametreler hesaplandı ve boyaların adsorpsiyonunun ekzotermik ve kendiliğinden yürüyen olduğu bulundu. Ayrıca, ESM'nin yapısal karakterizasyonu FTIR ve SEM analizleri ile gerçekleştirildi.

Anahtar Kelimeler: Yumurta kabuğu zarı, reaktif kırmızı 195, reaktif siyah 5, adsorpsiyon.

1. INTRODUCTION

Dyes are used in many areas including food colorants, printing, cosmetic, textile-processing and pharmaceutical industries and they are deemed as an important class of pollutants.[1] Azo dyes have one or more N=N bonded groups as chromophore group widely used in the textile industries.[2-4] Production of azo dyes are easy but degradation of these dyes are hard. They have toxic effects on health, many of them are considered as carcinogenic and mutagenic.[5-6] Also, colorization of water causes reduction in photosynthesis and afterwards adversely effects many organisms.[3,7] Reactive red 195 (RR195) is a monoazo, monochlorotriazine and vinylsulfone dye which is extensively used in dyeing processes.[8] Reactive black 5 (RB5) is one of the most common dyes that have been used in textile industries and falls into the diazo dye category, as it contains two Ar-N = N-Ar bonds in its structure.[9]

Azo dyes are highly soluble in water and decolourization of these dyes has received increasing attention. To remove these dyes from wastewater, ion exchange, electrocoagulation, reverse osmosis, flocculation, adsorption, membrane filtration, ozonation

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and photooxidation methods have been used.[10] Adsorption technique is widely used in general wastewater treatment in the industrial processes and has many advantages such as simplicity of operate, cost and high removal efficiency.[11-14]

In the present work, the removal of RB5 and RR195 dyes from aqueous solutions were studied by using eggshell membrane (ESM). ESM can be easily obtained as a natural waste product in large quantities. Collagen (type I, V and X), sialoprotein and osteopontin are found mainly in the protein structure of ESM.[15] ESM can be used in many areas as an adsorbent because it has high surface area, water-insoluble fibers and mechanical stable.[16] The experiments were performed by batch system and adsorption conditions were optimized. Equilibrium isotherms and thermodynamic parameters were also studied. ESM characterization was done by FTIR and SEM analyses.

2. EXPERİMENTAL

2.1. Materials

2.1.1 Chemicals

RR195 (Synozol Red HF- 6BN 150% C.I. Reactive Red 195) and RB5 were obtained from dyestuff fabric (Figure 1). Methanol, hydrochloric acid, sodium hydroxide and acetic acid were purched from Sigma Aldrich (USA) grade.

2.2. Preparation of eggshell membrane

The ESM was obtained from eggshells. First, the eggshells were washed and then incubated in 5% (v/v) acetic acid solution until the calcite totally dissolved. After washing with distilled water, the membrane structures were dried at room temperature for 72 h and ground into small pieces using a blender and homogenizer.

2.3. Dye analysis

Standard solutions of the dyes (0.005-0.05 mg ml^{-1} for RR195 and 0.005-0.04 mg ml^{-1} for RB5) were prepared with deionized water. Dye removal studies were analyzed by monitoring the absorbance changes at the maximum wavelengths which are 540 nm for RR195 dye and 597 nm for RB5 using a UV-Vis spectrophotometer (Shimadzu UV-1800) with a 1 cm cell.

2.4. Characterization of ESM

FTIR (Spectrum BX, Perkin Elmer) was used to determine the characteristic functional groups of ESM. The spectra measurements were taken in the range from 4000 to 400 cm^{-1} at room temperature. The morphology of ESM was examined after dried under vacuum using Scanning electron microscope (SEM) (Quanta 250 FEG/FEI).

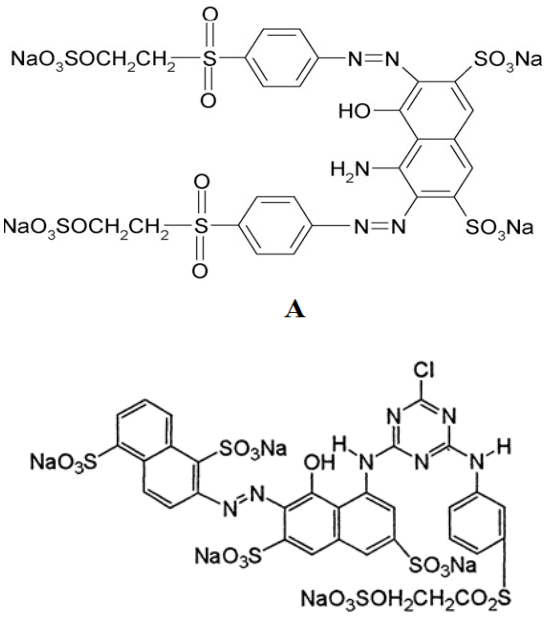

Figure 1. Structures of azo dyes: a) Reactive Black 5, b) Reactive Red 195.

