

Humic Acid Covered Alumina as Adsorbent for the Removal of Organic Dye from Coloured Effluents

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Abstract

Humic Acid (HA) covered Alumina (ALHUM), as a novel adsorbent material, was found to exhibit good sorption behavior toward organic cation (Methylene Blue, MB), in aqueous solution batch experiments. The covering efficiency was assessed by comparing the surface chemistry, the surface charge and the microstructure, of the bare and the HA covered Alumina samples, and by using various tools such as Streaming Induced Potential and Scanning Electronic Microscopy. The data indicate that the coverage increase of the Alumina support by HA enhances strongly the dye removal from water. Further, the MB adsorbed amount onto the ALHUM was found to increase by increasing either the aqueous phase pH or the temperature of the adsorption medium. However, decreases in the MB adsorbed amount were observed upon the increase of the divalent cation (Ca^{2+} , Ba^{2+} and Cu^{2+}) affinity toward the ALHUM and/or the aqueous solution ionic strength. These features highlight the suitability of ALHUM adsorbent for the treatment of water polluted with organic dyes.

Finally, the experimental adsorption data were compared to various theoretical predictions and the best fits were found by Dubinin-Radushkevich isotherm models as compared to the Langmuir and the Freundlich theoretical isotherms. The overall data suggest that the ALHUM can be used as an adsorbent for removal of MB from the coloured effluents and the treatment of the wastewater.

Keywords: Alumina, Humic Acid, Organic dyes, Adsorption,

Introduction

Organic dyes are widely used in textile, tanning the leather, paper, plastic and other industries (Crini 2006, Wu et al. 2008). These substances represent one of the problematic pollutants occurring in wastewater. Dyes having usually synthetic origin are generally characterized by complex aromatic molecular structures which resist to environmental conditions such as light and microbial attack (Dogan et al. 2006). Most dyes have toxic as well as carcinogenic, mutagenic and teratogenic effects (McKay et al. 1985), on aquatic life and also on humans (Gregory et al. 1991). In order to preserve the environment, notably hydrosphere, the elimination of synthetic dye from aqueous solution is of great concern. Removal techniques of dyes may be included three categories; physical, chemical and biological (Slokar et al. 1998, Hao et al. 2000). However, biological wastewater treatment processes were found to be ineffective in the removal of the dyes (Kannan et al. 2001, Fernandes et al. 2007) because of their low biodegradability (Preethi et al. 2006). Among the physical methods available, adsorption process has proven to be effective in the removal of color from wastewater, and it is one of the powerful and low cost treatment processes (Bonetto et al. 2015). Many adsorbents are used to reduce dye concentration from aqueous solutions. Activated carbon is regarded as an effective but expensive adsorbent due to its high cost of manufacturing and regeneration (Ahmad et al. 2014). Hence, there is a need for an effective and cheaper material as an alternative adsorbent for removing the dyes from water. Hence, some natural adsorbents including quartz (Jada et al. 2012), kaolinite (Adebawale et al. 2014), Montmorillonite modified with chitosan (Umpuch et al. 2013), clay minerals, and some natural biomass and polymeric resin have also been reported (Unuabonah et al. 2014, Yagub et al. 2014). For these natural adsorbent, a considerable amount of work has been reported in the literature, regarding the adsorption of some dyes on their surfaces. However, very few studies have dealt with the use oxides minerals modified with humic acid as natural adsorbent for dyes removal from water. Indeed, in natural environment, most inorganic particles surfaces are coated with adsorbed natural organic matter such as humic substance (O'Melia 1990). Such organic coatings are known to alter the surface charge and aggregation behaviour of mineral particles. The focus of the present study was to assess the potentiality of oxide aluminium (Alumina) modified with humic acid (HA) as a low cost adsorbent for the removal of Methylene Blue (MB) dye from aqueous solution. For this purpose, humic-coated Alumina (ALHUM) particles were firstly synthesized and characterized. Adsorption kinetics and isotherms were investigated as a function of contact time, pH, ionic strength, temperature and the nature of divalent cations present in the aqueous solution. Finally, the equilibrium data were analysed using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models.

Experimental

Materials

Cationic dye

The Methylene Bleu (MB) used in this study was an analytical grade reagent of 99% purity from Sigma Chemical Co. Its chemical formula is $C_{16}H_{18}N_3ClS$.

