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Enhanced Dye Adsorption by Microemulsion-Modified Calcined Diatomite (μE-CD)

M.A.M. KHRAISHEH*
Department of Civil and Environmental Engineering, University College London, Chadwick Building, London WC1E 6BT, UK
m.khraisheh@ucl.ac.uk

M.S. AL-GHOUTI
Industrial Chemistry Centre, Applied Technology Division, P.O. Box: 1438 Amman 11941, Jordan

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Abstract. This study attempted to improve the adsorption performance of calcined diatomite for the removal of colour from wastewaters through modification with microemulsions. The surface area, pH_{ZPC}, Fourier transform infrared (FTIR) of calcined diatomite and μE-CD were studied. It is found that an increase in the BET surface area, pH_{ZPC} and total pore volume after modification was obtained. A decrease in average pore volume was observed after modification. This suggests that the pore opening deceased to be in the micro- and meso-pore region hence the adsorption capacity for the modified adsorbent will be enhanced by reducing the escaping of dye molecules. The influence of concentration, pH and particle size on the adsorption capacities of methylene blue (MB), hydrolysed reactive black (RB) and hydrolysed reactive yellow (RY) was investigated. It was concluded from FTIR and pH analysis that the predominant mechanism of RY molecules onto μE-CD is by an electrostatic attraction between the carboxylate anion and the dye. In the case of MB and RB, the adsorption mechanism could be a combination of different mechanisms such as electrostatic attraction, capturing by microemulsion micelles in the pores of the calcined diatomite or the hydrophobic attraction. The adsorption capacities were higher than unmodified calcined diatomite. In the case of adsorption of MB molecules, a high adsorption capacity onto μE-CD was obtained.

Keywords: calcined diatomite, microemulsion, adsorption, methylene blue and reactive dye, modified adsorbents

1. Introduction

Diatomite is siliceous sedimentary rock comprising of an amorphous form of silica ($SiO_2 \cdot H_2O$) containing a small amount of microcrystalline material, chemically stable and inert. The silica surface contains silanol groups that spread over the matrix of the silica. When the diatomite was calcined, i.e. heated to high temperature, the active group on the diatomite surface (—OH groups) was removed and the surface acquires more and more hydrophobic properties by forming siloxane groups. Through the presence of these siloxane groups, it may be possible to impregnate a surfactant onto the diatomite surface.

Microemulsion is a system comprising mixture of water, hydrocarbons and amphiphilic compounds (small chain alkanols (called cosurfactants)) forming thermodynamically stable, transparent dispersion of two immiscible liquids, stabilised by an interfacial film of surfactants, homogeneous, optically isotropic solutions. Typical cosurfactants are short chain alcohols, ethanol to butanol, glycols, or medium chain alcohols, amines, or acids (Paul and Moulik, 1997). Abe et al. (1986) concluded that the role of the cosurfactant is to

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*To whom correspondence should be addressed.

destroy liquid crystalline or gel structures that form in place of a microemulsion phase. It was also concluded that cosurfactant free microemulsions in most systems cannot be made except at high temperatures to achieve a microemulsion phase in the 25–40°C range, cosurfactant must be used. Basically, cosurfactant have three functions: (a) provide very low interfacial tensions required for the formation of microemulsion and their thermodynamic stability, (b) modify the curvature of the interface and (c) act on the fluidity of the interfacial film. If the film is too rigid, it prevents the formation of microemulsion (Vandamme, 2002). Surfactant structures, such as micelles, are well known for their ability to solubilise nonpolar organic molecules in their hydrophobic cores and thereby promote the solubilisation of lipophilic substances in aqueous media.

Ramose et al. (1997) demonstrated that the microemulsions are quite efficient in recovery processes of metallic ions in laboratory scale. They developed and used a new technique of unconventional process of liquid–liquid extraction using a microemulsion as solvent. Dantas et al. (2001) also developed and used microemulsions to impregnate diatomite, making it capable to adsorb heavy metals from industrial effluents.

The aim of this work was to provide fundamental equilibrium adsorption isotherms information and to investigate the mechanism of adsorption in the adsorption of methylene blue and reactive dyes from aqueous solution onto μE-CD. The results summarised herein are also part of an investigation conducted to evaluate the adsorption capacity by taking into consideration the experimental parameters such as pH, particle size and initial dye concentration.

2. Material and Methods

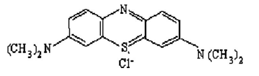
The diatomite samples used in this study were obtained from borehole BT-36, depth 34–36 m in Al-Azraq region in the East Jordan. The diatomite was washed several times with deionised water and dried in an oven at 100°C overnight and was allowed to cool in a desiccator. Calcination of diatomite was carried out by placing 30 g of diatomite in a crucible in the furnace at 980°C for four hours and then the samples were allowed to cool in a desiccator.

Microemulsion was prepared by mixing of 10 wt% surfactant (saponified coconut oil; mostly lauric acid, $CH_3(CH_2)_{10}COOH$, with some myristic acid, $CH_3(CH_2)_{12}COOH$);) and 25 wt% aqueous phase (deionised water). Coconut was saponified by standard procedure ASTM D-5558/1995 to form $CH_3(CH_2)_{10}COO^-Na^+$. Then the mixture was mixed with 40 wt% cosurfactant (isoamyl alcohol) 99% P.A., and 25 wt% oil phase (heavy distillate) (Dantas et al., 2001). Due to the spontaneous formation of microemulsions, they can be prepared in one step by mixing the constituents. The order of the addition of the constituents is not considered a critical factor for the preparation of microemulsions, but it can influence the time required to obtain equilibrium. This time will increase if the cosurfactant is added to the organic phase, because its greater solubility in this phase will prevent the diffusion in the aqueous phase (Vandamme, 2002). To prepare μE-CD, 10 g of diatomite and 20 cm^3 of microemulsions were mixed together. Then, the mixture was shaken and dried at 65°C for 48 h.