2.5. Adsorption studies

The adsorption studies between RR195 and RB5 dyes and ESM were performed by using batch system at various pH, contact time, temperature and concentrations. The adsorption characteristics of RR195 dye and RB5 were studied by varying pH range from 2.0 to 10.0. Dye removal studies were done at various contact time intervals (5-30 min), temperature values (20-60°C) and the concentrations (0.1-1.2 mg ml^{-1} for RR195 dye and 0.01-1.75 mg ml^{-1} for RB5 dye). After the adsorption, the ESM was removed by centrifugation and remaining dye concentration was determined spectrophotometrically.

The amount of dye adsorbed on the ESM was calculated according to Eq. (1).

$$q_e = \frac{(C_0 - C_e)\, x\, V}{m} \quad (1)$$

where qe is the amount of dye adsorbed (mg g^{-1}), C_0 and C_e is the initial and the equilibrium concentrations of dye (mg ml^{-1}), respectively, V is the volume of solutions (ml) and m is the amount of adsorbent (g).

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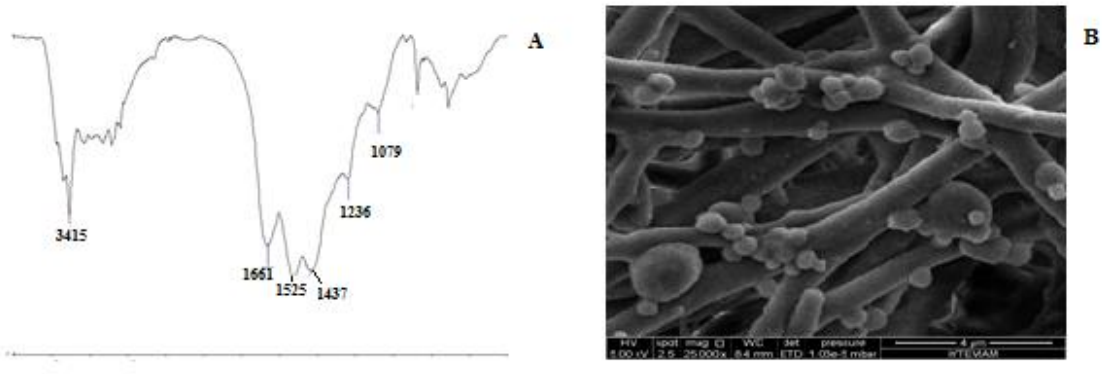

Figure 2. a) FT-IR spectrum of ESM, b) SEM micrograph of ESM.

