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Adsorption behaviors of anionic and cationic dyes on ionic liquid-modified silica gel as sorbent

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ABSTRACT

In this study, adsorption behaviors of typical anionic (red congo (RC)) and cationic (methylene blue (MB)) dyes on new synthesized [C_8mim][PF_6]-modified silica gel sorbent were examined. Outstanding differences were observed in adsorption behaviors of studied dyes on synthesized sorbent. The most percent adsorption of RC molecules was related to acidic pH values, while basic pH values were more effective than acidic ones for adsorption of MB molecules. Adsorption of RC molecules on sorbent was exothermic, but temperature had no considerable effect on MB adsorption. Thermodynamic parameters such as Gibbs free energy change of dyes partitioning (ΔG_0^T), their enthalpy change of partitioning (ΔH_0^T), and also their entropy change of partitioning (ΔS_0^T) related to partition coefficient (K) of studied dyes between [C_8mim][PF_6]-modified silica gel and aqueous solution were obtained. Desorption of adsorbed dyes, their preconcentration factors, and adsorption capacity of sorbent for each dye were also studied.

Keywords: Red congo; Methylene blue; Modified silica gel; Ionic liquid; Adsorption

1. Introduction

The industry of printing, dying, rubber, cosmetics, paper, food coloring, plastics, textiles, and related industries produce wastewaters containing various dyes that can pollute environment. Dyes can cause skin irritation, allergic dermatitis, mutations, and cancer [1]. Therefore, the removal of dyes from industrial effluents before entrance to natural waters is necessary for environmental safety. For treating the wastewater containing dyes, different physicochemical processes such as photocatalytic degradation [2], ionexchange [3], membrane nanofiltration [4], coagulation and flocculation [5], electrochemical oxidation [6], and catalytic ozonation [7] have been used. However, poor efficiency of these methods has limited their application. The adsorption is a suitable methodology due to its simplicity and effectiveness in removal of dyes with low concentration from wastewaters [8–10]. Chemically modified silica is an attractive sorbent for dyes removal from wastewaters [11–13]. Because of the relative inertness of silica surface, direct interaction of modifying reagents towards silica surface is difficult. So, activation process facilitates direct bonding of modifying reagents to silica surface [14,15]. The silanol groups (≡Si–OH) on the surface of silica are activated during the activation process and act as precursors for immobilization of various reagents. By loading of lipophilic functional groups on silica surface, its lipophilic properties are increased and adsorption efficiency of silica improves [16].

Liquid–liquid extraction based on ionic liquids (ILs), as a novel separation technology, was found to have some disadvantages such as lower rate of mass transfer, longer equilibrium time, difficulty in complete phase separation, and loss of IL to aqueous phase [17,18]. These problems can be overcome by immobilization of ILs on different solid substrates. Supported IL phases were applied as HPLC stationary phase and sorbent for solid phase extraction technique [19].

In this work, $[C_8mim][PF_6]$-modified silica gel was synthesized and applied as a new sorbent for studying the adsorption behaviors of cationic and anionic dyes.

2. Experimental

2.1. Instruments

The UV–Vis absorption spectra were recorded against the solvent blank using Perkin Elmer Precisely lambda 25 UV–Vis spectrometer. A SCHOTT lab850 pH meter with a combined glass electrode was applied for pH measurements. IR spectra were recorded by using Bruker Tensor FTIR 27 series apparatus.

2.2. Reagents

Ammonium hexafluorophosphate was purchased from Fluka; red congo (RC) and methylene blue (MB) were of Sigma-Aldrich; 1–bromooctan, 1–methylimidazolium, silica gel (230–400 mesh), and other reagents were purchased from Merck with the highest purity and were used without further purification. The $[C_8mim][PF_6]$ was synthesized as described in literature [20] and its chemical structure was verified by using NMR spectroscopy. Doubly distilled deionized water (0.5 $\mu S\ cm^{-1}$) was used throughout this work.

2.3. Preparation of IL-modified silica

Activation of silica gel was done by stirring in nitric acid water (50:50, v/v) solution at room temperature for 2.0 h and refluxing for 8.0 h. Then the activated silica was filtered and washed with distilled water and acetone, and finally vacuum dried. IL-modified silica was prepared, as it has been reported previously [21]. To a stirring solution of $[C_8mim][PF_6]$ (2.0 g) in acetone, 6.0 g of silica powder was added. The volatile components of the mixture were evaporated by water bath, after stirring for 2.5 h. The resulting material was washed thoroughly with methylene chloride and distilled water, and after that vacuum dried at 150°C for 3.0 h. The produced white powder was $[C_8mim][PF_6]$-modified silica and its chemical structure was verified by using FTIR spectroscopy.

