

Transport, sorption and desorption of organic dye through quartz sand particles

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Abstract

In the present work, step-input column experiments were carried out to investigate the transport, sorption and desorption mechanisms of Methylene Blue (MB) through quartz sand (QS) porous medium. Hence, five parameters related to the adsorption experimental conditions, such as the ionic strength, the pH, the temperature, the flow rate and the nature of divalent cations present in the aqueous phase, were varied in order to elucidate the adsorption-desorption mechanisms of MB through the QS medium. The MB adsorbed amount was found to decrease by decreasing either the pH, in the range 9.5-4, or the temperature, in the range 333-293°K. Similar decrease of MB adsorbed amount was obtained by increasing the flow rate, Q , in the range 45-90 ml. h⁻¹, or by increasing the affinity of the divalent cation (Ca²⁺, Cu²⁺, Zn²⁺ and Ba²⁺) toward the quartz surface. However, slight decrease in the MB adsorbed amount, was observed by increasing the ionic strength, in the range 10⁻³-10⁻¹M. The overall data indicate that, electrostatic interaction forces, which occur between the cationic organic pollutant and the negative surface of the quartz substrate, mainly control the adsorption process. In addition, the increase of the adsorbed amount with the temperature, suggests that the adsorption is endothermic in nature.

Keywords: Quartz Sand, Methylene Bleu, sorption, desorption, depollution, environment, column experiments

Introduction

The release into various aquatic systems of dyes that result from different sources such as textile industries, paper and pulp industries, dye industries, pharmaceutical industries, tannery, and Kraft bleaching industries, lead to the undesirable environmental pollution. In particular, the discharge of organic dye-containing effluents, such as aromatic compounds, into the water environment is unwelcome, not only because of their colour, but also because almost of them and their breakdown products, have toxic, carcinogenic or mutagenic effects on aquatic life and on human's health (McKay et al. 1985; Gregory et al. 1991; Liakou et al. 1997). Thus, for reasons related to human health and to protect the environment, the removal of synthetic dyes from aqueous effluents is of great importance. Various methods of dye removal, such as, coagulation (Vandevivere et al. 1998), electrochemical deposition (Martinez-Huitle and Brillas 2009), adsorption on different adsorbents, chemical decomposition by oxidation, photodegradation and microbiological discoloration, were used. Biological wastewater treatment processes, were found to be ineffective for the removal of dyes (Walker and Weatherley 1997). However, the removal of dyes from water by their adsorption on solid supports is one of powerful and low cost treatment processes. In this method, adsorbents such as activated carbon and clays are used. Activated carbon is the most successfully used adsorbent (Jia-Ming and Chia-Yuan 2001; Yang and Al-Duri 2001; Kannan and Sundaram 2001; Karaca et al. 2008; Walker and Weatherley 1998), but its cost limits its use, especially in developing countries. Therefore, there is a need to find an effective and low cost material as an alternative adsorbent for removing the dyes from water. Among the materials that fulfil these requirements, natural adsorbents such as clays and clay minerals, (Dogan and Alkan 2003; Ho and Chiang 2001; Ghosh D, Bhattacharyya 2002; Rytwo and Tropp 2002), zeolites, (Benkli et al. 2005), agricultural materials, (McKay et al. 1988; Robinson et al. 2002; Annadurai et al. 2002), cellulosic materials, and various industrial wastes have been investigated in various water depollution studies, (Wang et al. 2004). However, very few studies have focused on the use of quartz sand, as an adsorbent for the removal of dyes from water (Espantaleón et al. 2003; Al-Asheh et al. 2003). The aim of the present work is to study the adsorption of methylene blue (MB) from water onto the surface of quartz sand or Fontainebleau sand, which is a cheap and abundant adsorbent. The use of quartz sand as adsorbent will allow us to mimic the natural conditions found in hydro systems (soils, aquifers.). In addition, the purpose of this study is to elucidate the mechanism of MB adsorption on the quartz surface, and to investigate the

influence on the dye retention of various parameters such as the ionic strength, the flow rate, the pH of the aqueous phase, the temperature, and the nature of the divalent cations present in the aqueous phase.