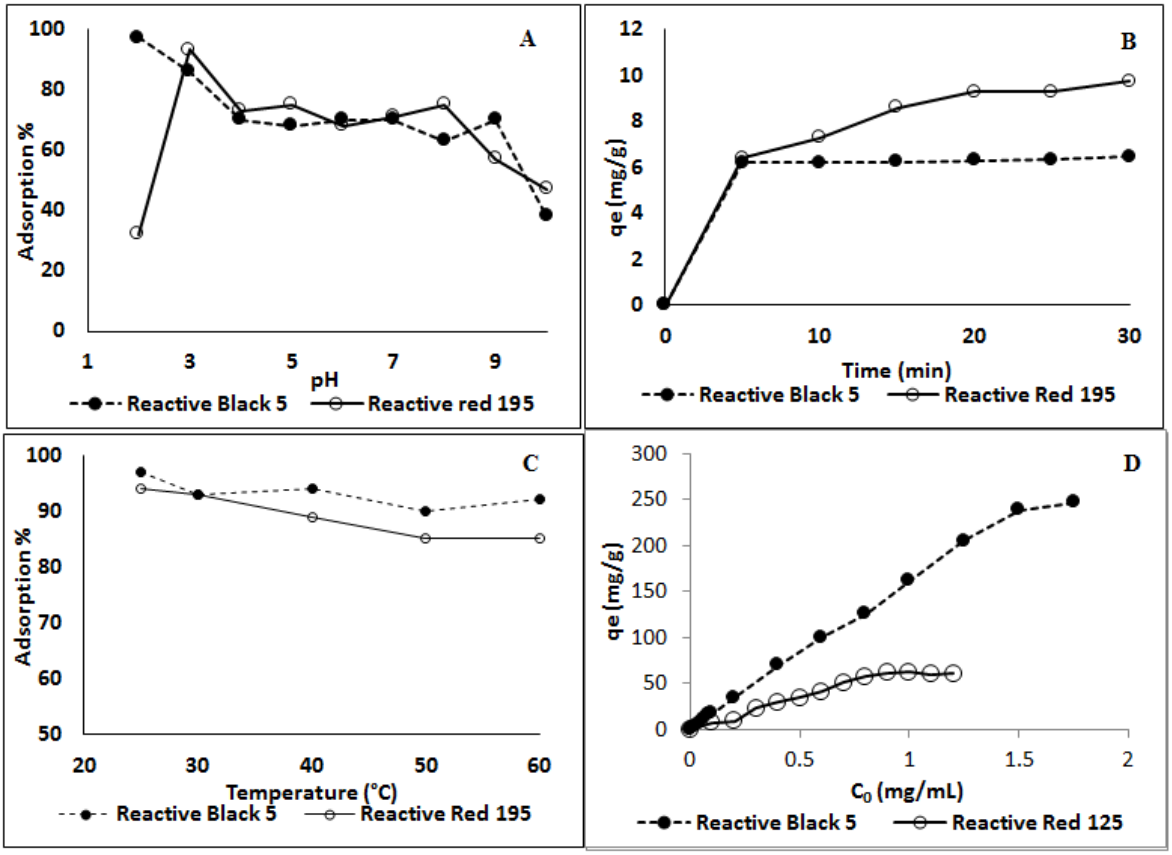

Figure 3. a) Effect of pH on the adsorption of azo dyes on the ESM (contact time 30 min, adsorbent dose 20 mg, temperature 25°C, RB5: 0.04 mg ml^{-1}, RR195: 0.05 mg ml^{-1}); **b)** Effect of contact time on the adsorption of azo dyes on ESM (RB5: 0.04 mg ml^{-1}, pH 2.0; RR195: 0.05 mg ml^{-1}, pH 3.0; adsorbent dose 20 mg; temperature 25°C); **c)** Effect of temperature on the adsorption of azo dyes on ESM (RB5: 0.04 mg ml^{-1}, pH 2.0, 15 min; RR195: 0.05 mg ml^{-1}, pH 3.0, 25 min; adsorbent dose 20 mg); **d)** Effect of initial concentrations of azo dyes on the adsorption (RB5: pH 2.0, 15 min; RR195: pH 3.0, 25 min; adsorbent dose 20 mg; temperature 25°C).

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3. RESULTS AND DISCUSSION

3.1 Characterization of the ESM

3.1.1 FT-IR analysis

FT-IR spectrum of ESM was recorded in the range of 4000–400 cm^{-1} (Figure 2a). ESM was first dried for 24 h at 50°C to prevent water related interferences. The peak positions are noticed at 3415, 1661, 1525, 1437, 1236 and 1079 cm^{-1}. The band at 3415 cm^{-1} showed the N–H and O–H groups.[17] The bands at 1661 and 1525 cm^{-1} reflect the amide I (-COO^- stretching vibration), amide II respectively. Bands at 1437 cm^{-1} and 1236 cm^{-1} indicate C–C stretching and amide III bands, respectively.[18] The absorption peak at 1079 cm^{-1} probably indicates the presence of C-O stretching/bending vibration (and/or amine C-N stretching) and CH_2 vibration.[19]

3.1.2. SEM analysis

Physical properties and the morphology of the adsorbent were characterized by SEM.[20] It was used to determine shape, size distribution and porosity of the particle. Scanning electron micrographs of ESM is shown in Figure 2b. ESM has protein fibers which form three-dimensional network structure.[18] ESM has numbers of pores which provide an increase surface area and dye molecules may be easily diffused into these pores.

