

Adsorption of dyes from aqueous solutions onto sand and their kinetic behavior

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Abstract

Three organic dyes namely, Coomassie Blue, Malachite Green and Safranin Orange were removed from solution by adsorption on sand at 298 K. Characteristics of local sand sample used as an adsorbent in this work were initially found from the low-temperature adsorption of nitrogen on sand samples at 77 K. Conditions for maximum adsorption of these dyes on sand sample were then optimized. It was seen that under these conditions, 65–70% of dye could be removed from solution onto the sand surface. Adsorption data was fitted to Freundlich equation for the calculation of various parameters and it was found that for all the three dyes $1/n < 1$, which indicates that adsorption was favorable. The adsorption kinetics followed the pseudo second order equation for all the three dyes investigated in this work with the k values lying in the region of 6.2×10^5 to 3.0×10^6 . The intra-particle diffusion rate coefficient values obtained by using the Morris–Weber equation showed that Malachite Green reached equilibrium faster than Coomassie Blue and Safranin Orange. The diffusion coefficient values calculated for the three dyes were in the range of 7.8×10^{-8} to 9.3×10^{-8} cm²/s and are compatible with other studies reported in the literature. The adsorption behavior of the dyes was also investigated in terms of added cations and anions and it was found that adsorption of Coomassie Blue and Safranin Orange decreased substantially in the presence of sulphate, thiosulphate, acetate, potassium, nickel and zinc ions.

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1. Introduction

Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Commonly suggested methods include biodegradation, photocatalytic, photolytic and advanced oxidative degradation of these solutions [1–5]. A considerable amount of interest has recently been focused on using the adsorption technique for the removal of some dyes from solutions on various adsorbent surfaces such as clays [6,7], flyash [8,9], peat [10], activated carbon [11–13], polymers [14,15] and alumina [16,17]. The process is known to be simple and efficiently treat dyes in concentrated form. Although the adsorption technique is versatile and easy to adopt in practical forms, the adsorbent materials are either costly or cannot be regenerated for large-scale applications. There is thus a growing need to use a low cost, renewable and easily available adsorbent material for such purposes. One potential adsorbent

material can be sand, which can be utilized for such purposes as it can also bring unlimited number of economic and environmental benefits to the industrial waste water treatment. Sand has been used as an adsorbent in removing inorganic ions from solutions [18,19], however, there is limited study available on sand surfaces for the removal of dyes [20,21].

The objective of the present study was to assess the ability of locally available sand for the removal of Coomassie Blue (CB), Malachite Green (MG) and Safranin Orange (SO) from aqueous solutions. The study was carried out with the aim to optimize conditions for maximum removal of these dyes from aqueous solutions on sand surface in the absence and presence of various ions. Besides this, the adsorption data was fitted to various equations to obtain constants related to the equilibrium and kinetics of the adsorption phenomena.

2. Experimental

Organic dyes with a labeled purity of more than 98% were procured from either Sigma or Fluka and used as such. Dye solutions of desired concentrations were made in deionized

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water. Preliminary experiments were carried out on these dye solutions to ascertain the working concentration range in the Lambert–Beer region. All the dye solutions are colored and show intense absorption peaks in the visible region. The λ_{\max} value of these dyes are; CB = 585 nm, MG = 618 nm and SO = 525 nm. A change in intensity of an absorption peak of a given dye solution in an adsorption process can thus be targeted to characterize the removal of dye from the solution.

In the present studies, sand was used as an adsorbent material because of its enormous availability in the local environment. Sand sample was procured from the dunes in the vicinity of Al-Ain city located in the south-eastern region of UAE. The sand sample was not treated in any other way except sieving it to obtain different portions of it.