Methylene blue (C.I 52015), reactive black (Cibacron C-NN)) and reactive yellow (Cibacron MI-2RN) dyes were selected as a basic and reactive dye, respectively for studying the adsorption behaviour of these dyes onto μE-CD; a summary of the main characteristics of these dyes is given in Table 1. The charge of RB and RY are negative (anions) as they have sulphonic groups. The chemical structure and molecular weight of these dyes are unknown and they have been confirmed by elemental analysis, Flourier transform infrared (FTIR) and mass spectrometric analysis. The molecular weights of RB and RY are 1622 and 722 g/mol, respectively. The number of sulphonic groups for RB and RY are 6 and 3, respectively. Working solutions were prepared by appropriate dilution with deionised water to a final concentration of 1000 mg/dm^3. Because the reactive dyes, present in the effluents, are hydrolysed, it was necessary to study the adsorption behaviour of these dyes onto μE-CD in a hydrolysed form. The hydrolysis of RB and RY dyes was carried out by the Laszlo method (Laszlo, 1995).

The texture characteristics of adsorbent were determined by the standard N_2 adsorption isotherms using Quantachrome instruments NOVA *e*-Series, followed by evaluating the porous parameters. Surface charge density, acidity and basicity, pH_{ZPC}, Fourier transform infrared (FTIR-Perkin Elmer Spectrophotometer RX I) of μE-CD were studied. The adsorption isotherm experiments were carried out in 60 cm^3 glass bottle where 0.05 g of μE-CD and 50 cm^3 of the appropriate concentrations of the test dye solution were added. After the equilibrium period, the samples were filters through a 0.45 μm cellulose nitrate membrane filter (Swinnex-25 Millipore). The final dye

Table 1. Main characteristics of the dyes used in this study.

Dye	MB	RB	RY
Type	Basic Dye C.I.52015	Cibacron reactive black C-NN	Cibacron reactive Golden Yellow MI-2RN
Phase	Solid	Liquid, 33 wt%	Liquid, 33 wt%
λ_{max}, nm	663	597	430
ε, dm^3 g^{-1} cm^{-1}	170.1	22.6	23.0
Chemical structure	$C_{16}H_{18}N_3S^+Cl^-$ 	Unknown	Unknown

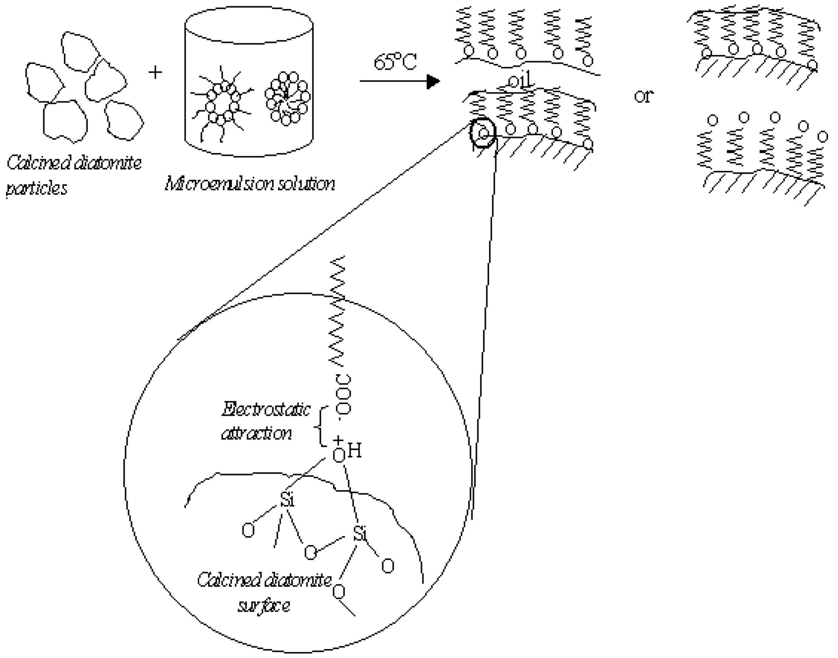


Figure 1. Schematic showing the interaction of the surfactant on the surface of the calcined diatomite.

concentrations were determined using a Perkin-Elmer UV-Vis spectrophotometer corresponding to λ_{max} of each dye. Further details on the adsorption isotherms are given else where (Al-Ghouti et al., 2003).

3. Results and Discussion

3.1. Structure and Surface Properties of the Adsorbents

The interaction of the surfactant $(CH_3(CH_3)_{10}COO^-Na^+)$ and the surface of the calcined diatomite may be envisaged as shown in Fig. 1. The mechanism of the surfactants adsorption on the calcined diatomite may occur via the hydrophilic part of the molecules (i.e. electrostatic attraction between the positive and negative charge) or via the hydrophobic parts.

The proposed interaction is based on the fact that the surfactants molecules are adsorbed electro-statically and are aligned with their charged heads towards the surface of the calcined diatomite (Fig. 1). The hydrocarbon chains, on other hand, protrude into the aqueous phase forming a hydrophobic property on the surface. Further adsorption occurs through the growth of aggregates that are formed. The adsorbed layer is

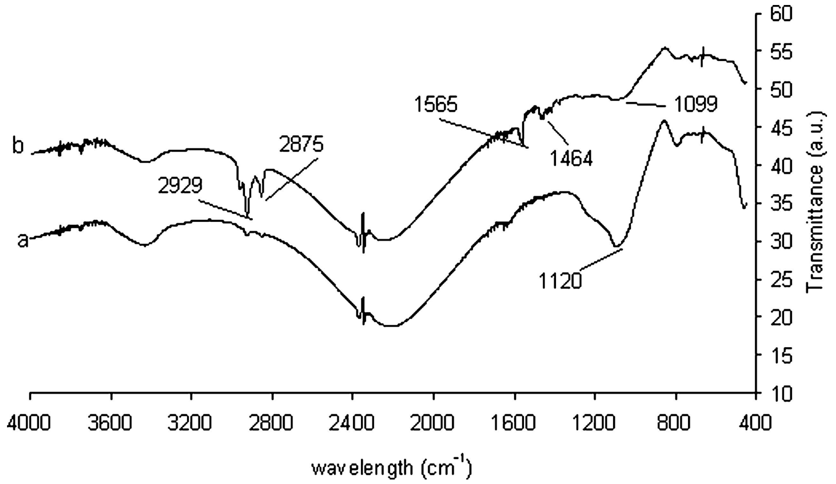


Figure 2. Infrared spectra of: (a) calcined diatomite and (b) μE-CD.