Material and methods

Porous medium and Dye (Methylene Blue, MB)

The quartz sand used is a Fontainebleau sand purchased from Prolabo (Fig. 1). It contains mainly quartz according to the elementary analysis (Si = 45.03%, O = 52.18%, C <0.3%, H <0.3%, Ca = 100 ppm, 185 ppm = Al, Mg <10 ppm, Na <50 ppm, Fe = 150 ppm). The mean grain diameter, D_m , of the sand, is $D_m = 120 \pm 12 \cdot 10^{-6}$ m, as determined by Scanning Electron Microscopy (SEM) image analysis (Fig. 1), and its isoelectric point IEP = 2.44, as measured by microelectrophoresis. In addition, the sand's surface area was measured by using Micromeritics ASAP 2000 surface area analyser. The adsorption-desorption isotherms were obtained by measuring, respectively, the adsorbed and desorbed volumes of N_2 at 77 K and relative pressure P/P_0 ranging from 0 to 1. The sample specific surface area is $5.1 \pm 0.1 \text{ m}^2 \cdot \text{g}^{-1}$, as determined in the relative pressure range $0.05 < P/P_0 < 0.35$ according to the BET method (Brunauer et al. 1938). It should be noted that in the present work, the quartz sand specific surface area, was also measured in aqueous medium by titration of the negatively charged sand particles by the MB cations. The data gives a specific surface area value of $6.6 \pm 0.1 \text{ m}^2 \cdot \text{g}^{-1}$, which is 25% higher than the value found for the quartz sand powder by the BET method.

The dye used is methylene blue (MB), supplied from Merck. This basic dye belongs to the class of thiazine dyes. Its chemical formula is $C_{16}H_{18}ClN_3S$. The MB dye is used in various chemical industries, such as textile dyeing, biology, pharmacy, and as an antiseptic. The maximum solubility of MB in water, at 20°C, is equal to 50 g. L^{-1} .

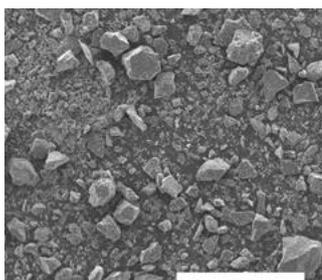


Fig. 1. SEM image of natural quartz sand particles. The scale bar at the bottom right is $500 \cdot 10^{-6}$ m.

Reactants

All chemical reagents employed in this work are of purity >99.5%, and the aqueous solutions were prepared using, in all instances, bidistilled water. The ionic strength was fixed by using sodium chloride (NaCl) as salt, (except when indicated). The pH values of the samples were varied in the range 4; 6 and 9.5, by adding to the aqueous phase small amounts of sodium hydroxide (NaOH) or hydrochloric acid (HCl) aqueous solutions. Aqueous solutions of calcium chloride ($CaCl_2$), copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$) and barium chloride ($BaCl_2$), were prepared and used to study the effects of nature of the divalent cations on the transport and deposition of MB in a saturated porous medium of quartz sand.

Experimental device

The experimental device consisted of three following components:

- a cylindrical column containing the quartz sand made of Altuglas and fitted with a jacket thermostated (length, $L=10$ cm; inner diameter, $D=1$ cm).
- a syringe pumps (Perfusor segura) to control the flow rate.
- a fraction collector, and a pH-meter allowing the continuous measurement of pH at the column outlet.

The experimental device, held vertically, is fed from bottom to top, in order to facilitate degassing and to reduce the non-uniform flow rise. It should be noted that all the materials used in the experimental device, had demonstrated by preliminary experiments to be non adsorptive toward MB in the conditions used.