Following composition of the sand sample was obtained after sieving; Coarse sand, 0.02%; 350 μm , 0.41%; 250 μm , 65.75%; 180 μm , 21%; 125 μm , 7.5%; 88 μm , 3.6% and the remaining fraction below 88 microns. Since the sand fraction of particle size 250 μm was the major portion of the sample, it was therefore used in the present study. The BET surface area of this sand fraction was found to be 5.226 m^2/g by the nitrogen adsorption method [22]. Average pore diameter for this fraction was determined to be 37.25 Å, whereas the micropore area and micropore volume were estimated to be 3.50 m^2/g and 1.65 $\times 10^{-3}$ cm^3/g , respectively. However no attempt was made to determine the mineral composition of the sand sample. Removal of dyes from aqueous solutions on sand surface was calculated by monitoring the changes in absorption values and hence the concentrations of the dye solutions. The absorption intensity changes corresponding to λ_{\max} of the dye solution were monitored on a CARRY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell.

Initially, dye stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a flask followed by necessary dilutions of this stock solution. A given amount of sand sample (usually 0.05–0.1 g) was then added to 5 mL of the diluted solution. The contents of the dye solution were then agitated for a given amount of time using a magnetic stirrer operated at a constant speed. The contents were then centrifuged and the supernatant solution was taken out with a pipette and monitored instantaneously on a spectrophotometer for absorption. The change in absorbance of the dye solution was then used to calculate the dye concentration in solution and the percentage adsorption of the dye on sand.

$$\text{Dye adsorption (\%)} = (1 - A_f/A_i) \times 100 \quad (1)$$

where A_i and A_f are the initial and the equilibrium concentration values of the dye solution, respectively.

Since the solution pH has a considerable effect on dye removal, the pH of the solution was also changed to monitor the adsorption behavior of dyes on sand samples. The pH was changed by adding incremental amounts of either dilute HCl or NaOH to the solution. Changes in absorption was then used to calculate the concentration and adsorption for each dye used in this study.

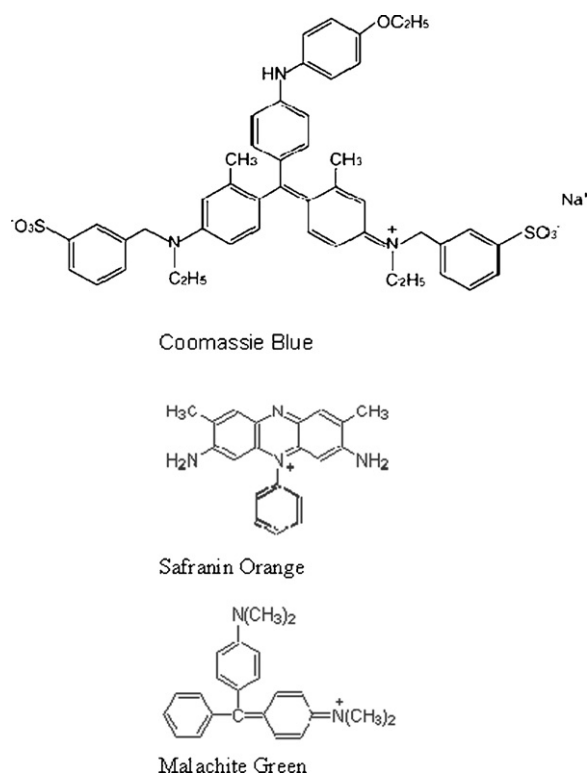


Fig. 1. Molecular structures of the dyes.

3. Results and discussion

Three dyes namely Coomassie Blue (CB), Malachite Green (MG) and Safranin Orange (SO) were investigated in this work. Their structures are given in Fig. 1. Conditions for maximum removal of these dyes from aqueous solution by adsorbing them on sand were initially optimized. In this regard, amount of sand, concentration of the dye solution, pH and the shaking time were varied over a wide range. To optimize each parameter, one of the parameters (e.g., mass of sand) was varied while keeping other conditions (e.g., concentration of dye, shaking time, etc.) the same. The same procedure was adopted to optimize the remaining conditions. It may be mentioned here that adsorption of dyes increased with an increase in their initial concentration value and became constant after the equilibrium time. The results of such studies for all these dyes are summarized in Table 1. These optimized conditions were then fixed for subsequent studies. The adsorption of dyes on sand can most probably arise by both the physical or chemical processes. Fig. 2 shows the effect of pH on percentage adsorption of Coomassie Blue on sand. The adsorption of this dye was found to be maximum in neat solution as