thought to form the structure of a bi-layer (Fan et al., 1997). The removal of the hydroxyl groups from the surface of the diatomite by calcination lead to a decease in the hydrophilic properties and an increase in the hydrophobic properties. After that, the surfactant molecules interact with the surface of the calcined diatomite. This is probably due to the hydrophobic interaction of the hydrophobic tail of the surfactant and the hydrophobic character of the calcined diatomite surface. As a result, the negative charge of the surfactant head will be towards the solution or the negatively charged part of the head of the surfactant may interact with the silanol groups on the surface of the calcined diatomite. These arrangements may lead to a multilayer-type adsorption by simply accumulating of a layer after layer of the surfactant on the calcined surface. Furthermore, this interaction may take place by a micellar adsorption and not by individual molecules. However, it was not clear if the micellars were produced within the solution and adsorbed in the form of micellar or whether initially individual molecules were adsorbed in the adsorbent surface, building a monolayer and afterwards micellars (Narkis and Ben-David, 1985).

It is also assumed that in the first stages, when the concentration of surfactants in the solution is low, molecules of the surfactant arrange themselves on the adsorbent surface in such a way that the hydrophilic and hydrophobic constituents are parallel to the surface and occupy a region corresponding to the plan projection area. While at high concentrations, the hydrophilic head moves in the direction of the liquid and above the critical micelle concentration (CMC) aggregates of two and three dimension micelles are formed on the adsorbent surface.

To examine the surface of the calcined diatomite after modification, the treated calcined diatomite was subjected to FTIR analysis. The most important peaks of the treated calcined diatomite were recorded (see Fig. 2). After modification with microemulsions, new peaks appeared. 1565 and 1464 cm^{-1} refers to (COO^{-}) stretch bands and 2929 and 2875 cm^{-1} refers to C—H stretching in —CH$_3$ and —CH$_2$— (Shriner et al., 1980). As a result, a chemisorption occurred by the adsorption of carboxylic acids (saponified coconut oil) on the surface of the calcined diatomite to form surface carboxylate groups. Thus, chemisorptive interactions at the solid/liquid interface may be characterised by the observation of infrared bands due to the vibrations of the surface species generated by chemisorption (Parfitt and Rochester, 1983).

The peak of Si—O—Si bond of the calcined diatomite was 1120 cm^{-1}. When the surfactant was adsorbed on the calcined diatomite the intensity of that peak became smaller and shifted to 1099 cm^{-1} (see Fig. 2), suggesting that the interaction of the surfactant and the calcined diatomite took place on the Si—O—Si bond. However, it is worth mentioning that due to the large size of the surfactant, modification of every siloxane group will be hindered and few may still be found on the surface.

The surface properties of the adsorbents were presented in Table 2. It indicates an increase in the BET surface area, pH$_{\mathrm{ZPC}}$ and total pore volume after modification. A decrease in average pore volume was

Table 2. Surface properties of calcined diatomite and μE-CD.

Adsorbent	Surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore radius (nm)	pH_{ZPC}	Acidity (mmol/g)	Basicity (mmol/g)
Calcined diatomite	0.35	0	0.0014	0.0014	7.824	7.6	0.230	0.035
μE-CD	3.68	0	0.0064	0.0064	3.479	8.1	0.280	0.280

observed after modification suggesting that the pore opening deceased to be in the micro- and meso-pore region hence the adsorption capacity for the modified adsorbent will enhance by reducing the escaping the dye molecules. Table 2 also shows that the surface area of the modified calcined diatomite increased by 10.5 folds, indicating that the modification process by microemulsions created many active sites for adsorption. Furthermore, the acidity and basicity of calcined diatomite and μE-CD were studied by applying Boehm's method (Otowa et al., 1997). The basicity of μE-CD was dramatically increased from 0.035 to 0.28 mmol/g. Capacity towards H^+ reflects the basicity of the surface, which is highly affected by presence of heteroatoms, such as oxygen. Treatment of the samples with the microemulsions increased noticeably the capacity towards H^+. This may be due to the functional groups (COO^-, carboxylic group), which may be created on the surface of calcined diatomite. Microemulsions modifications changed the surface of calcined diatomite by creating acid and basic surface groups, which may change the surface behaviour. From this explanation, MB adsorption onto μE-CD should have higher adsorption capacity than RB and RY adsorption. Therefore, the dye adsorption could be strongly affected by the presence of acid-base surface groups on the surface of μE-CD.

Surface charges may arise from chemical reactions at the surface. Surface charge of μE-CD can be estimated by alkalimetric titration method (Chen and Lin, 2001). Figure 3 shows the surface charge density of calcined diatomite and μE-CD as a function of pH. The intersection of the curve with x-axis at σ equals zero gives the zero point of charge, pH_{ZPC}, where the total charge from the cations and anions at the adsorbent surface is equal zero.