3.2. Effect of pH

In the adsorption process, pH has critic effect, particularly on adsorption capacity. The pH of the dye solutions was adjusted to 2.0-10.0 by using 0.1 M NaOH or HCl solutions. 20 mg ESM was treated with 0.04 mg ml^{-1} RB5 and 0.05 mg ml^{-1} RR195 dye solutions (4 ml) for 30 min. Dye adsorption on ESM was highly dependent to the pH of the medium. The dye adsorption capacity of ESM decreased when the pH values increased from 2.0 to 10.0. Maximum adsorption was reached at pH 3.0 and pH 2.0 for RR195 (93% adsorption) and RB5 (97% adsorption), respectively (Figure 3a). Therefore, further experiments were performed at these pH values. RR195 and RB5 dyes which possess anionic (Dye–SO_3^-) groups are interacted with the positive charge of the ESM. pH changes affect the net charge of the functional groups of ESM such as carbonyl and amine groups.[13] Under acidic conditions, the adsorption of two dyes on ESM may be favorable because of the electrostatic interactions. At high pH values, the number of negatively charged groups on ESM increased, so electrostatic repulsion between the adsorbent and dye molecules occurred. Also, at alkaline region, the adsorption of the dye ions may be prevented by OH^- ions, so a decrease in adsorption of the dyes were observed.[21,22]

3.3. Effect of contact time

The contact time between the dye and the adsorbent has an important role in wastewater treatment by adsorption. 20 mg of ESM was added to 0.05 mg ml^{-1} RR195 (pH 3.0) and 0.04 mg ml^{-1} RB5 (pH 2.0) solutions. As seen from Figure 3b, in first 5 min of adsorption process, a very fast increase in the adsorption was observed which was due to large number of accessible pores of the adsorbent.[23,24] The equilibrium was reached at 25 minutes for RR195 and 15 minutes for RB5. At the beginning of the contact time, the adsorption of the dyes was found to be rapid. At 15 and 25 minutes, the adsorption remained almost unchanged and reached to the equilibrium.

3.4. Effect of temperature

In this work, 0.05 mg ml^{-1} RR195 (pH 3.0) and 0.04 mg ml^{-1} RB5 (pH 2.0) dye solutions were added to the ESM and shaken gently at various temperature values (25-60°C) for 25 and 15 minutes, respectively. The adsorption percentage of the RR195 and RB5 dyes slightly decreased with an increase in the temperature from 25 to 60°C (Figure 3c). For this reason, the temperature was chosen as 25°C in the following experiments. When the temperature was increased, the solubility of the dyes increased, so stronger interaction forces between dyes and solvent than those between dyes and ESM occurred.[12,25-27] As the temperature was increased, Brownian movement of dye molecules in solution increased, so the adsorption of both dyes RB5 and RR195 decreased.[28] Hydrogen bonding between dye molecules and ESM, which has an important role at the adsorption process, might also lead to be broken because of high temperature.[28]

3.5. Effects of initial dye concentration

In the experiments, ESM was treated with the solutions of various dye concentration (0.025-0.5 mg ml^{-1} for RR195 and 0.01-1.75 mg ml^{-1} for RB5) by mild shaking and the other operational parameters were kept at optimum values. When the initial concentrations of the dyes were increased, the amount of dye adsorbed was found to be increased. The adsorption of RB5 and RR195 reached equilibrium at initial concentrations of 1.75 and 1 mg ml^{-1} respectively, and then the adsorption remained constant. When the dye concentration was increased, dye adsorption capacities rapidly increased from 1.4 to 247 mg g^{-1} for RB5 dye and from 4.3 to 60 mg g^{-1} for RR195 (Figure 3d). An increase in the initial dye concentration may cause an increase in the driving force of the concentration gradient.[29,30]

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3.6. Adsorption thermodynamics

The thermodynamic parameters can be used to estimate effect of temperature on adsorption. The amount of dye adsorbed was calculated from Eq. (2).

$$K_c = X_e/(C_i - X_e) \quad (2)$$

where X_e (mg ml^{-1}) is the concentration of dye adsorbed on ESM at equilibrium, C_i the initial dye concentration, mg ml^{-1}. The equilibrium constant for the adsorption process, K_c, was calculated at various temperatures (298-333 K) according to Eq. (2). Eq. (3) allows to calculate $\Delta H°$ and $\Delta S°$ of the adsorption by plotting ln K_c versus $1/T$ in Figure 4.