Table 1
Optimized conditions of various dye adsorptions on sand

| Dye | Mass of sand (g) | [Dye]/ μM | Shaking time (min) | pH | % Adsorption |
|-----------------|------------------|----------------------|--------------------|-----|--------------|
| Coomassie Blue | 0.2 | 20 | 20 | 6.0 | 65 |
| Malachite Green | 0.03 | 20 | 4 | 4.8 | 70 |
| Safranin Orange | 0.03 | 20 | 4 | 5.2 | 70 |

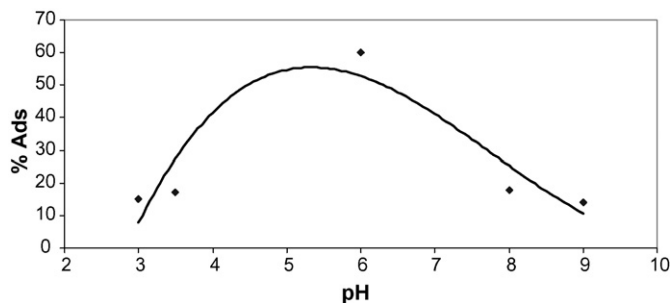


Fig. 2. Effect of pH on %adsorption of Coomassie Blue on sand.

compared to that in acidic or basic media. Similar results were obtained for the other two dyes used in this study.

Since industrial effluents are always contaminated with various additives such as inorganic salts, it is therefore important to study the effect of these ions on the adsorption property of dye solutions. The adsorption of dye in the presence of anions (added as sodium salts) and cations (added in the nitrate form) were therefore carried out. The concentrations of all these ions in solution were kept at 1×10^{-3} M in each case. The results are tabulated in Table 2. It can be seen that adsorption of Malachite Green remained largely unchanged in the presence of both anions and cations (except nickel and zinc), whereas, all the ions had a substantial effect on the adsorption of Coomassie Blue and Safranin Orange. Thus these ions should be removed from the dye solutions prior to their adsorption on sand.

The adsorption of dyes from aqueous phase onto a solid surface can be well described as a reversible reaction under an equilibrium condition established between the two phases [23]. The rate at which the species are removed from solution onto an adsorbent surface is an important factor for designing treatment plants. Thus in order to characterize the adsorption process of the dyes on sand, three different kinetic models were investigated namely the pseudo first order, pseudo second order and the mass transport and intra particle diffusion model. These models are commonly used to describe the adsorption behavior of pollutants on solid surfaces. Parameters of the kinetic models were extracted from the experimental data of this study.

Table 2

Effect of various ions on the percent adsorption of various dyes on sand under optimized conditions shown in Table 1

| Name of dye | Anions (%adsorption) | Cations (%adsorption) |
|-----------------|----------------------|-----------------------|
| Coomassie Blue | Sulphate (12) | Potassium (15) |
| | Thiosulphate (–) | Nickel (15) |
| | Acetate (11) | Zinc (13) |
| Malachite Green | Sulphate (64) | Potassium (70) |
| | Thiosulphate (70) | Nickel (47) |
| | Acetate (73) | Zinc (23) |
| Safranin Orange | Sulphate (22) | Potassium (27) |
| | Thiosulphate (22) | Nickel (28) |
| | Acetate (25) | Zinc (8) |

Anions were added as sodium salts, whereas cations were added as nitrates (concentration of each ion in solution = 1×10^{-3} M).