The pH_{ZPC} of μE-CD was estimated as 8.10. In the pH solution < 5.5 and high pH > 8.5, the surface charge densities (σ) of μE-CD were high in positive and negative values, respectively. For example, σ of μE-CD

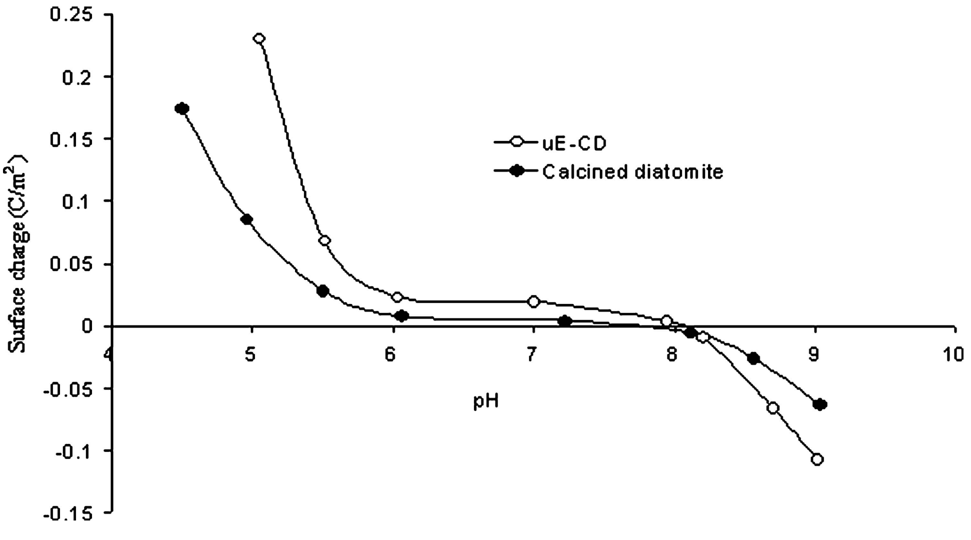


Figure 3. Surface charge densities and pH_{ZPC} of μE-CD.

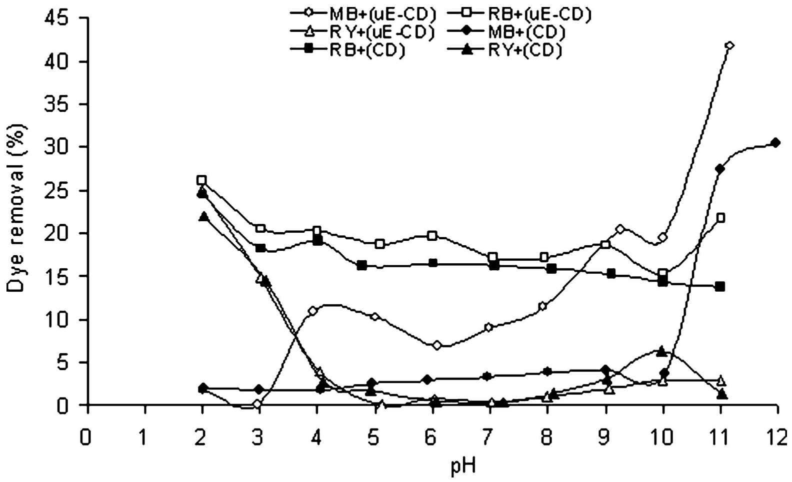


Figure 4. Effect of pH values on dye adsorption onto μE-CD and calcined diatomite (CD). Experimental conditions: initial dye concentration: 100 mg/dm^3, mass of adsorbent: 0.05 g, particle size: 106–250 μm, equilibrium time: 48 h, temperature: 22°C, and shaking speed: 125 rpm.

at pH = 5 and 9 are +0.23 and −0.11, respectively. If the microemulsion droplets are assumed to be spherical then the high surface charge can be expected to produce sufficient electrostatic repulsion between droplets to maintain the stability of the system (Al-Shamrani et al., 2002). For example, the surface charge density of μE-CD and calcined diatomite at pH = 5 are 0.24 and 0.02, respectively. From Fig. 3, if pH is greater than 8.10, the surface of μE-CD would have a negative charge and at lower than pH 8.10, the surface is expected to be positively charges. Therefore, the surface charge of μE-CD is a strong function of pH. The experimental results indicated that μE-CD has moderately positive and negative charged. The negative charge is probably due to adsorption of hydroxyl ions at the surface of μE-CD (Al-Shamrani et al., 2002), which is expected to have an influence on the dye adsorption. It is also noted that the pH_{ZPC} of μE-CD higher than calcined diatomite. This may be attributed to that the way of the surfactants interaction on the calcined surface upon modification. The higher value of pH_{ZPC} confirmed that the most surfactant molecules interacted by electrostatic interaction (see Fig. 1). The surface charge and its distribution on the μE-CD surface are important factors, which may determine the behaviour of μE-CD in the adsorption process.

3.2. *Effect of pH on Dye Adsorption onto μE-CD*

The establishment of such microemulsion on the surface of the calcined diatomite can have beneficial effect. One such effect proposed is that the hydrophobic character of the surface might be changed hence the adsorption of dye with high hydrophobic character will increase. Furthermore, the microemulsion formed on the surface of calcined diatomite can change the surface charge density of the calcined diatomite, which might enhance its adsorption capacity for the dye molecules. It showed that the pH_{ZPC} of μE-CD is quite higher than calcined diatomite and the surface charge density of μE-CD is higher than calcined diatomite at specific pH. These considerations indicate that the modification of the calcined diatomite by microemulsion is quite important. The effect of solution pH on the adsorption of MB, RB and RY onto μE-CD was studied. The experimental data was analysed by plotting the percentage dye removal against pH of the dye solution and the results are illustrated in Fig. 4. The results of the pH survey can be easy explained by taking into account the main functional groups on the μE-CD surface. After modification of the calcined diatomite by microemulsion, most of the calcined diatomite was covered by microemulsion (i.e. surfactant $RCOO^-Na^+$). The most important equilibrium reactions in solution during dye adsorption onto μE-CD are:

$$\mathrm{RCOO}\,Na + \mathrm{MB}^{+} \rightarrow \mathrm{RCOOD} + \mathrm{Na}^{+}(\mathrm{D} : \mathrm{dye}) \tag{1}$$

$$\mathrm{RCOONa} + \mathrm{H}^{+} \rightarrow \mathrm{RCOOH} + \mathrm{Na}^{+} \tag{2}$$

Thus, the difference in the amount of adsorption between MB, RB and RY is dependent on the equilibrium constants of these dyes according to Eqs. (1) and (2).