Humic acid (HA)

The humic acid used in the study product obtained from Aldrich-Chimie in the form of sodium humate. It was used as received without further purification. Characteristics of humic acid, such as its molecular weight, which is around 2000 g/mol, and its elemental analysis which gives C (38.02%), H (3.76%), N (0.52%), O (57.4%), and S (<0.3%), were described elsewhere (Jada et al. 2006).

Alumina (Al_2O_3)

Commercial oxide aluminium Al_2O_3 (Alumina) mineral particles was supplied by Merck, and used without further purification. The zeta potential measurement of alumina have shown that pH_{PZC} is about 9. (Kumar et al. 2011.)

Reagents

All chemical reagents employed in this work were p.a. quality, and the aqueous solutions were prepared using, in all instances, bidistilled water. The ionic strength was fixed by using sodium chloride (NaCl) as salt. The pH of the solution was adjusted to the desired values [pH=4-10] by using solutions of HCl or NaOH (0.1 M). Aqueous solutions of Calcium chloride ($CaCl_2$), Copper chloride ($CuCl_2$), and Barium chloride ($BaCl_2$), were prepared and used to investigate the nature's effect of divalent cation on sorption of BM onto humic- covered alumina (ALHUM).

Preparation of humic coated -Alumina

For the preparation of humic acid coated alumina, 50 mg of alumina was placed in stopped bottle and 50 ml of $NaCl$ $10^{-2}M$ containing 50 mg/l of Humic acid was added. The pH's suspension was adjusted to 5 and agitated at 20°C for 24h, then the resulting mixture was centrifuged, at ambient temperature, for 30min at 4000 rpm to settle HA-covered Alumina particles. These particles were dried at 40°C for 12h. The final HA-covered Alumina sample was thereafter characterized by various techniques.

Characterization of the dried and the aqueous dispersion of the solid samples

The bare and HA covered Al_2O_3 solid samples were analysed by Scanning Electron Microscopic (MEB) in order to get further insight into the solid particle size and morphology. Further, the modification of Al_2O_3 particles surface charge, upon HA adsorption, was assessed by titration of the bare and HA covered Al_2O_3 solid samples with Cetyltrimethylammonium chloride (CTACl) aqueous solution, and by using a potential measuring device (Particle Charge Detection, PCD, Müteck instrument). The measuring cell is composed of a cylindrical poly (tetrafluoroethylene) (PTFE) container with a PTFE piston inside. The titratable aqueous solid dispersion (10 ml) was filled into the gap (0.5 mm) between the container wall and the piston, and various amounts of the aqueous CTACl solution were then added. The resulting streaming induced potential (SIP) was measured between two gold electrodes located at the top and the bottom of the gap. During the measurements the piston moves sinusoidally up and down at a frequency of 4 Hz and forces the aqueous suspension to move and to stream through the gap along the container wall. The SIP measured during the piston movement, results from the separation of the counter ions from the solid particles (bare Al_2O_3 or HA covered Al_2O_3) adsorbed on the container wall.

Sorption experiments

To study the effects of various parameters (pH, ionic strength, temperature, and nature of divalent cation) on the adsorption isotherm of MB dye onto ALHUM, various series of ALHUM- Dye aqueous dispersions were prepared. An aqueous MB solution with a concentration of 1g/l was prepared as stock solution, being used for preparing the rest of the solutions by dilution.

All adsorption tests were carried out in a stoppered bottles immersed in a thermostatic bath at a constant agitation speed.

The kinetic study was carried out by adding 60 mg of HA-coated Alumina to 60mL of dye solution having a dye concentration of 50 mg/l at pH =6 and at ionic strength equal to 10^{-2} M of NaCl. The mixtures were put under a constant agitation ranging from 10 to 500 mn.

In the subsequent series dealing with the effects of pH, the ionic strength, and the divalent's cation nature, an amount of ALHUM solid (60mg) was placed in flasks and a volumes (60ml) of salt solutions (monovalent or

divalent cation) containing various amounts of dye, (initial dye concentration, C_{in} , ranging from 10 to 150mg/l), were added. The effect of pH was investigated by adjusting the dyes - HA-coated Alumina aqueous dispersions to desired pH values (pH =4, 6, 8 and 10) in 10^{-2} M of NaCl solution.