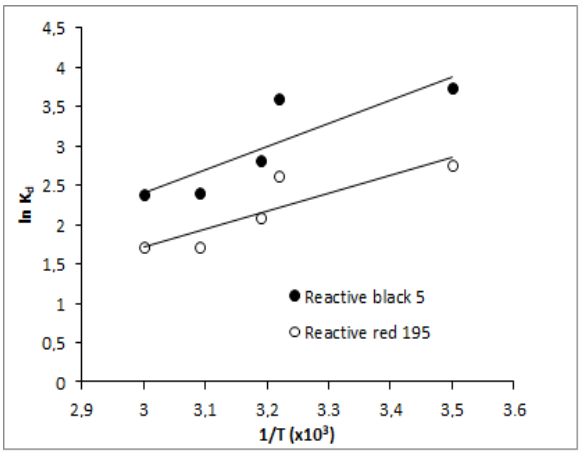

Figure 4. Plots of ln K_d versus $1/T$. (RB5: 0.04 mg ml^{-1}, pH 2.0, 15 min; RR195: 0.05 mg ml^{-1}, pH 3.0, 25 min; adsorbent dose 20 mg).

$$In\ K_c = (\Delta S°/R) - (\Delta H°/RT) \quad (3)$$

where R (8.314 kJ mol^{-1} K^{-1}) is the gas constant and T is the absolute temperature, respectively. The slope and the intercept of the plots in Figure 4 is equal to $-\Delta H°/R$ and $\Delta S°/R$, respectively. The values of $\Delta H°$ and $\Delta S°$ for the adsorption of dye on the ESM were calculated from The slope and the intercept of the plots, respectively. $\Delta G°$, $\Delta H°$, $\Delta S°$ values obtained are presented in Table 1.

Table 1. Thermodynamic parameters

	T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
Reactive Black 5	298	-8.53	-24.6	-0.054
Reactive Red 195	298	-6.72	- 24.07	-0.059

The negative value of $\Delta H°$ of adsorption indicated an exothermic nature thus is less favorable at higher temperatures. Negative value of $\Delta S°$ shows the affinity of the adsorbent for RR195 and RB5 dyes and indicates the randomness adsorption. To calculate the $\Delta G°$ value of the adsorption, Eq. (4) was used.

$$\Delta G° = \Delta H - T\Delta S \quad (4)$$

The $\Delta G°$ values were calculated as -8.53 kJ mol^{-1} and -6.72 kJ mol^{-1} for RB5 and RR195, respectively. Negative value of $\Delta G°$ shows that the feasibility of the adsorption process is less favored at higher temperatures and nature of the adsorption is spontaneous[7,31,32] Kyzas and co-workers studied RB5 adsorption on magnetic graphene oxide. They reported negative values of $\Delta H°$ (-21.13 kJ mol^{-1}), $\Delta G°$ (-0.66 kJ mol^{-1}) and $\Delta S°$ (-0.082 kJ mol^{-1} K^{-1}) for 300 mg ml^{-1} RB5 concentration at 298 K.[33] From the thermodynamic parameters, Munagapati and co-workers reported that RB5 adsorption on banana peel powder (BPP) was endothermic, feasible and spontaneous.[21] They found the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ as -0.198 kJ mol^{-1}, 14.15 kJ mol^{-1} and 0.056 kJ mol^{-1} K^{-1}, respectively.[21]

3.7. Adsorption isotherms

Equilibrium study is important to gain information on the interaction of adsorbate and the adsorbent, so the adsorption capacity of an adsorbent can be evaluated. [29] In this work, the experimental data were evaluated by the Freundlich and Langmuir models.[34] The logarithmic form of the Freundlich model is defined by Eq.(5).[12,35]

$$log\ q_e = log\ k_F + 1/n\ log\ C_e \quad (5)$$

where q_e is the amount dye adsorbed. K_F and n are Freundlich constants. K_F is related to the adsorption capacity and $1/n$ is related to the adsorption intensity. When log qe was plotted against log C_e (Figure 5), $1/n$ and K_F values were calculated from the slope and intercept of the plot and the values at 25°C are given in Table 2.