It can be seen in Fig. 4 that the maximum percentage of MB removal was in basic media at pH > 10 and it was at acidic media pH < 3 for RB and RY. The enhancement of uptake of basic dye (MB) and reactive dye (RB and RY) at basic and acidic media, respectively, may be explained by in terms of electrostatic interactions between the surface charge of μE-CD and the charge of dye molecules. As has been mentioned before, that the surface charge of μE-CD was influenced by pH of the dye solution. At a basic media (pH > 8.1), the surface charge of μE-CD is more negative and thus the adsorption of the positively charge dye (MB) will be increased. In contrast, at acidic media (pH < 3) the surface charge of μE-CD is more positive and as result the adsorption of the reactive dyes will be increased. It means that decreasing the solution pH increases the repulsive force between MB molecules and the surface of μE-CD and thus hinders the transport of MB molecules from the bulk solution to the surface. Therefore, it was concluded the positively charged surface is appropriate for RB and RY dyes adsorption and the negatively charged surface is responsible for MB adsorption. Furthermore, the low dye removal at low pH of MB may also be explained by the competitive between the H^+ ions competition and MB molecules. The RB removal was slightly constant when the pH changed from 2 to 11. In contrast, the RY had a good adsorption at low pH (pH $= 2$). It is a common observation that anions are favourably adsorbed on the surface of adsorbents at low pH because the presence of hydrogen ions hinders the surface active from the adsorption of cations (Singh and Rawat, 1994). Moreover, it can be shown in Fig. 4 that the adsorption behaviour of MB molecules onto μE-CD is quite different from adsorption onto the calcined diatomite. It may be referred to the adsorption mechanism and to the affinity of MB molecules for adsorbing on μE-CD surface. While the adsorption behaviour of RB and RY molecules onto the calcined diatomite and μE-CD is quite similar. In addition, it is clear that the RB uptake is higher than RY at all pH values (2–11). However, a full description of the dye adsorption onto calcined diatomite was shown in Khraisheh et al. (2005).

3.3. *Effect of Particle Size on Dye Adsorption onto μE-CD*

The adsorption isotherms curves can be interpreted in order to obtain information about the adsorption mechanism strictly connected with interactions between adsorbent and the adsorbate molecules and give the possibility to assess the efficiency of the adsorbent in the removal of pollutants. During the adsorption process, the dye molecule is drawn from the bulk solution to the adsorbent surface. The net attractive forces involving the dye, water, and the adsorbent are assumed to be responsible for adsorption. To study the effect of particle size on the dye adsorption onto μE-CD, several particle size ranges were chosen, (<106), (<106–250), and (250–500) μm. The experimental results were illustrated in Fig. 5. In case of adsorption of MB onto μE-CD, Fig. 5 shows that existence of an intermediate plateau at initial MB concentration between 500–800 mg/dm^3. The existence of two plateaus in the adsorption isotherms of MB adsorption could be attributed to different explanations: (i) the formation a double layer, the saturation of each layer corresponding to a plateau, (ii) different orientation of the adsorbed MB molecules on surface of μE-CD, and adsorption on different types of sites (Haydar et al., 2003). It is mentioned before that the adsorption of MB onto μE-CD could happen by different mechanisms. It may be proposed that the lower plateau is due to the adsorption of MB by forming a hydrophobic attraction with tails of the surfactants or by dissolving in the micelles and then to be adsorbed in pores. The second plateau can be attributed to the adsorption of MB by forming electrostatic attraction.

The capacities and the essential adsorption parameters for RB, RY and MB were calculated using a number of the most frequently used adsorption models and the results are shown in Table 3. In the case of RB and RY, Langmuir isotherm was not utilized to evaluate the results, since the obtained adsorption isotherms did not present the typical Langmuirian form. However, from Table 3, it can be concluded that the adsorption isotherm of MB exhibits Langmuir behaviour, which indicates a monolayer adsorption and the adsorption of RB and RY was best represented by the Freundlich model, which indicates a heterogeneous surface binding (Robinson, 2002; Kibe et al., 2000). The Freundlich adsorption isotherm equation predicts that the dye concentrations on the adsorbent will increase so long as there is an increase in the dye concentration in the aqueous solution. The Freundlich model does not predict the adsorption capacity of adsorbent surface for specific adsorbate, but the K_F value can be taken as a relative indicator of the adsorption capacity