To study the effect of ionic strength, dispersion containing various NaCl concentrations (10^{-3} - 10^{-1} M) at pH 6 were prepared. The effect of divalent cation nature was studied by adding various salts ($CuCl_2$, $BaCl_2$, $CaCl_2$) to the dispersions at fixed salt concentration of 10^{-2} M at pH =6.

The control of the temperature was carried out by a thermostatic bath regulated at temperatures ranging from 293 to 323 K. For this purpose, dispersions containing 60 mg of HA-coated alumina mixture with 50 mg/l of dye were prepared in 60 ml of NaCl salt (10^{-2} M). These dispersions were agitated for a contact time varying from 10 min to 500min.

Once the experiments were finished, the adsorbent was separated from the liquid phase by centrifugation at 4000 rpm for 30 min. The residual concentration of the supernatant was measured by a spectrophotometer at 665nm. The adsorbed amount, Q_{ads} , as expressed in milligram of dye per gram of the solid, was determined from the difference between the initial concentration (C_{in}) and the residual concentration (C_e), according to the equation:

$$Q_{ads} = (C_{in} - C_e)/m_s \quad (\text{Eq.1})$$

where m_s is the amount of the ALHUM adsorbent (g/l), C_{in} and C_e are initial and residual dye concentrations respectively (mg/l).

Theoretical

Adsorption isotherm

All adsorbent/adsorbate systems are not behaving the same way. The adsorption phenomena are often addressed by their isotherm behavior. Isotherms describe the existing relationship between the adsorbed amount and the solute concentration at equilibrium and at constant temperature. These isotherms were studied using a several well-known isotherm models such as Langmuir, Freundlich and Dubinin-Radushkevich (D-R).

- Freundlich isotherm (Eq.2) is widely used to describe adsorption on a surface having heterogeneous energy distribution. This energy varies as a function of surface coverage (Freundlich et al. 1939).

- Langmuir isotherm (Eq.4) assumes that adsorption take place on a homogeneous adsorbent surface of identical sites that are equally available and energetically equivalent (El Qada et al. 2006). Further, this model is applicable to monolayer chemisorption (Bhattacharyya et al. 2005).

The mathematical expression of the both Freundlich and Langmuir models, and their linearized form are given by the following equation:

$$q_e = k_f C_e^n \quad \text{Eq. 2}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{Eq. 3}$$

$$q_e = \frac{q_m k_L C_e}{1 + K_L C_e} \quad \text{Eq. 4}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e q_m} \quad \text{Eq. 5}$$

Where q_e is the amount of solute adsorbed per links of adsorbent (mg/g); C_e is the concentration of solute remaining in solution at equilibrium (g/L); k and n are Freundlich constants. One of the Freundlich constants k indicates the adsorption capacity of the adsorbent. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption. n values indicates the type of isotherm to be irreversible ($n=0$), favourable ($0 < n < 1$), unfavourable ($n > 1$) (Alley, 2000).

C_e is the equilibrium dye concentration in aqueous phase (mg/L), K_L is Langmuir equilibrium constant (L/mg) and q_m the maximum adsorption capacity (mg/g).

- The Dubinin - Radushkevich isotherm model assumes that the adsorption potential is variable and that the free enthalpy of adsorption is related to the pore filling degree, unlike the Langmuir model (Dubinin et al. 1947). The D-R expression is represented by the following equation:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad \text{Eq. 6}$$

$$\varepsilon^2 = RT \ln \left(1 + \frac{1}{C_e} \right) \quad \text{Eq. 7}$$

where q_m is the maximum adsorption capacity (mg/g), ε is the Polanyi potential, β is a constant related to the adsorption energy, E (Kj/mg), by following equation:

$$E = \frac{1}{\beta^{0.5}} \quad \text{Eq. 8}$$

The linear form of Dubinin - Radushkevich model is:

$$\ln q_e = \ln q_m - \beta RT \ln \left(1 + \frac{1}{C_e} \right) \quad \text{Eq. 9}$$

Kinetics of adsorption

In order to gain a better understanding of the kinetics and the rate determining step of adsorption processes, the pseudo-first-order (Eq. 10a) (HO 2004), the pseudo-second-order (Eq. 11) (HO (2000) and the intraparticle diffusion models (Eq. 12) (Tunali et al. 2006) were employed.