Table 3

Kinetic parameters for the pseudo second order equation

| Name of dye | k_2 (g/mol min) | q_e (mol/g) | R^2 |
|-----------------|-------------------|-----------------------|-------|
| Coomassie Blue | 3.0×10^6 | 3.33×10^{-7} | 0.976 |
| Malachite Green | 6.2×10^5 | 1.93×10^{-6} | 0.934 |
| Safranin Orange | 2.0×10^6 | 5.0×10^{-7} | 0.934 |

In the first instance pseudo first order reaction model was used which in general is given by [24]

$$q_t = q_e \{1 - \exp(-k_{1,ads}t)\} \quad (2)$$

In the linear form this equation can be written as

$$\ln(q_e - q_t) = \ln q_e - k_{1,ads}t \quad (3)$$

where q_e and q_t are amounts of dye adsorbed at equilibrium and at any time t , $k_{1,ads}$ the pseudo first order rate constant and t is the time.

In many cases the above equation does not fully describes the adsorption kinetics. In such cases, a pseudo second order equation can be used, which is given by [24]

$$\frac{t}{q_t} = \frac{1}{k_{2,ads}q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are amounts of dye adsorbed at equilibrium and at any time t , and $k_{2,ads}$ is the pseudo second order rate constant.

The adsorption data did not fit linearly to pseudo first order kinetics over the entire region as shown from Fig. 3A–C. However, the data fitted very well to pseudo second order kinetic equation as seen from Fig. 3D–F. The rate constant values, $k_{2,ads}$ along with the correlation coefficients are summarized in Table 3 for the three dyes used in the present work.

Experimental data for the dye adsorption on sand was also subjected to Freundlich equation, which has the following form [13]

$$\log A_{ads} = \log A + n \log A_i \quad (5)$$

where A_i and A_{ads} are the concentrations of the dye in solution, and on the sand surface at equilibrium, respectively, and A the Freundlich capacity factor and n is the Freundlich intensity parameter for a particular system. A plot of $\log A_{ads}$ versus $\log A_i$ should give a straight line, whereas, the slope and the intercept of this line will give the value of n and A .

Graphical conformity to this equation for the three dyes is shown in Fig. 4A–C, whereas, the values of n , A and other constants obtained in each case are shown in Table 4.

Table 4

Values of various constants of Freundlich isotherms

| Name of dye | Freundlich coefficients | | |
|-----------------|-------------------------|-------|-------|
| | n | A | R^2 |
| Coomassie Blue | 1.83 | 0.820 | 0.940 |
| Malachite Green | 1.045 | 0.694 | 0.997 |
| Safranin Orange | 1.044 | 0.729 | 0.996 |