2.4. Recommended procedure

Aqueous solutions containing MB and RC (2.0 mL) with suitable pH values were separately brought into contact with synthesized sorbent to remove dyes from aqueous solution. For back extraction purpose, a suitable buffer solution was brought into contact with sorbent containing adsorbed dyes. The phase-contacting experiments were carried out in a conical glass test tube. In the both steps, system was stirring with magnetic stirrer (500 rpm) during the optimum times and then two phases were carefully separated using a centrifuge device.

3. Results and discussions

3.1. Preliminary experiments

Preliminary experiments showed that $[C_8mim][PF_6]$-modified silica gel can be used as a new sorbent for MB and RC extraction from aqueous solutions. As MB and RC (Fig. 1) have strong absorbance in visible region, amount of dyes during this study was determined by using spectrophotometric method.

3.2. The pH of the sample solution

The effect of the feed pH on the percent adsorption of studied dyes was studied (Fig. 2). Aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} of each dye solution in phosphate buffer 1.0×10^{-3} mol L^{-1} with different pH

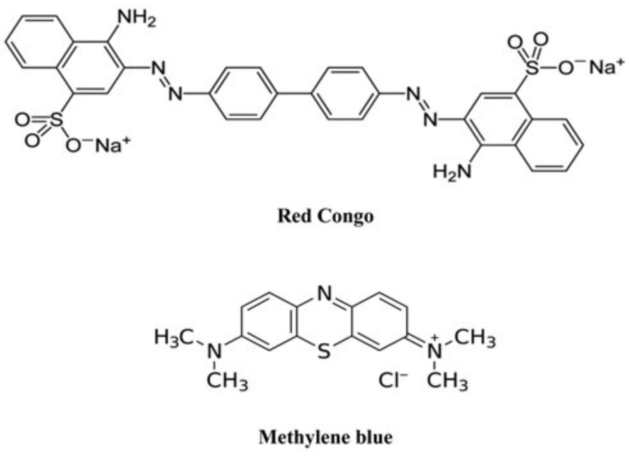

Fig. 1. Chemical structures of studied dyes.

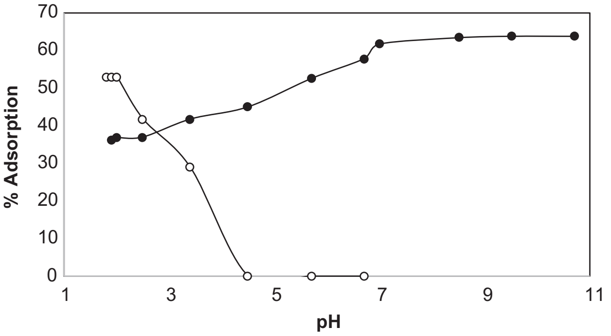

Fig. 2. Effect of pH of aqueous solution; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-3} mol L^{-1} with different pH values, amount of sorbent: 0.04 g, contact time: 30 min; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-3} mol L^{-1} with different pH values, amount of sorbent: 0.04 g, and contact time: 30 min.

values were brought into contact with 0.04 g of sorbent and extraction process was done during 30 min.

As it is seen in Fig. 2, RC can be effectively adsorbed on IL-modified silica sorbent at pH values less than 2.0. At these pH values, the most percent of $–SO_3H$ groups of RC molecules are in neutral (non-ionized) form. So, H-bonding formation of anionic part of IL (PF_6^-) and –OH groups of silica with $–SO_3H$ groups of RC is an effective parameter for RC adsorption on sorbent. With pH increasing and more ionization of $–SO_3H$ groups, hydrophobicity of RC molecules is decreased and their tending for leaving aqueous solution and adsorption on sorbent diminishes. Furthermore, decrease in the adsorption of RC on sorbent can be attributed to decrease in H-bonding formation of RC molecules with IL-modified silica sorbent because of the ionization of $–SO_3H$ groups of RC and ≡SiOH groups of silica [11]. In the other hand, repulsion between $–SO_3^-$ of RC and sorbent containing anionic groups (PF_6^- and ≡SiO^-) is an effective parameter for decreasing in RC adsorption on IL-modified silica sorbent. So, a pH 1.9 was selected as the optimum pH to prevent any abrupt change in percent extraction of RC.