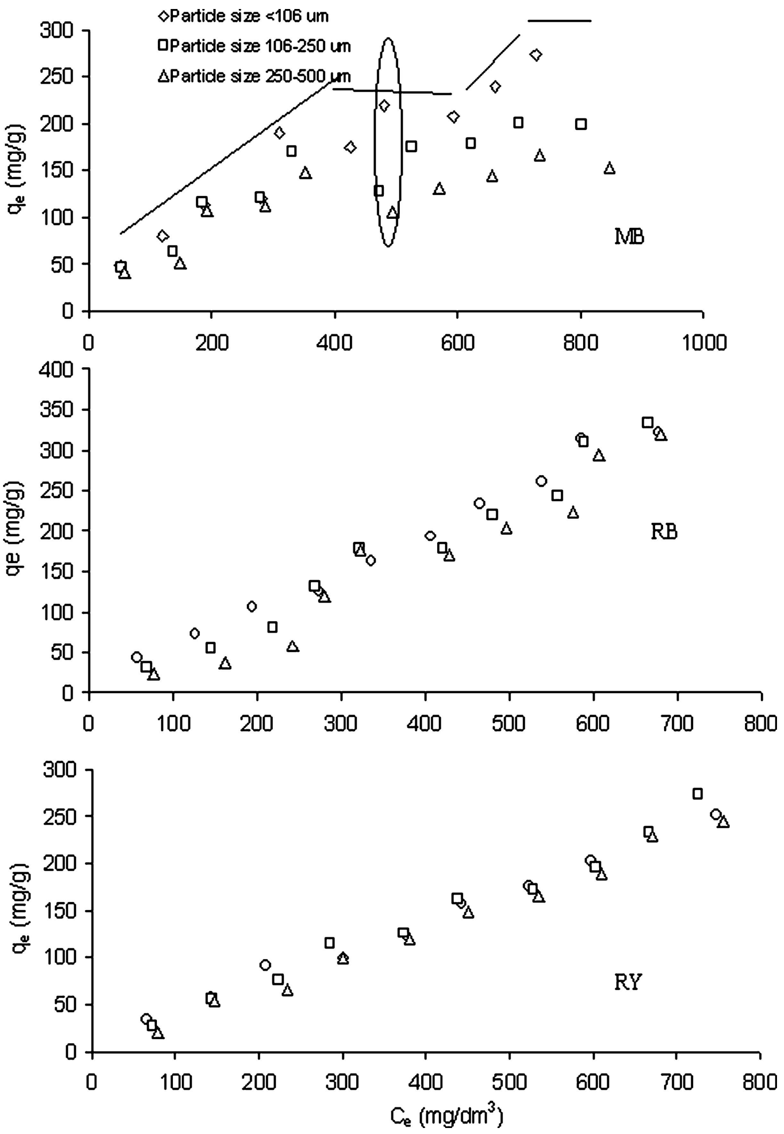


Figure 5. Adsorption isotherms of MB, RB and RY onto μE-CD at various particle sizes. Experimental conditions: mass of adsorbent: 0.05 g, volume of dye solution: 50 cm^3, temperature: 20°C, shaking speed: 125 rpm, shaking time: 48 h, pH of MB, RB and RY solution: 2, 2 and 11, respectively.

for a narrow sub-region having equally distributed energy sites toward specific adsorbate (Gemeay, 2002). However, the values of q_e were predicted by introducing corresponding values of K_F and $1/n$ as well as the initial dye concentration ($C_o = 100\,\text{mg/dm}^3$). Therefore, it is clear from the experimental results, Table 3, that the adsorption capacity corresponding to the initial equilibrium concentration was increased in order: MB > RB ≈ RY. The ($1/n$) value from Freundlich equation indicates that the relative distribution of energy sites and depends on the nature and strength of the adsorption process. For example, the value of ($1/n$) of adsorption MB onto μE-CD surface is 0.63; in fact this value refers to 63% of the active sites that have equal energy where adsorption takes place.

Table 4 shows the adsorption parameters of the dye adsorption onto calcined diatomite and μE-CD. The adsorption capacities were higher than unmodified calcined diatomite. In the case of adsorption of MB molecules, a high adsorption capacity onto

Table 3. Representation of Henry and Freundlich parameters of adsorption isotherms of MB, RB, and RY onto μE-CD at various particle size ranges.

Dye	Particle size distribution (μm)	K_F (mg/g) (mg/dm^3)^n	1/n	Equation	Adsorption capacity*, (mg/g)	k_H (dm^3/g)
MB	<106	4.02	0.63	$\log q_e = 0.604 + 0.63 \log C_e$	47.81	(1)
	106–250	5.36	0.55	$\log q_e = 0.729 + 0.55 \log C_e$	47.70	(2)
	250–500	5.87	0.50	$\log q_e = 0.769 + 0.50 \log C_e$	40.77	(3)
RB	<106	1.26	0.85	$\log q_e = 0.100 + 0.85 \log C_e$	39.33	0.49
	106–250	0.29	1.08	$\log q_e = -0.538 + 1.08 \log C_e$	28.13	0.48
	250–500	0.08	1.28	$\log q_e = -1.097 + 1.28 \log C_e$	20.74	0.43
RY	<106	1.00	0.83	$\log q_e = 0.83 \log C_e$	32.25	0.34
	106–250	0.46	0.96	$\log q_e = -0.337 + 0.96 \log C_e$	28.32	0.35
	250–500	0.24	1.05	$\log q_e = -0.620 + 1.05 \log C_e$	23.57	0.32

Note: Langmuir equation was applicable and the Langmuir parameters were: (1) $K_L = 0.85\,\text{dm}^3/\text{g}$, $a_L = 0.002\,\text{dm}^3/\text{mg}$, and $Q = 418\,\text{mg/g}$, (2) $K_L = 0.83\,\text{dm}^3/\text{g}$, $a_L = 0.003\,\text{dm}^3/\text{mg}$, and $Q = 277\,\text{mg/g}$, and $K_L = 0.77\,\text{dm}^3/\text{g}$, $a_L = 0.0038\,\text{dm}^3/\text{mg}$, and $Q = 205\,\text{mg/g}$.

* Adsorption capacities correspond to the initial equilibrium concentration at $C_o = 100\,\text{mg/dm}^3$.

Table 4. Representation of Henry and Freundlich parameters of adsorption isotherms of MB, RB and RY onto calcined diatomite and μE-CD.

	Calcined diatomite				μE-CD			
Dye	K_F (mg/g) (mg/dm^3)^n	1/n	Adsorption capacity*, (mg/g)	k_H (dm^3/g)	K_F (mg/g) (mg/dm^3)^n	1/n	Adsorption capacity* (mg/g)	k_H (dm^3/g)
MB	1.07	0.746	27.11	*	4.02	0.63	47.81	**
RB	0.32	1.042	26.64	0.43	1.26	0.85	39.33	0.49
RY	0.51	0.855	21.39	0.20	1.00	0.83	32.25	0.34

Note: * Langmuir equation was applicable and the Langmuir parameters were: $K_L = 0.48\,\text{dm}^3/\text{g}$, $a_L = 0.0035\,\text{dm}^3/\text{mg}$, and $Q = 137\,\text{mg/g}$. ** $K_L = 0.85\,\text{dm}^3/\text{g}$, $a_L = 0.002\,\text{dm}^3/\text{mg}$, and $Q = 418\,\text{mg/g}$.

μE-CD was obtained. Moreover, the closer the n value to 1 indicates homogenous surface. It is clear from Table 4 that calcined diatomite has more homogeneous surface that μE-CD.