- The pseudo-first-order model is given by equation Eq 10a.

$$\frac{dq(t)}{dt} = K_1(q_e - q(t)) \quad \text{Eq. 10a}$$

where $q(t)$ and q_e are respectively the amounts adsorbed per unit mass of the adsorbent (both in mg/g) at any time and at equilibrium, and K_1 is the pseudo-first-order rate constant of adsorption (min^{-1}). The linearized form of equation 10a is expressed by equation 10b:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad \text{Eq. 10b}$$

- The pseudo-second-order model is expressed as:

$$\frac{dq(t)}{dt} = K_2(q_e - q(t))^2 \quad \text{Eq. 11a}$$

where K_2 is the rate constant of pseudo-second-order adsorption. Integration of this equation (Eq. 11a) gives equation 11b:

$$q(t) = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad \text{Eq. 11b}$$

- Intra-particle diffusion model:

The transfer of the solute from the aqueous phase to the surface of the adsorbent involves multi-step such as external diffusion and internal diffusion, pore diffusion, surface diffusion and adsorption into the pore surface. The intra-particle diffusion model used to study the diffusion in adsorption system is originated from Fick's second law and is written as (Ho 1998, Juang et al. 2000)):

$$q(t) = K_i t^{0.5} + \text{Constant} \quad \text{Eq. 12}$$

where K_i is the intra-particle diffusion rate constant ($\text{mg.g}^{-1}.\text{min}^{-0.5}$) and Constant (mg/g) is a constant.

Results and discussions

Characterization of the bare and Humic Acid-coated Al_2O_3 particles (ALHUM)

The titration curves of the bare and Humic Acid-coated Al_2O_3 particle aqueous dispersions with the cationic surfactant, CTACl, are presented, respectively, in Figs. 1 and 2. It should be noted that in these titration experiments the solid particles are adsorbed on cylinder and piston surfaces, and adding cationic surfactant molecules compensates their negative surface charges until the bare or the Humic Acid-coated Al_2O_3 particles turn to neutral. This point of neutral charge or the end point of titration corresponds to the isoelectric point. It should be mentioned that the sign charge reversal of the solid particles from negative to positive upon addition of CTACl, indicates specific adsorption of the surfactant on the bare or on the Humic Acid-coated Al_2O_3 surface. By using the known equivalent charge of the cationic surfactant, i.e. equivalent charge for CTACl=312. 5 meq/100g, the calculations give the solid's values of about 0.40 and 0.24 meq/100g, for respectively, the bare and Humic Acid-coated Al_2O_3 particles. Such decrease in the equivalent charge value for the Humic Acid-coated

Al_2O_3 particles as compared to the bare particles, is attributed to the surface charge screening of the Al_2O_3 which occurs upon adsorption on its surface of Humic Acid.

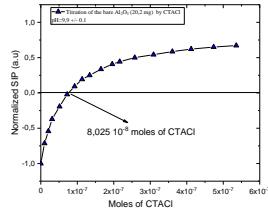


Fig 1. Variation of the streaming induced potential (SIP) with CTACl concentration for the bare Al_2O_3 particles aqueous dispersions, $\text{pH}=9.9 \pm 0.1$

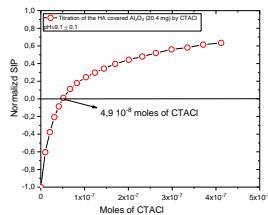


Fig 2. Variation of the streaming induced potential (SIP) with CTACl concentration for the Humic Acid (50 mg/l) covered Al_2O_3 particles aqueous dispersions, $\text{pH}=9.1 \pm 0.1$

The decrease in the Al_2O_3 particles surface charge which is observed upon the adsorption of Humic Acid leads to an increase of the solid particle size as observed Figs 3 and 4. Hence in Fig. 3, from the SEM image, the mean size of the bare Al_2O_3 particles is about 100 microns whereas the mean size of the Humic Acid covered Al_2O_3 particle is about 180 microns as can be seen from the SEM image depicted in Fig. 4.