As it is seen in Fig. 2, MB molecules can be adsorbed on IL-modified silica sorbent at acidic and basic pH values. This behavior can be attributed to electrostatic interactions of cationic MB and anionic part of IL (PF_6^-). With pH increasing, electrostatic interactions of cationic MB and sorbent containing anionic group of ≡SiO^- [11], in addition to PF_6^-, increases percent adsorption of MB on sorbent. It is considerable that the competition between cationic MB and excess H^+ ions at lower pH values lessens the MB adsorption on sorbent, but a decrease in the proton concentration with increasing pH is in favor of adsorption process [22]. Percent adsorption was almost constant in the pH range of 8.5–11.0. So, a pH 9.5 was selected as an optimum pH value for MB adsorption on sorbent.

3.3. Effect of sorbent amount

In order to study the effect of sorbent amount, aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} solution of each dye with optimum pH values were brought into contact with different amounts of sorbent. Extraction process was done during 30 min and percent adsorption of each dye on different amounts of sorbent was determined. As it is seen in Fig. 3, the most amount of RC was adsorbed on sorbent when more than 0.060 g of sorbent was used. Hence, a mass of 0.070 g of sorbent was chosen for further studies. The most MB adsorption was obtained when amount of sorbent was more than 0.050 g. So, a mass of 0.060 g of sorbent was selected for the following studies.

3.4. Effect of ionic strength

To study the effect of ionic strength of feed solution, aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} of each dye solution with optimum pH values containing different amounts of phosphate salts were brought into contact with optimum amounts of sorbent and extraction process was done during 30 min. As it is seen in Fig. 4, with increase in buffer concentration (increase in ionic strength of feed solution) until 0.01 mol L^{-1},

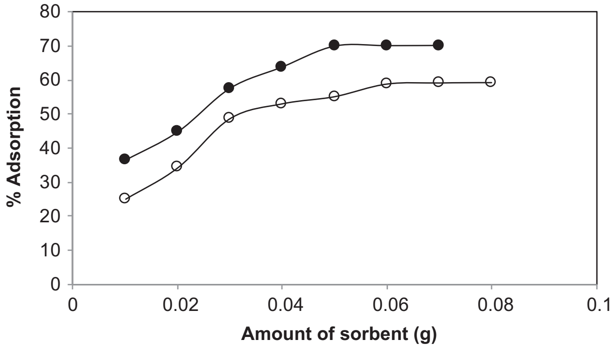

Fig. 3. Effect of sorbent amount; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-3} mol L^{-1} with pH 1.9, contact time: 30 min, different amounts of sorbent; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-3} mol L^{-1} with pH 9.5, contact time: 30 min, and different amounts of sorbent.

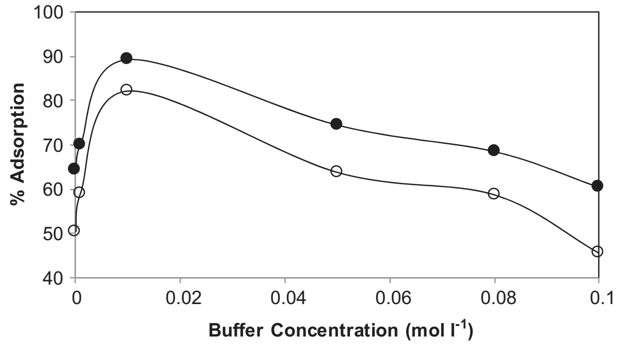

Fig. 4. Effect of ionic strength; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} solution with pH 1.9 containing different amounts of phosphate salts, contact time: 30 min, amounts of sorbent: 0.07 g; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} solution with pH 9.5 containing different amounts of phosphate salts, contact time: 30 min, and amounts of sorbent: 0.06 g.

percent adsorption of dyes on sorbent is increased. This behavior can be explained by salting out effect [23]. When concentration of ions in solution is increased, water molecules migrate into ions and hydrate them. So, more percent of dye molecules are released from water molecules, migrate into sorbent, and are adsorb on its surface. With more increase in ionic strength, because of competition between dye molecules and ions of buffer in interaction with active sites of sorbent, percent adsorption of dyes on sorbent is decreased. So, a concentration of 1.0×10^{-2} mol L^{-1} for buffer solution was selected.

3.5. Effect of contact time of aqueous solution with sorbent

For studying the effect of contact time of aqueous solution with sorbent, aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} solution of each dye with optimum pH values were brought into contact with optimum amounts of sorbent and extraction process was done during different times. As it is seen in Fig. 5, with contact time increasing, percent adsorption of studied dyes on sorbent was increased. RC molecules were almost completely adsorbed during 90 min and MB molecules during 80 min. To prevent any abrupt change in percent adsorption of studied dyes, the times of 100 and 90 min were, respectively, selected as optimum contact times for RC and MB adsorption on sorbent.