Experiments were conducted at room temperature ($20 \pm 2^\circ\text{C}$) (except when indicated). In addition, the bottle containing the MB injected solution is made with amber glass to prevent photochemical degradation of the dye molecule, and it was kept under nitrogen atmosphere during all the column experiments.

Column experiments

The column pore volume and porosity were determined by using a Tracer (Potassium Iodide, KI, 20 mg. L^{-1}). The column outflows for conservative tracer experiments were monitored with a UV-visible spectroscopy at $\lambda = 234 \text{ nm}$. Typical column parameters were: $V_p = 2.29 \text{ mL}$ and $\varepsilon = 0.42$, for $9.5 \pm 0.2 \text{ g}$ sand mass.

Injecting aqueous solutions through the porous medium

In a first step, the porous medium is saturated by continuous injection, at constant flow and during one day, of MB free aqueous solution (blank experiments at given pH and ionic strength, I), until a steady state is reached. Then, in a second step, MB solution is injected continuously, under the same conditions as those made for the blank tests into the column, until equilibrium. In a third step, elution of sorbed MB is performed with MB free aqueous phase having the same values of pH and ionic strength, than those previously used in injecting the dye into the porous medium.

Collecting and analysing the column outlet fractions

The fractions at the outlet of the column were collected at constant volume, and their fluorescence excitation spectra were measured by using a spectrofluorimètre (Shimadzu RF-5001). The fluorescence excitation spectra were recorded at the excitation wavelength range 450-720 nm and emission wavelength = 750 nm. From the integrated fluorescence intensities of, the outlet or effluent fractions, and the known MB aqueous solutions series (recorded under identical conditions), the MB residual concentrations in the collected fractions, C, were then determined.

In the following, only the breakthrough curves dealing with the effect of the ionic strength, I, will be presented. These curves will be expressed as C/C_0 versus V/V_p . The ratio (C/C_0) is the normalized effluent concentration and the (V/V_p) is normalized injected solution volume; C is the total MB concentration measured in each effluent fraction, V is the cumulated volume eluted since the beginning of the MB injection, V_p the pore volume, and C_0 the inlet MB concentration. From the breakthrough curves dealing, with the effects of various parameters (flow rate, pH, temperature and the nature of divalent cation), we determined the amounts of MB adsorbed, Q_{ads} , and the MB desorbed, Q_{des} , at the quartz sand-aqueous solution interface. Note that in all the experiments, each breakthrough curve is composed of two fronts: an adsorption front followed by a desorption one.

Results and discussions

Effect of the ionic strength

Fig. 2 shows the adsorption and desorption fronts of the breakthrough curves dealing with the effect of the ionic strength, I. This figure indicates clearly the influence of ionic strength on the transport, adsorption and desorption of methylene blue (MB) through the quartz sand column. As can be seen in Fig. 2a, they are small differences between the adsorption fronts obtained at various values of the ionic strength. The sorption of MB on the quartz grains in the presence of NaCl salt can be explained by competition between the MB and Na^+ cations, towards the negative sites of the quartz surface ($\text{pH} > \text{IEP}$), and the zeta potential magnitude, which decreases, as the concentrations of various ionic species, increase at the quartz sand-solution interface. The elution curves as depicted in Fig. 2b, show at the beginning the presence of plateaus which are followed, at $V/V_p > 20$, by diffuse fronts of desorption.

The calculated values of the MB amounts sorbed, Q_{ads} , and released, Q_{des} , at three values of the ionic strength, I, are presented in Table 1, which shows that Q_{ads} decreases slightly when the ionic strength, I, of the solution increases. The sorption of MB on the quartz grains in the presence of NaCl salt can be explained by competition between the MB and Na^+ cations, towards the negative sites of the quartz surface ($\text{pH} > \text{IEP}$), and the zeta potential magnitude, which decreases, as the concentrations of various ionic species, increase at the quartz sand solution interface. The MB adsorption on the quartz surface

results from the ionic nature of the interaction occurring between the MB cations and the negative surface sites of the quartz sand (Jada et al. 2006).