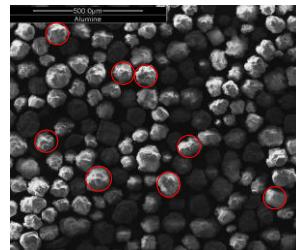


Fig 3. SEM image of the bare Al_2O_3 particles

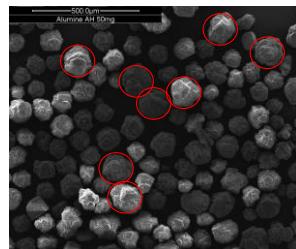


Fig 4. SEM image of the Humic Acid (50 mg/l) covered Al_2O_3 particles

Effect of HA amount on the adsorption of MB dye, by the bare and HA covered Al_2O_3 samples

To investigate the influence of humic acid content on the sorption of MB dye from water onto HA covered Al_2O_3 sample, a series, of adsorption experiments of dye on the bare alumina and on the alumina modified by different HA concentrations (50 and 100 mg/l), was carried out at ambient temperature. The adsorption isotherms of MB by alumina are shown in Fig. 5. As can be seen, the presence of humic acid coated to alumina, exhibited a rather pronounced effect on the adsorption of MB. Consequently, coating alumina surface with a large amount of humic acid improves the removal of BM from aqueous solution. Indeed, the adsorption of HA on surface of alumina causes modification of surface charge; this latter would become negative. This promotes the attraction between the cationic dye (MB) and the alumina coated with humic acid (ALHUM) via electrostatic interaction.

This result is consistent with the reported work of Almeida et al 2009. These authors reported higher adsorption of MB on montmorillonite clay having a negatively charged surface similar to that observed on ALHUM particles in the present work.

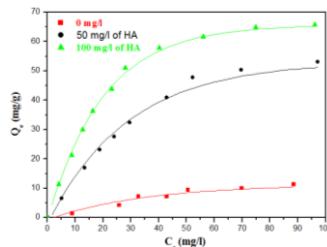


Fig 5. Effect of amount of Humic acid on adsorption of MB by alumina ([Solid] = 1g/l, Ionic strength, I=10⁻² M, pH=6, Ambient temperature).

In the following, we will consider only the alumina particles mixed with 50 mg /l of humic acid (ALHUM).

Effect of contact time

In order to determine the required time to reach equilibrium, an adsorption experiment of MB at a fixed concentration on ALHUM, as a function of contact time was investigated. The data are presented in Fig. 6. As can be in this figure, the equilibrium adsorption of MB dye onto ALHUM is reached after 2h of contact. After this time, the adsorbed amount remains constant despite the increase in contact time. In addition, it's noted that almost 50% of dye has been removed in less than 50 min. It should be noted that in the next adsorption experiments, the contact time MB dye/ ALHUM adsorbent will be fixed at 3 h. The kinetics involved in the process of MB adsorption onto ALHUM particles was studied using the following models: the pseudo first-order, the pseudo-second-order and the intra-particle diffusion; in order to determine the rate constant of MB dye adsorption on ALHUM solid. The parameters of each model are presented in Table 1. These parameters are estimated using the non-linear regression.

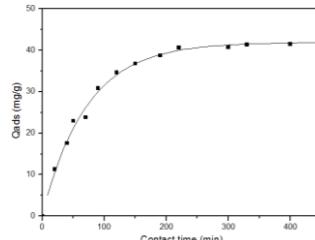


Fig.6 Kinetics of the adsorption of MB onto HA-coated Alumina solid ([MB]=50 mg/l, [Solid]=1g/l, pH=6, I=10⁻²M NaCl, Ambient temperature).

Table 1: Kinetic constants of MB adsorption on HA-coating Alumina

Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
Q _{eq} (mg/g)	K ₁ (min ⁻¹)	r	Q _{eq} (mg/g)	K ₂ (g/mg.min)	r	K _{id} (mg/g.min ^{0.5})	C _{ste} (mg/g)	r
41.05	0.014	0.996	41.69	1.55*10 ⁻³	0.948	2.884	0.470	0.988

As can be observed in Table 1, since the values of the correlation coefficient (r) and the rate constant (K₁ or K_{id}), calculated by fitting the pseudo first-order and the intra-particle diffusion models to the experimental data, are high, it is then likely that the adsorption of cationic dye (MB) from the aqueous solution may be well described and controlled by these two models. In literature, several authors have reported that the MB adsorption on various adsorbents followed a pseudo-first-order kinetic model (Bhattacharyya et al. 2005, Low et al. 1995). The values of the rate constant, K₁, of pseudo-first-order kinetic model obtained in the present work is almost identical to that found by Shawabkeh, et al. 2003.