3.6. Effect of temperature

In order to study the effect of temperature, aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} of each dye solution

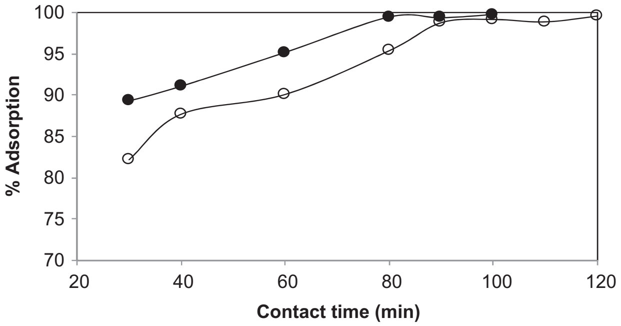

Fig. 5. Effect of contact time of aqueous solution with sorbent; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 1.9, amounts of sorbent: 0.07 g; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 9.5, and amounts of sorbent: 0.06 g.

with optimum pH values were brought into contact with optimum amounts of sorbent and extraction process was done at different temperatures during 30 min. RC adsorption on sorbent was diminished with temperature increasing (Fig. 6). This behavior shows the exothermic adsorption of RC molecules on sorbent. Temperature had no considerable effect on MB adsorption and with temperature increasing, its adsorption was only increased slowly. At a given temperature, Gibbs free energy change (ΔG_0^T), enthalpy change (ΔH_0^T), and also entropy change (ΔS_0^T) of dye partitioning between [C$_8$mim][PF$_6$]-modified silica gel and aqueous solution are related to partition coefficient (K) of dye through following equations:

$$\Delta G_0^T = -RT \ln K \tag{1}$$

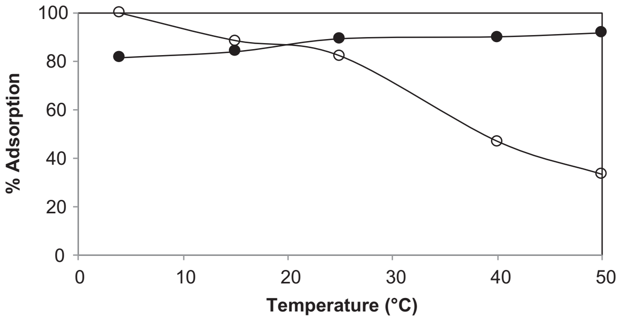

Fig. 6. Effect of temperature; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 1.9, contact time: 30 min, amounts of sorbent: 0.07 g; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} in phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 9.5, contact time: 30 min, and amounts of sorbent: 0.06 g.

$$\ln K = -\frac{\Delta H_0^T}{RT} + \frac{\Delta S_0^T}{R} \tag{2}$$

Therefore, the enthalpy and entropy changes associated with partitioning of studied dyes between [C_8mim][PF_6]-modified silica gel and aqueous solution can be calculated from the slope and intercept of an ln K vs. T^{-1} plot and subsequently the Gibbs free energy change can be obtained by using the above equations. The results are shown in Table 1.

3.7. Desorption of adsorbed dyes on sorbent

As it is seen in Fig. 2, RC molecules at pH values more than 5.0 have almost no adsorption on sorbent. So, buffer solutions with pH values more than 5.0 are suitable solutions for desorption of RC molecules from sorbent. For obtaining the best results and effective desorption of adsorbed dyes from sorbent, pH 9.0 was selected as optimum pH value of eluent solution. Other experiments showed that the complete RC desorption was related to buffer concentrations more than 8.0×10^{-3} mol L^{-1} during 30 min. To prevent any abrupt change in percent desorption of studied dyes, a phosphate buffer solution with pH 9.0 and concentration of 1.0×10^{-2} mol L^{-1} was selected as eluent solution for desorption of adsorbed RC.

In spite of decrease in MB adsorption at acidic pH values (Fig. 2), buffer solutions with acidic pH values have no enough ability for quantitative desorption of adsorbed MB molecules. To determine a suitable solution for MB desorption, HCl solutions with different concentrations were examined. The HCl solutions with concentrations more than 9.0×10^{-1} mol L^{-1} could almost completely remove MB molecules from sorbent surface during 30 min. So, a solution of HCl 1.0 mol L^{-1} was selected as a suitable eluent solution to remove adsorbed MB molecules from sorbent.