3.4. *Mechanism of Adsorption*

Two mechanisms of the dye adsorption onto μE-CD are possible: (i) adsorption by an electrostatic force of the anionic head group of the surfactant and the positive charge of the dye (MB^+), (ii) adsorption by tail groups of the surfactant and the hydrophobic character of the dye. MB is a basic dye and has basic characteristics and therefore is expected to interact strongly with the anionic head groups of the surfactants ($RCOO^-$). In the contrary, RB and RY contain anionic clusters and are not expected to interact with the anionic head groups of the surfactants where the number of these clusters may explain the differences between RB and RY adsorption capacities (Hanna et al., 2002).

Upon modification, microemulsions may also fill the pores of the calcined diatomite; as a result, dye molecules may dissolve in the hydrophobic core of the surfactants (Fig. 6(A)). Considering the possible locations of the dye in the microemulsion system, the dye may be found (i) in the water core in, (ii) the aqueous solution-surfactant interface region, (iii) the surfactant domain, i.e. the curved surfactant monolayer that compartmentalises the water or (iv) the oil-continuous solvent (Ortona et al., 1988). Figure 6(A) represents a proposed model showing the possible location of the

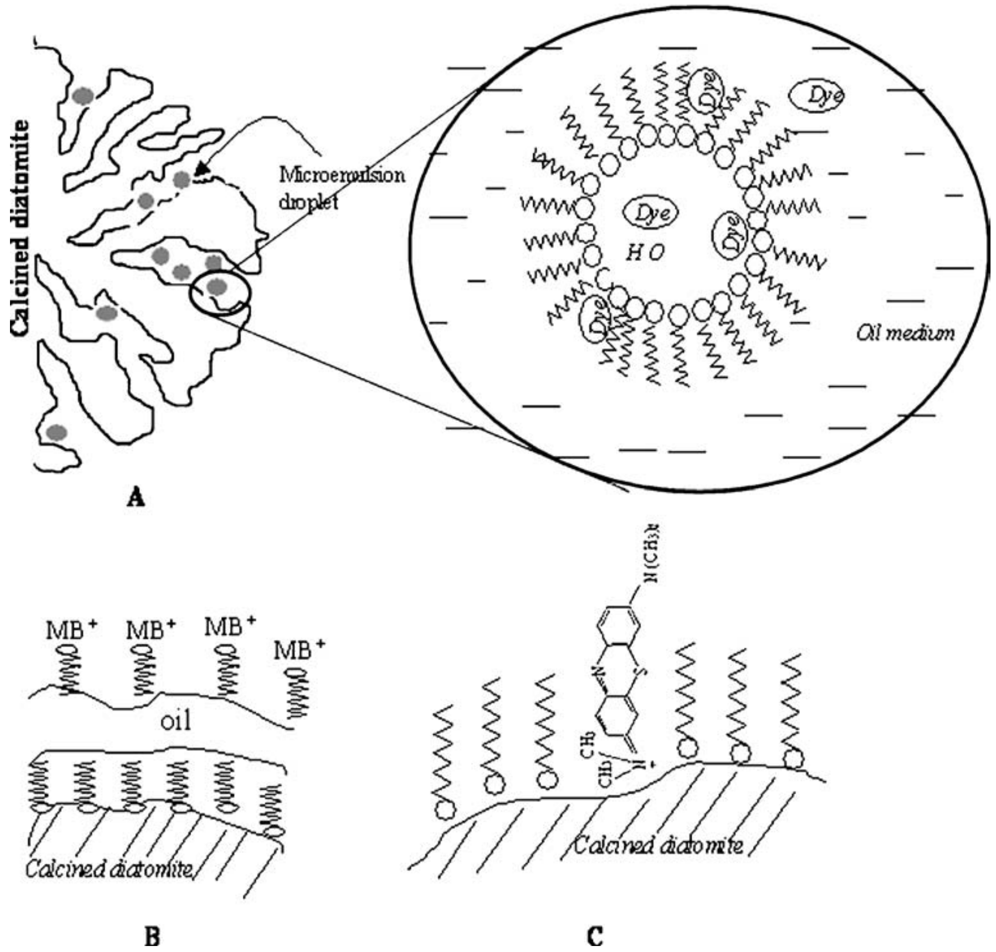


Figure 6. Schematic diagram of adsorption of MB molecules onto μE-CD: (A) Microemulsion filling calcined pores showing the possible location of the dye molecules in the microemulsion system, (B) electrostatic attraction between the MB and the polar head of the surfactant and (C) hydrophobic interaction.

dye molecules in the microemulsion system. The diffusion of the dye within the droplets is relatively easy, regardless of whether the dye is located in the surfactant skin or in the aqueous core. Because the adsorption process of MB, RB and RY was pH dependent, then the prominent mechanism of adsorption may that by electrostatic adsorption. Thus, three kinds of the dye adsorption mechanisms onto μE-CD may be described: (i) on the external surface, by forming an electrostatic attraction between the dye molecules and the head group of the surfactant or by forming a electrostatic attraction between the dye molecules and the functional groups of the calcined diatomite (i.e. siloxane bridge), (ii) filling the channel (pores) of the calcined diatomite by dissolving in the microemulsion micelles and (iii) hydrophobic interaction between the hydrophobic part of the dye and the hydrophobic part of the surfactant. However, the exact nature of this adsorption depends on the details of the surface such as its structure, chemical nature (hydrophobic or hydrophilic), surfactant-solid interaction and bulk solution structure. MB molecule is taken as model to describe the adsorption mechanisms onto μE-CD and the results are schematically described in Fig. 6.