Effect of pH on the adsorption of dye

Fig. 7 shows the MB adsorption isotherms from water onto the HA-coating Alumina particles at ambient temperature and at various values of pH=4, 6, 8 and 10. These figures indicate that the adsorption is strong at high pH. The MB adsorbed amount increase from 35 mg/g to 79 mg/g when the pH of the aqueous phase pH increases from 4 to 10. From these observations, it was suggested that the sorption of MB is dependent on the properties of the adsorbent surface. In addition, these behaviours can be attributed to electrostatic interaction between the ALHUM group's surface charged negatively and the functional groups of dye molecule charged positively. However at basic pH, the magnitude of ALHUM negative surface charge reaches its maximum value as resulting from the higher ionisation of humic acid carboxylic groups. Furthermore, the MB adsorption can be attributed to electrostatic interaction that occurs between the surface groups of HA-coating Alumina and the MB molecule functional groups. In a reported work, Ait Akbour et al. 2013 have observed an increase of HA zeta potential magnitude, from -30mV to -50mV with increasing the aqueous phase pH value. These results were explained by the ionization of HA acidic groups, mainly carboxylic that occurs when the aqueous phase pH increases from 3 to 10. This negatively charged solid surface of ALHUM sample attracts more MB molecules via electrostatic attractions. Our results are in a good agreement with similar effects previously reported for adsorption of textile dyes by natural clays (Elmoubarki et al. 2015), and by (Umpuch et al. 2013) for adsorption of methyl orange by chitosan intercalated montmorillonite.

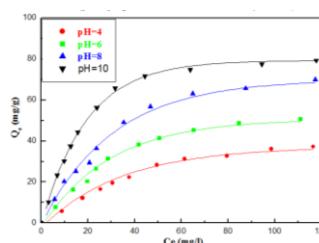


Fig.7. Adsorption isotherms of MB onto HA-coated Alumina particles at various pH values of the aqueous phase. ([Solid]=1g/l, I=10⁻² M NaCl, Ambient temperature).

Effect of ionic strength

Fig. 8 represents the effect of NaCl concentration on the adsorption isotherms of MB from water onto HA-coating Alumina at ambient temperature and at pH 6. It is found that MB adsorption onto ALHUM particles increases by lowering the ionic strength. In fact, significant decrease of the amount adsorbed from 61.33 to 35.50 mg/g as the ionic strength increases from 10⁻³ to 10⁻¹ M. Such data are similar to earlier finding for the adsorption of organic cation (MB) on quartz sand solid bearing negative surface charge (Jada et al. 2012). Thus, in the present work, the presence of NaCl in the aqueous phase may affect the electrostatic interaction that occurs between the negatively charged ALHUM surface and the positively charged basic dye (MB). The data indicate that increasing the inorganic cation concentration (Na⁺) in the solution competes with the organic cation (MB) to be adsorbed on ALHUM surface. Therefore, it is expected that the adsorbed MB amount should decrease with an increase of NaCl concentration.

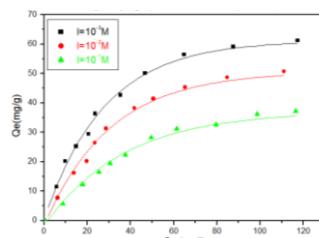


Fig.8. Adsorption isotherms of MB onto HA-coated Alumina particles at various ionic strength of the aqueous phase. ([Solid]=1g/l, pH=6, Ambient temperature).

Effect of the nature of the divalent cation

In this experiment series, we examined the effect of divalent metal ion on the adsorption isotherms of MB dye from water onto HA-coating Alumina solid. The divalent cations used were in the form of chloride salts (CaCl₂, BaCl₂, CuCl₂) used at a fixed concentration of 10⁻²M. The obtained data are presented in Fig. 9, and indicate that the adsorption capacity of MB is dependent on the nature of divalent cation present in the aqueous solution. These results show that the MB adsorbed amount decreases in the sequence: Cu²⁺ > Ba²⁺ > Ca²⁺. This difference in MB adsorption behaviour may be explained by the difference in the cation (Cu, Ba, Ca) affinity toward the ALHUM surface. Thus, the presence of divalent cation in the solution modifies and reduces the ALHUM surface