3.8. Preconcentration factor

Preconcentration factor is calculated through dividing of breakthrough volume (the maximum volume of aqueous solution containing dye that dye adsorption from this solution is maximum) by minimum volume of eluent solution that can completely remove adsorbed dyes from sorbent [24]. By applying the optimum conditions, different volumes of phosphate buffer solution were added to aliquots of 2.0 mL of 1.0×10^{-5} mol L^{-1} solution of each studied dye. Then, each solution was brought into contact with optimum amounts of sorbent and extraction process was done. As it is shown in Fig. 7, breakthrough volumes for RC and MB solutions were 20.0 and 22.0 mL, respectively. Adsorbed RC molecules on sorbent could almost completely be desorbed by minimum volume of 0.5 mL of phosphate buffer solution with pH of 9.5. Minimum volume of HCl solution of 1.0 mol L^{-1} that could almost completely remove MB molecules from sorbent surface was 1.0 mL. So, calculated preconcentration factors for RC and MB were 40 and 22.0, respectively.

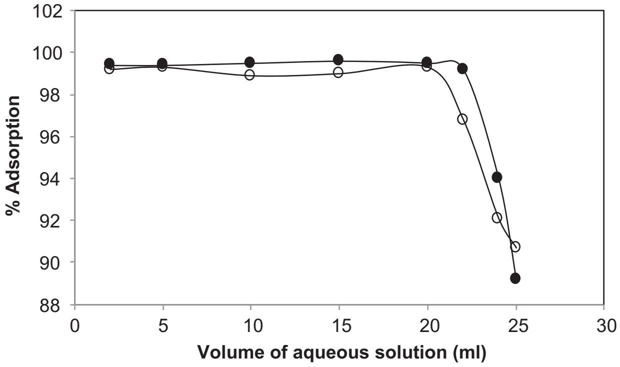

Fig. 7. Effect of volume of aqueous solution containing RC and MB; RC solution (○): 2.0 mL of 1.0×10^{-5} mol L^{-1} in different volume of phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 1.9; amounts of sorbent: 0.07 g, contact time: 100 min; MB solution (●): 2.0 mL of 1.0×10^{-5} mol L^{-1} in different volume of phosphate buffer 1.0×10^{-2} mol L^{-1} with pH 1.9; amounts of sorbent: 0.06 g, and contact time: 90 min.

Table 1
Thermodynamic parameters associated with partitioning of studied dyes between [C_8mim][PF_6]-modified silica gel and aqueous solution

			ΔG_0^T (kJ mol^{-1})					
Dye	ΔS_0^T (kJ mol^{-1})	ΔH_0^T (kJ mol^{-1})	4℃	15℃	20℃	25℃	40℃	50℃
RC	−0.40	−125.06	−14.64	−10.26	−8.26	−6.27	−0.29	3.69
MB	0.02	0.19	−6.56	−6.86	−6.98	−7.10	−7.47	−7.72

3.9. Adsorption capacity of sorbent

To determine the adsorption capacity of sorbent for dyes, aliquots of 2.0 mL of 1.0×10^{-4} mol L^{-1} of RC and MB solutions were brought into contact with sorbent in the optimum experimental conditions. Adsorption capacity of sorbent for RC and MB was 17.0×10^{-4} and 29.0×10^{-4} mmol g^{-1} of sorbent, respectively. These results show more tendency of sorbent for MB adsorption than RC adsorption.

4. Conclusions

Adsorption behaviors of RC and MB as anionic and cationic dyes on $[C_8mim][PF_6]$-modified silica gel as a new sorbent were studied. Results showed that noticeable differences exist in adsorption behaviors of these dyes on sorbent. Quantitative adsorption of RC molecules was done in acidic pH values while about MB, basic pH values were more effective than acidic ones. Adsorption of RC molecules on sorbent was exothermic. Temperature had no considerable effect on MB adsorption. The effects of other parameters such as ionic strength, contact time, and amount of sorbent were also studied. A phosphate buffer solution of 1.0×10^{-2} mol L^{-1} with pH 9.0 and HCl solution of 1.0 mol L^{-1} were selected as suitable eluent solutions for desorption of adsorbed RC and MB molecules, respectively. Preconcentration factor of each dye and adsorption capacity of sorbent for them were also determined.

It is noticeable that the sorbent $[C_8mim][PF_6]$-modified silica can be used for efficient, simple, and inexpensive removal of anionic and cationic dyes from aqueous solutions.

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