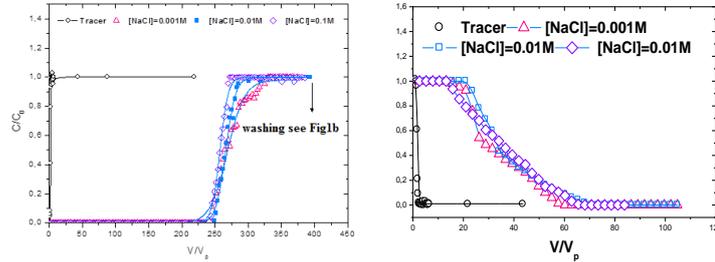


Fig. 2. Effect of the ionic strength, I as fixed by NaCl, on MB adsorption (Fig 2a, left) and desorption (Fig 2b, right) through quartz sand. Initial MB concentration, $C_0=1$ ppm; $\text{pH}=6$, flow velocity, $Q=60$ ml/h, temperature $T=293^\circ\text{K}$.

Table 1: Effect of the ionic strength on the adsorbed, Q_{ads} , and the desorbed, Q_{des} ,

Ionic strength, I (mol. L ⁻¹)	Q_{ads} (mg/m ²)	Q_{des} (mg/m ²)
0.001	0.125	0.015
0.01	0.120	0.018
0.1	0.117	0.018

Effect of the flow velocity

The MB adsorbed and released amounts, respectively, Q_{ads} and Q_{des} , at the quartz sand-water interface, and at three different flow velocities values, are presented in Table 2, and were found to increase both when the flow rate, Q , decreases from $Q = 90$ ml/h to $Q=45$ ml/h.

Table 2: Effect of the flow rate, Q , on the adsorbed, Q_{ads} , and the desorbed, Q_{des} , amounts of MB through QS, $C_0= 1$ ppm, $\text{pH}= 6$, $T=293^\circ\text{K}$, ionic strength, $I = 10^{-3}\text{M}$ (NaCl).

Flow rate, Q (ml.h ⁻¹)	Q_{ads} (mg/m ²)	Q_{des} (mg/m ²)
45	0.166	0.02
60	0.116	0.016
90	0.076	0.016

These variations may be due to the decrease, at high flow rate, of the diffusion and the penetration of the MB solute, to the quartz sand surface. Qualitatively, the Peclet number, Pe , which is a relevant parameter in the study of transport phenomena in fluid flows, represents the ratio of two time characteristics, one characteristic time corresponding to the transfer by convection and an other one to the transfer by diffusion. The Peclet number, Pe , encompasses in a dimensionless form, the impact of both the flow rate and the particle size, on the MB adsorbed mass on the quartz sand surface (Rousseau et al. 2008).

Moreover, it was shown that the collection efficiency, η , defined for a spherical collector, as the ratio between, the flow of particles retained by the collector and the incident flux, is related to Pe by a power law having an exponent of $-2/3$ or -1 , depending on whether the deposit is limited, respectively, by diffusion (DLD) or by reaction (RLD) (Rousseau et al. 2008). Thus, according to these power laws, the fraction of MB retained on the quartz surface decreases when the flow rate, Q , increases. Our experimental data are in a good agreement with the theoretical predictions using the colloidal approach. Our results agree also with the data reported by others authors (Lin et al. 2004). According to these authors, the increase in the flow rate, Q , disadvantages the acidic dye adsorption on montmorillonite. Our findings are consistent with the work reported by (Benkli et al. 2005), showing that the adsorption of hexadecyl trimethyl ammonium bromide on zeolites, depends on the flow rate. The effect of flow rate on the retention of MB, results from the duration time when the fluid is in contact with the quartz surface (contact time). Thus, when the flow rate is low, the number of adsorbed MB cations on the solid surface is higher, as resulting from the long contact time occurring between the fluid molecules and the quartz surface.