Another widely used equation in adsorption processes is the Langmuir equation (Eq. (6)) [35]

$$1/q_e = 1/Q°b.1/C_e + 1/Q° \quad (6)$$

where $Q°$ is the amount of dye adsorbed (mg g^{-1}), which gives the maximum adsorption capacity of ESM and the Langmuir isotherm constant, b (l mg^{-1}) is related to adsorption energy. The calculated Langmuir constants, Q^o and b are given in Table 2.

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Table 2. Parameters of adsorption isotherms and kinetic models

	Adsorption Isotherms		Kinetic Models		Experimental Capacity (q_{exp})
	Langmuir Isotherms	Freundlich Isotherms	Pseudo-first-order model	Pseudo-second-order model	
Reactive Black 5	$R^2 = 0.955$	$R^2 = 0.754$	$R^2 = 0.974$	$R^2 = 0.998$	247 mg g^{-1}
	Q_{max}= 333.3 mg g^{-1}	K_F = 56.23 mg g^{-1}	q_e = 77.1 mg g^{-1}	q_e = 256.4 mg g^{-1}	
	b = 0.11 ml mg^{-1}	1/n = 0.392	k_1 = 0.096 min^{-1}	k_2 = 2.76 10^{-3} g mg^{-1} min^{-1}	
Reactive Red 195	$R^2 = 0.918$	$R^2 = 0.2622$	$R^2 = 0.8922$	$R^2 = 0.9971$	62.5 mg g^{-1}
	Q_{max}= 76.9 mg g^{-1}	K_F = 63.2 mg g^{-1}	q_e = 13.25 mg g^{-1}	q_e=62.5 mg g^{-1}	
	b = 2.17 ml mg^{-1}	1/n = 0.046	k_1 = 0.07 min^{-1}	k_2 = 0.02 g mg^{-1} min^{-1}	