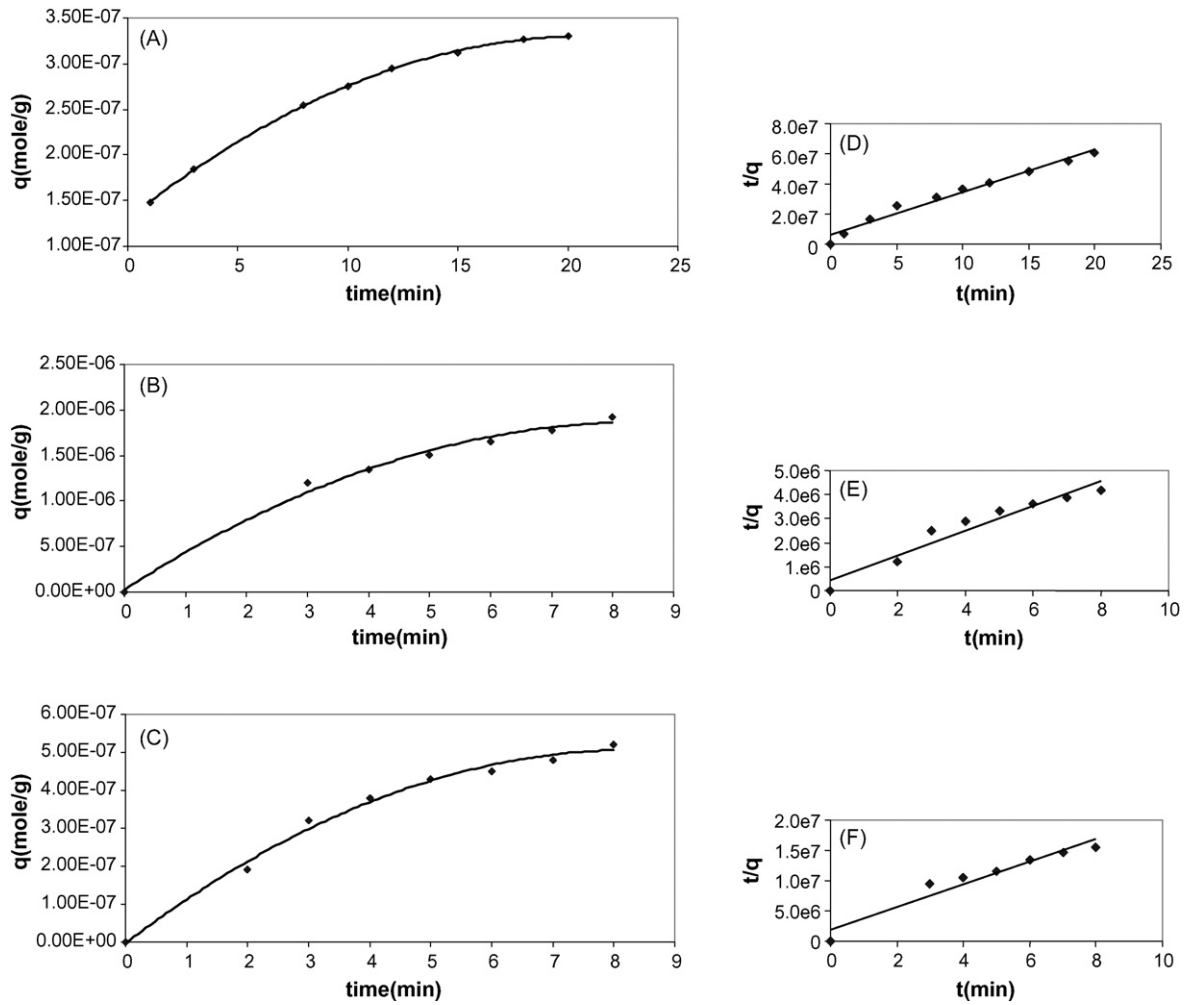


Fig. 3. (A) Pseudo first order kinetics of CB adsorption on sand. (B) Pseudo first order kinetics of MG adsorption on sand. (C) Pseudo first order kinetics of SO adsorption on sand. (D) Pseudo second order kinetics of CB adsorption on sand. (E) Pseudo second order kinetics of MG adsorption on sand. (F) Pseudo second order kinetics of SO adsorption on sand.

The Freundlich isotherm is applicable to heterogeneous systems and reversible adsorption [12]. The n value in this equation suggests deviation from linearity. If $n=1$, the adsorption is homogeneous and there is no interaction between the adsorbed species. If $1/n < 1$, the adsorption is favored and new adsorption sites are generated. If $1/n > 1$, the adsorption is unfavorable, bonds become weak and adsorption capacity decreases. In our studies, we have found that for all the three dyes $1/n < 1$, which indicates that adsorption is favorable; though it is more favorable in the case of Malachite Green ($1/n = 0.55$) as compared to other dyes.

Most of the adsorption processes may be described by either the external mass transfer (boundary layer diffusion) or intra-particle diffusion model. The later is given by the Weber–Morris equation [18]

$$q_t = k_i t^{1/2} \quad (6)$$

where the parameter k_i is the diffusion coefficient value, t the time and q_t is the amount of dye adsorbed. Fig. 5A–C shows the data fitting to the above equation for the three dyes, whereas, the diffusion coefficient rate values, k_i , obtained from this equation

are tabulated in Table 5 for the three dyes investigated in the present study. These values are comparable and one can see that the diffusion rate coefficient for Malachite Green is higher than Safranin Orange and Coomassie Blue, thus leading it to reach equilibrium faster.