Effect of the aqueous phase pH

We carried out adsorption experiments of MB on the quartz sand surface, at three values: of the aqueous phase pH: pH = 4, pH = 6 and pH = 9.5. As shown in Table 3, both Q_{ads} and Q_{des} were found to increase with the increase of the aqueous phase pH.

Table 3: Effect of the aqueous phase pH, on the adsorbed, Q_{ads} , and the desorbed, Q_{des} , amounts of MB through QS, $C_0= 1$ ppm, $T=293^\circ\text{K}$, ionic strength, $I = 10^{-3}\text{M}$ (NaCl), flow rate= 60 ml/h.

pH	Q_{ads} (mg/m^2)	Q_{des} (mg/m^2)
4	0.104	0.016
6	0.116	0.016
9.5	0.240	0.048

The observed increases of Q_{ads} and Q_{des} with the increase of the aqueous phase pH, as shown in Table 3, indicate that the pH is a parameter that strongly affects the adsorbed MB amount. The influence of the aqueous phase pH on the variation of the MB sorbed amount, results in the bonding forces involved in the formation of the MB-silica complex. Such bonding interactions include electrostatic, as well as Van der Waals forces (Kaouna et al. 1987). Others authors (Kar et al. 1991), have reported similar pH effect, on the adsorption of dye molecules, at mineral-water interface. According to these authors, the dye adsorption capacity on silicates increases with increasing the pH of the aqueous phase. Moreover, it has been found recently, (Tsai et al. 2005) that the adsorption of basic dye from aqueous solution onto clay surface, reached its maximum value in basic medium (i.e., at pH = 10).

Effect of temperature

The influence of the temperature on the transport of the MB basic dye through the porous medium was investigated and the adsorbed Q_{ads} ; and desorbed, Q_{des} , MB amounts were calculated from the obtained breakthrough curves. The data are presented in Table 4 and indicate that an increase in the temperature from 293 °K to 333 °K, leads to an increase in Q_{ads} from 0.12 to 0.17 mg/m^2 , i.e. an increase of about 42%. However, as can be shown in Table 4, the same increase in temperature does not show significant change of Q_{des} .

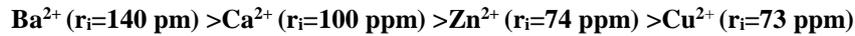
Table 4: Effect of the temperature, T, on the adsorbed, Q_{ads} , and the desorbed, Q_{des} , amounts of MB through QS, $C_0= 1$ ppm, pH=6, ionic strength, $I = 10^{-3}\text{M}$ (NaCl), flow rate= 60 ml/h.

Temperature, T (°K)	Q_{ads} (mg/m^2)	Q_{des} (mg/m^2)
293	0.124	0.016
313	0.150	0.020
333	0.166	0.016

Such dye behaviour proves that the adsorption of MB at the quartz sand aqueous solution interface is an endothermic process. The same thermal behaviour was observed by others authors (Ghosh and Bhattacharyya 2002), when they studied the adsorption of MB on kaolinite. In additions, others authors (Dogan and Alkan, 2003), examined the retention of methyl violet onto perlite, and they found that the rate of methyl violet adsorption increased with increasing temperature and pH of the aqueous phase. The data in table 4 can be explained by the fact that an increase of the temperature leads to an increase of thermal agitation, and also to an increase of the diffusion rate of the ions, resulting in an enhancement of the exchange, and/or displacement, of Na^+ ions, immobilized near the surface solid, by MB cations. Finally, the adsorption of MB on the quartz sand particles involves two main steps: a first transport step, during which the MB molecules diffuse from the aqueous phase to the quartz surface, and a second step (anchoring or binding step) in which the MB molecules adsorb on the solid surface. The kinetics of transport and binding of MB molecules at solid liquid interface, are controlled by different factors, such as ionic strength, pH of the aqueous phase, and the temperature of the medium.