Figure 7 represents the FTIR of μE-CD and spent μE-CD after the dye adsorption. It is obvious, from Fig. 7, that the intensity of the surfactant peaks was remarkably decreased. The peaks from 1790–1450 cm^{-1} are related to the dye stretching groups and the dye-carboxylate (RCOOD) binding. A remarkable increase

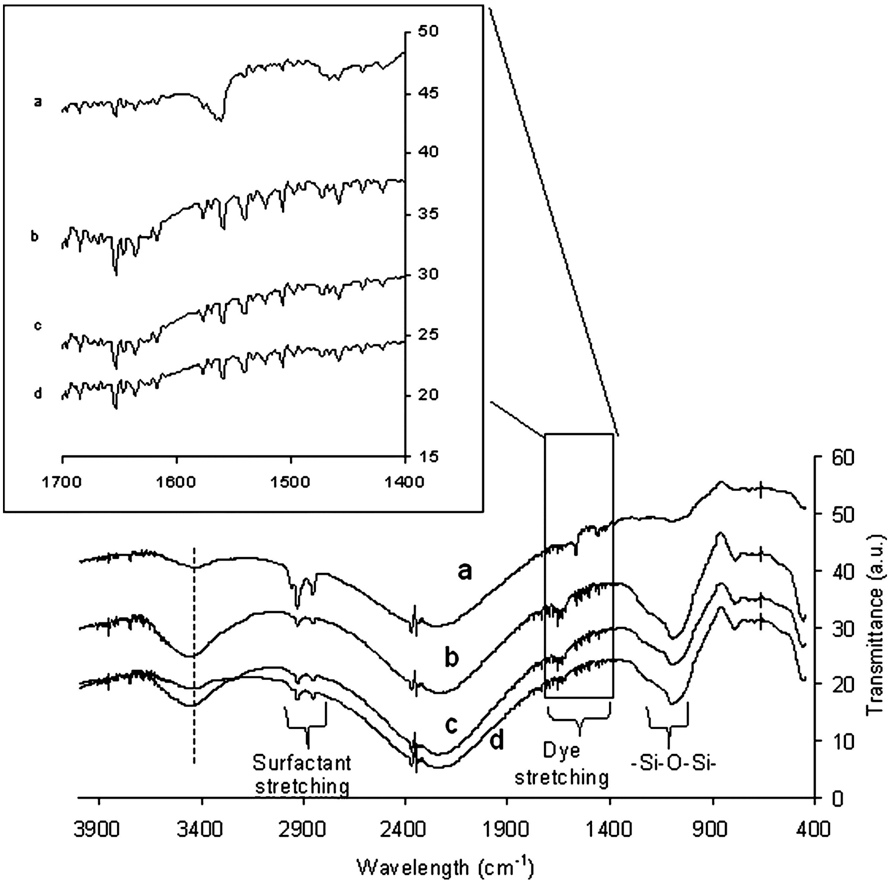


Figure 7. Infrared spectra of: (a) μE-CD alone and μE-CD after adsorption of: (b) MB, (c) RB and (d) RY.

of the intensity of siloxane (—Si—O—Si—) peaks was observed upon the dye adsorption onto μE-CD. Moreover, the intensity of the symmetrical and asymmetric stretching of the carboxylate anion was decreased and shifted to lower wavelengths (i.e. 1565 shifted to 1561 cm^{-1} and 1464 shifted to 1459 cm^{-1}), suggesting an electrostatic attraction between the carboxylate anion and the dye. The intensity of 2929 and 2875 cm^{-1} peaks, which is referred to C—H stretching in —CH_3 and —CH_2—, was also reduced, indicating that some of the dyes molecules adsorbed by forming a hydrophobic interaction between the tails of the surfactant and the hydrophobic part of the dye. In addition, it is clear from Fig. 7 that the intensity of 3434 cm^{-1} peak, which represents to the hydroxyl group absorption, decreased for RY adsorption and remarkably increased for MB and RB adsorption. This peak also was shifted to the higher wavelength in which this peak shifted to 3457, 3457, and 3443 cm^{-1}, respectively. This may indicate that the adsorption behaviour of RY molecules onto μE-CD is quite different than MB and RB molecules. The only conclusion, which may be drawn, is that the predominant mechanism of RY molecules onto μE-CD is by an electrostatic attraction between the carboxylate anion and the dye. This effect is clearly stated from the behaviour of adsorption of RY at different pH values. In the case of MB and RB, the adsorption mechanism could be a combination of different mechanisms such as electrostatic attraction, capturing by microemulsion micelles in the pores of the calcined diatomite, or the hydrophobic attraction.

4. Conclusion

Modification of calcined diatomite by microemulsions enhanced the removal of MB, RB and RY, MB in particular, from aqueous solution. This enhancement was correlated well with the pH and FTIR analysis in which they provided a reliable method in determining the mechanism of the dye adsorption onto μE-CD. Surface charge density and its distribution on the μE-CD surface are important factors, which may determine the behaviour of μE-CD is the adsorption process. The microemulsions formed on the surface of calcined diatomite can change the surface charge density of the calcined diatomite, which might enhance its adsorption capacity for the dye molecules. It is noted that the $\mathrm{pH_{ZPC}}$ value of μE-CD higher than calcined diatomite. This may be attributed to the way of the surfactants interaction on the calcined surface upon modification. The higher value of $\mathrm{pH_{ZPC}}$ confirmed that most surfactant molecules interacted by electrostatic interaction. It was concluded the positively charged surface is appropriate for RB and RY dyes adsorption and the negatively charged surface is responsible for MB adsorption. Furthermore, the adsorption of MB onto μE-CD is quite different from reactive dye adsorption, suggesting various kinds of adsorption. The adsorption capacities of μE-CD were higher than unmodified calcined diatomite. In the case of adsorption of MB molecules, a high adsorption capacity onto μE-CD was obtained.

Nomenclature

q_e	equilibrium solid phase solute concentration. It is usually expressed as the amount of solute adsorbed per unit mass of adsorbent (mg/g)
X	amount of solute adsorbed (mg)
m	mass of adsorbent (g)
K_L	adsorption constant (dm^3/g)
k_H	Henry adsorption constant (dm^3/g)
C_e	equilibrium liquid phase concentration (mg/dm^3)
a_L	Langmuir isotherm constant (dm^3/g)
Q	Langmuir monolayer capacity ($Q.\ a_L = K_L$)
K_F	Freundlich isotherm constant (dm^3/g)
n	refers to adsorption tendency
$\lambda_{\max}$	maximum wavelength (nm)
ε	molar absorptivity (dm^{3}g^{-1}cm^{-1})
σ	surface charge density (C/m^2)

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