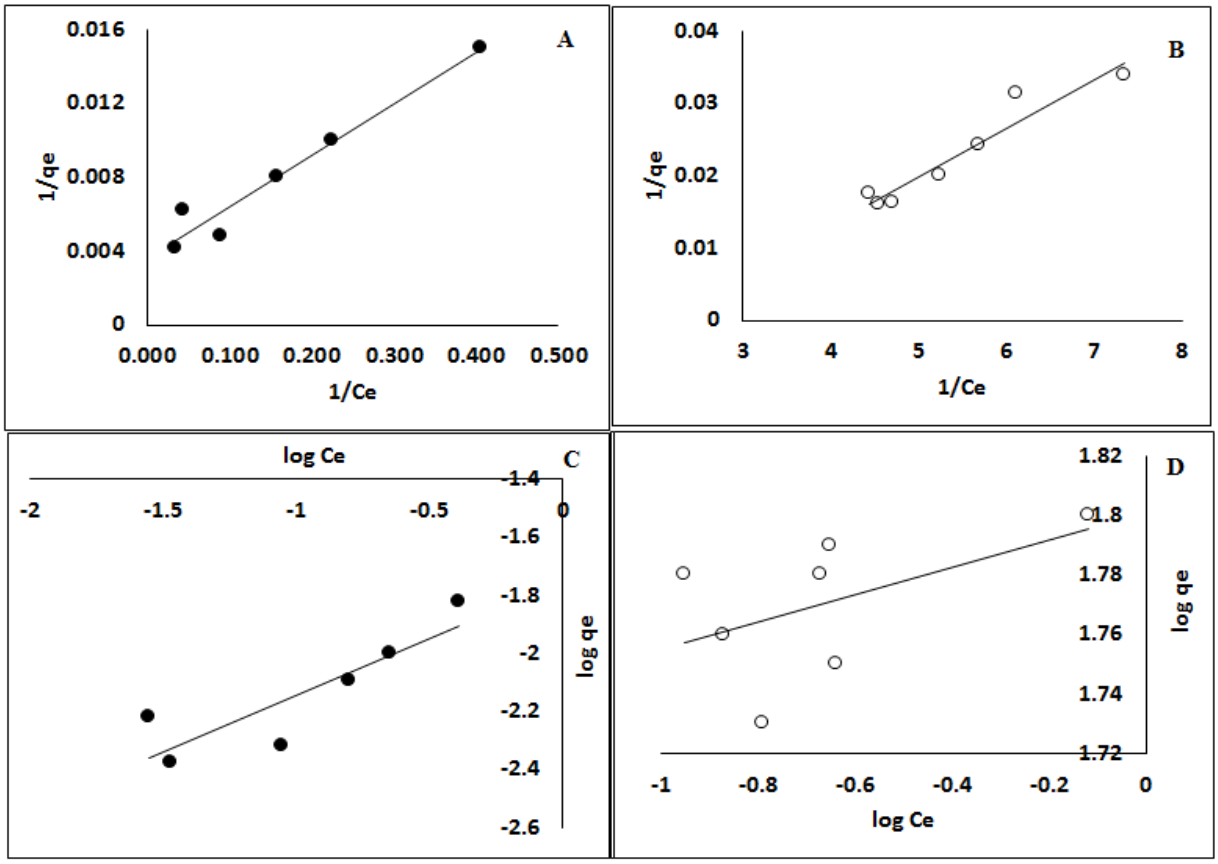

Figure 5. Langmuir (a and b) and Freundlich (c and d) isotherm graphs of RB5 (-●-) and RR195 (-○-) dyes.

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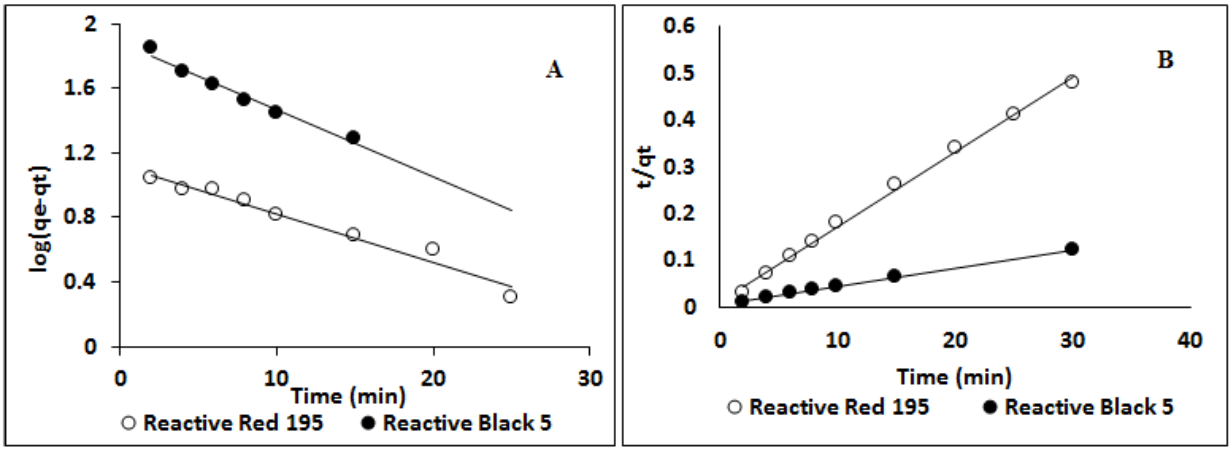

Figure 6. Pseudo first order (a) and pseudo second order (b) kinetics of RB5 (-●-) and RR195 (-○-) dyes.

The higher R^2 values of Langmuir over Freundlich model showed the suitability of the Langmuir model than the Freundlich model. The R^2 values from the Langmuir isotherm for the adsorption of RB5 and RR195 are 0.955 and 0.918, respectively. The maximum adsorption capacities obtained from the Langmuir isotherms were found to be 76.9 and 333.33 mg g^{-1} for RR195 and RB5, respectively. Dimensionless separation factor, R_L is a used to analyze the adsorption process. When the R_L value is between 0 and 1 or higher than 1, this means the adsorption process is favorable or unfavorable, respectively. If the R_L equals to 1 or 0, it shows the adsorption process linear or irreversible, respectively.[35] the R_L, can be expressed as:

$$R_L = 1/(1+bC_0) \quad (7)$$

Where b is the Langmuir constant and C_0 is the initial dye concentration (mg ml^{-1}).