Effect of the nature of divalent cations present in the aqueous phase

In this experiment series, we examined the effect of divalent metal ions on the MB adsorption from water onto quartz sand. The divalent cations used, were in the form of metal chloride salts (CaCl_2 , CuCl_2 , ZnCl_2 and BaCl_2), at a concentration of 10^{-3} M. The Q_{ads} and Q_{des} were calculated from the mass balances of the breakthrough data, and their variations with the divalent cation nature, are presented in Fig. 3. The results show that the MB adsorbed mass, Q_{ads} , decreases in the sequence: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$. This behaviour may be explained by the cation affinity toward the solid support. Thus, the saturation of the quartz sand by the divalent cations ($\text{Me}^{2+} = \text{Ca}^{2+}$, Cu^{2+} , Zn^{2+} and Ba^{2+}) reduce the number of the solid negative sites, resulting in reduction of the electrostatic attraction between the MB cations and the solid surface. However, the decrease in the electrostatic attraction between the MB cations, and the solid surface depends on the ionic radius, r_i , of the divalent cation, Me^{2+} , present in the aqueous solution. Thus, according to Coulomb's law, the divalent cation, Me^{2+} , having the largest ionic radius, r_i , (non-hydrated radius), is preferentially adsorbed on the solid surface (Alloway, 1995). The ionic radii of different divalent cations Me^{2+} , decrease in the following sequence:



Therefore, the strong adsorptions of MB cations on the quartz sand, as observed in the presence of Cu^{2+} and Zn^{2+} ions, result from the slight reduction of the quartz negative surface charge and/or the low affinities of the metal cations toward the solid. On the other hand, the low adsorptions of MB cations on quartz particles, in the presence of Ca^{2+} and Ba^{2+} ions, are due to the strong reduction of the quartz negative surface charge and/or to the higher affinities of the metal cations toward the solid.

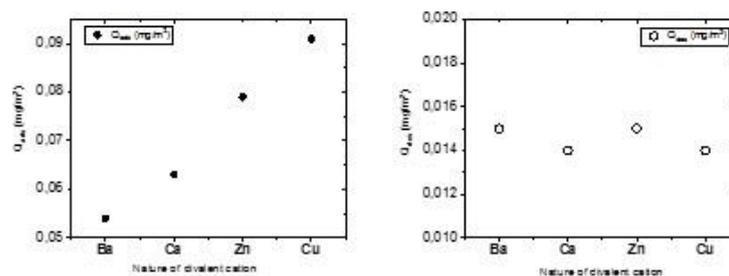


Fig. 3. Effect of the divalent cation nature Me^{2+} , on MB adsorption (Fig 3a, left) and desorption (Fig 3b, right) through quartz sand. Initial MB concentration, $C_0=1$ ppm; pH=6, flow velocity, $Q=60$ ml/h, temperature $T=293^\circ\text{K}$., $[\text{Me}^{2+}] = 10^{-3}$ M, $\text{Me}=\text{Ba}$; Ca ; Zn and Cu .

Conclusions

A natural quartz sand column was used to study the transport, retention, and release of Methylene Blue (MB). The quartz sand was selected as adsorbent, due to its availability and low cost. The data presented in this work show the effects of various parameters, such as ionic strength, flow rate, pH of the aqueous phase, the temperature of the medium, and the nature of the divalent cation, on the transport and the retention of MB dye, through the porous medium. The main results are summarized as follows:

- the retained MB amount, in the quartz sand porous medium, decreases significantly when the flow rate increases. However, a slight decrease in the retained MB amount occurs when the ionic strength of the aqueous phase increases;
- the fraction of MB deposited on the quartz increases by increasing either the temperature of the medium, or by raising the pH of the aqueous phase;
- the presence of metal divalent cations in the medium decreases in all instances, the adsorbed MB amount. However, such decrease depends on both, the metal cation affinity toward the solid surface, and its hydration by water molecules;
- the adsorption of MB on the quartz sand particles is endothermic nature and it is irreversible.

The overall data provide useful information to elucidate the mechanisms of complex formation, occurring in soil and groundwater, between inorganic or organic cations and the quartz sand surface.

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