The half-adsorption time $t_{1/2}$ is another parameter which can be calculated from the equilibrium concentration and the diffusion coefficient rate values. This was calculated by using the following equation [25]

$$t_{1/2} = 1/k_2 q_e \quad (7)$$

Table 5
Diffusion coefficient values for different dyes as calculated from Morris–Weber equation

| Name of dye | k_i (mol/g h ^{1/2}) | R^2 | $t_{1/2}$ (min) | D (cm ² /s) |
|-----------------|---------------------------------|-------|-----------------|--------------------------|
| Coomassie Blue | 6.0×10^{-7} | 0.983 | 1.00 | 7.8×10^{-8} |
| Malachite Green | 5.0×10^{-6} | 0.999 | 0.84 | 9.3×10^{-8} |
| Safranin Orange | 1.0×10^{-6} | 0.997 | 1.00 | 7.8×10^{-8} |

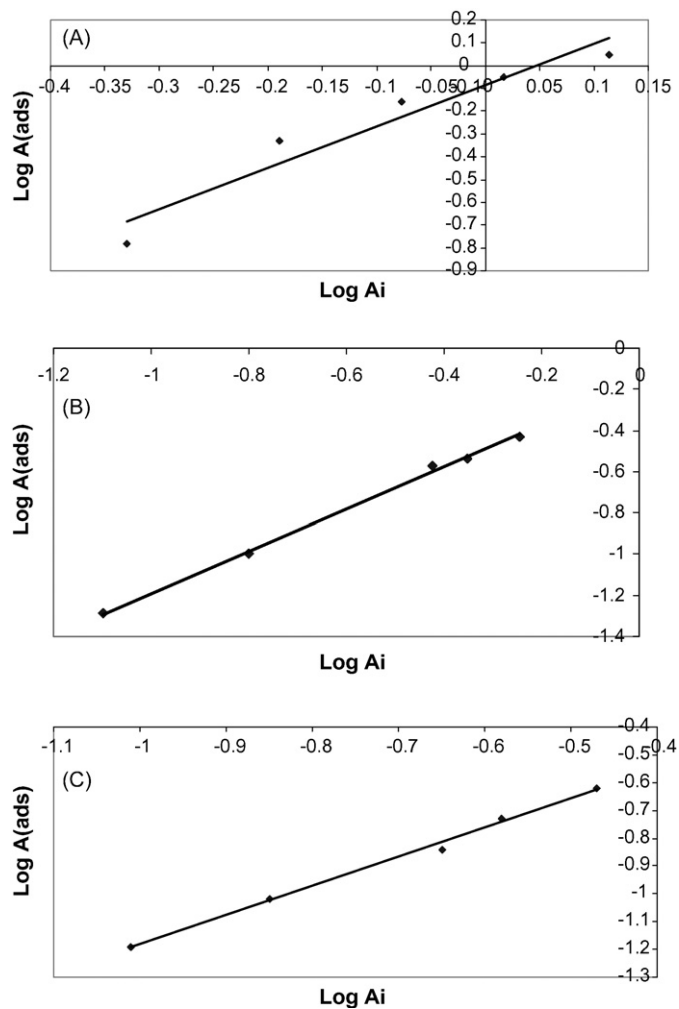


Fig. 4. (A) Application of Freundlich equation to the adsorption of Coomassie Blue on sand. (B) Application of Freundlich equation to the adsorption of Malachite Green on sand. (C) Application of Freundlich equation to the adsorption of Safranin Orange on sand.