The R_L values for the adsorption of RR195 and RB5 dyes onto ESM was determined as 0.33 and 0.84 respectively, showing that the adsorption process was favorable. Chang and Shih studied the adsorption of RB5 onto magnetic iron oxide nanoparticles (IONPs) and they reported the adsorption process were well compatible with the Langmuir and Freundlich equations.[36] They calculated that Langmuir isotherm capacity was 11.29 mg g^{-1} at 25°C. Kyzas co-workers studied the removal of RB5 by magnetic graphene oxide synthesized by impregnation (mGOi) and magnetic graphene oxide synthesized by co-precipitation (mGOp) at 25°C and pH 3.0, and they calculated that the maximum adsorption capacities (Q_{max}) were 164 and 188 mg g^{-1}, respectively.[33] Their results were fitted to the Langmuir model. Munagapati co-workers used banana peel powder (BPP) as an adsorbent to remove reactive black 5 and congo red from aqueous solutions. Their adsorption equilibrium results were compatible with Langmuir isotherm model and they calculated the adsorption capacity as 49.2 mg g^{-1}.[21] Belessi co-workers studied adsorption of RR195 dye on TiO_2 surface and they reported that equilibrium data fitted very well with the Langmuir isotherm. At 30°C and pH 3.0, Langmuir adsorption capacity was calculated as 87 mg g^{-1}.[14] Kamranifar and co-workers reported the removal of RR195 using powder and ash of barberry stem. Adsorption isotherm was fitted to both the Freundlich and Langmuir isotherms for the barberry stem powder. However, Freundlich isotherm was compatible for the adsorption of RR195 on barberry stem ash. Q_{max} (mg g^{-1}) values were calculated as 15.72 mg g^{-1} and 6.44 mg g^{-1} for barberry stem (powder) and barberry stem (ash) respectively.[6]

3.8. Adsorption kinetics

To obtain information about the performance of the sorbent material, the pseudo-first-order (Eq. (8)) and the pseudo-second-order (Eq. (9)) kinetic models were used.

$$\log(q_e - q_t) = \log q_e - \frac{q_1}{2.303} t \quad (8)$$

$$\frac{t}{q_e} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \quad (9)$$

where q_t (mg g^{-1}) represents the adsorption capacity of dyes adsorbed on eggshell membrane at any time t (min). k_1 (min^{-1}) is the rate constant of the pseudo-first-order model and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order model.[37-38]

The results of the pseudo first-order and pseudo second order models for RR195 and RB5 adsorbed on ESM are shown in Figure 6. All the kinetic parameters calculated from the intercepts and the slopes of the plots

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in Figure 6 are shown in Table 2. The R^2 (correlation coefficient) of the pseudo first-order kinetic model was determined as 0.974 and 0.8922 for RB5 and RR195, respectively. R^2 values from the pseudo second-order model were found as 0.998 and 0.9971 for RB5 and RR195 respectively. For the adsorption of both dyes, the theoretical qe values calculated from the pseudo- second order kinetics are much higher than those of the pseudo first order kinetics and they very closed to the experimental qexp values. This situation indicates that the adsorption is a good fit to the pseudo second order kinetic model. Kyzas and co-workers reported that the adsorption kinetics of RB5 on magnetic graphene oxide fitted to the pseudo-second order model.[33] Belessi and co-workers reported the sorption kinetics of RR195 on the surface of TiO_2 nanoparticles fitted to the pseudo-second-order kinetic model.[14]

4. CONCLUSIONS

ESM was used as an adsorbent for the removal of RR195 and RB5 dyes. Adsorption conditions were optimized as a function of pH, temperature, contact time and concentrations of the adsorbates. The adsorption of RR195 and RB5 on ESM was very dependent to the pH of the medium and maximum adsorption was observed at pH 3.0 for RR195 and 2.0 for RB5, respectively. The optimum contact time was found as 25 min and 15 min for RR195 and RB5, respectively. The negative values of $\Delta G°$ indicate the overall adsorption process is spontaneous. The $\Delta G°$ value was calculated as -6.72 kJ mol^{-1} for RR195 and -8.530 kJ mol^{-1} for RB5 at 298 K. The negative values of $\Delta H°$ showed that the adsorption of RR195 and RB5 by ESM was exothermic. Adsorption isotherm of the ESM was fitted to the Langmuir isotherm model and the Q_{max} value was calculated as 76.9 mg g^{-1} for RR195 and 333.33 mg g^{-1} for RB5, respectively. The present work reveals that the ESM is a promising material for the removal of dyes from aqueous solutions.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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ORCID

https://orcid.org/0000-0001-6158-1775 (A. Dinçer)

https://orcid.org/0000-0001-6883-8748 (M. Sevildik)

https://orcid.org/0000-0002-2968-4456 (T. Aydemir)