The diffusion coefficient for the intra particle transport of the three dyes were also calculated by using the following relationship [25]

$$t_{1/2} = \frac{0.03r^2}{D} \quad (8)$$

where $t_{1/2}$ is the half life in seconds as calculated from Eq. (7), r the radius of the adsorbent particle in centimeters and D is the diffusion coefficient value in cm^2/s . For the calculation of r value, it was assumed that the solid phase consists of particles which are spherical in nature. Calculated values of $t_{1/2}$ and D are given in Table 5. The D values obtained in our study are comparable to those available in the literature [25]. For example, the D values for phenol and benzene on wood are reported to be 9×10^{-8} and 8×10^{-9} cm^2/s , respectively, and that of astrazone blue and telon blue on wood were found to be 6×10^{-13} and 3.0×10^{-13} cm^2/s , respectively [25,26].

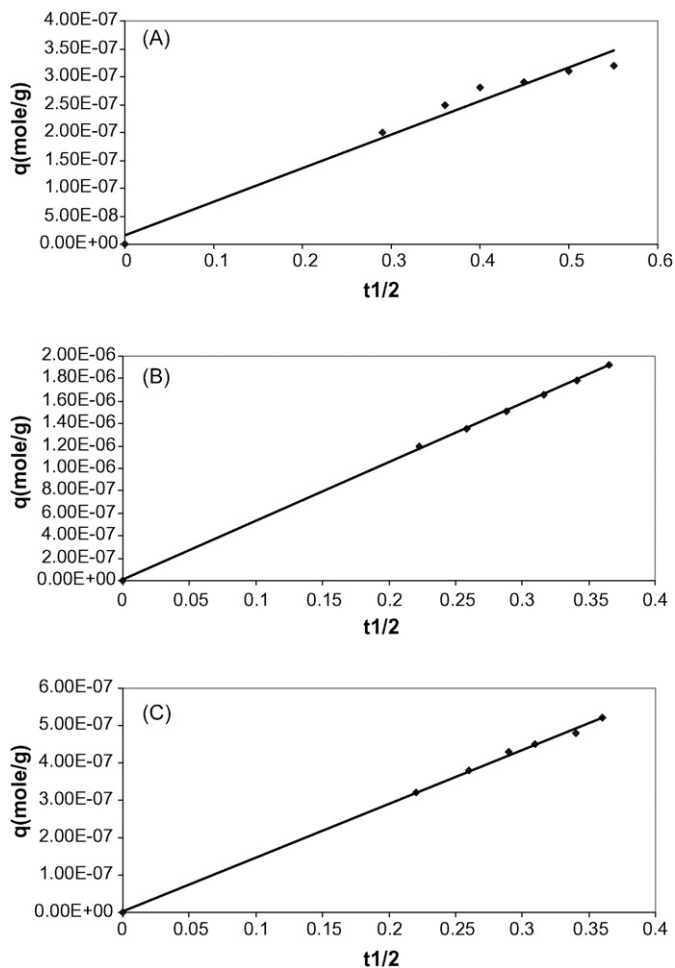


Fig. 5. (A) Application of Morris–Weber equation to the adsorption of Coomassie Blue on sand. (B) Application of Morris–Weber equation to the adsorption of Malachite Green on sand. (C) Application of Morris–Weber equation to the adsorption of Safranin Orange on sand.

4. Conclusion

Removal of various organic dyes from aqueous solution onto sand surface was carried out at room temperature. The conditions of adsorption of these dyes were optimized. It was seen that under these conditions, a maximum of 65–70% dye could be removed from the solution onto the sand surface. The adsorption of the two dyes namely Coomassie Blue and Safranin Orange decreased substantially in the presence of all the added ions, i.e. sulphate, thiosulphate, acetate, potassium, nickel and zinc ions. The adsorption data for all the dyes investigated in this work fitted well to Freundlich equation. Sorption kinetic data revealed that the adsorption kinetics followed the pseudo second order equation for all the three dyes investigated in this work. Furthermore, the Morris–Weber equation revealed that the diffusion coefficient values were comparable, and that Malachite Green reaches the equilibrium faster than the other two dyes.

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