negative charge, resulting in reduction of the electrostatic attraction between the basic dye (MB) and the solid surface. It has been shown that the divalent cation Cu^{2+} forms coordination complexes with the HA negatively charged groups and it is more efficient than Ba^{2+} and Ca^{2+} in reducing the Humic Acid charge (Jada et al. 2006, Ait Akbour et al. 2013). In fact, the adsorption of divalent cations such as Cu^{2+} , Ba^{2+} and Ca^{2+} from bulk water onto the HA-coating Alumina surface reduce the thickness of ALHUM colloids electrical double layer and/or the zeta potential (Elimelech et al. 1990). Thus the low adsorption of MB on HA-coating Alumina particles in the presence of Cu^{2+} is attributed to strong reduction of the number of negative sites on the solid surface. This behaviour is consistent with the reported work of (Ait Akbour et al. 2013). These authors have found that the order of divalent cation complexing capacity and affinity toward of HA macromolecules decrease in the sequence $\text{Cu}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+}$. However, the higher MB adsorbed amount observed in the presence of Ca^{2+} as compared to Ba^{2+} or Cu^{2+} is likely due to the weak adsorption of the Ca^{2+} on the HA-coating Alumina surface resulting a low reduction of the global negative charge of ALHUM particles.

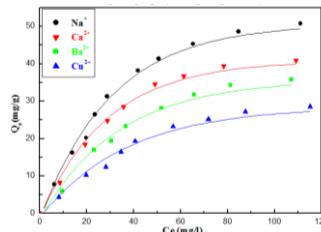


Fig.9. Adsorption isotherms of MB onto HA-coated particles in the presence of various divalent cations.
([Solid] =1g/l, pH=6, [Me²⁺] = 10^{-2} M)

Effect of temperature

Fig. 10 shows the variation of MB adsorption on ALHUM particles, versus contact times, at 20°C, 30°C, 40°C and 50°C and at fixed pH and ionic strength values (pH = 6, [NaCl]= 10^{-2} M). The quantities of MB adsorbed on ALHUM solid, at plateaux levels, as function of temperature are presented in Table 2. The obtained data indicate a slight increase in the adsorption capacity of MB basic dye, from 25.17 to around 30.73 mg/g, when increasing the solution temperature values from 20°C to 50°C. This behaviour proves that the adsorption of MB at HA-coating Alumina/aqueous solution interface is an endothermic process. Thus, the increase in the MB adsorbed amount with increasing temperature can be explained by the combination of two phenomena: (i) The strong adsorptive forces between the actives sites of ALHUM particles and MB molecule and (ii) a strong thermal agitation resulting in higher diffusion of MB molecules from the aqueous phase to ALHUM particles surface. Several authors have observed same effect of temperature on dye molecules sorption (Ghosh et al. 2002, Dogan et al. 2003, Tsai et al. 2005, Reyad et al. 2003). In another work, Karaca et al. 2008 indicated that the adsorption of methylene blue from aqueous solutions onto activated carbon is an endothermic process. Others authors (A. Jada et al. 2012) found also that the retention of MB organic cation through a porous medium consisting of negatively charged quartz sand particles, increased with increasing of solution temperature.

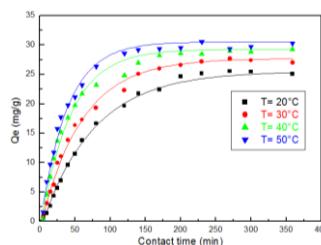


Fig. 10. Adsorption isotherms of MB onto HA-coated Alumina solid at various temperature.
([Solid]=1g/l,[MB]=50mg/l, pH=6, I= 10^{-2} M NaCl)

The thermodynamic parameters for adsorption of MB dye onto ALHUM were given by the following equation (Eq.13):

$$\Delta G^\circ = -RT \ln(K_0) \quad (\text{Eq. 13})$$

where ΔG° is the standard free energy change (J/mol), R is the universal gas constant (8.314 J/mol. K), T is the absolute temperature (K), and K_0 is the equilibrium constant given by equation (Eq.14):

$$\ln(K_0) = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (\text{Eq.14})$$

In Eq 14, ΔH° and ΔS° are, respectively, the enthalpy and entropy of the adsorption reaction. The values of ΔH° and ΔS° can be obtained, respectively, from the intercept and the slope of the plot of $\ln (K)$ versus $1/T$. The values of ΔH° and ΔS° calculated from (Eq. 14) and presented in Table 2. As shown this Table, the negative

values of ΔG° indicate that the adsorption process is a spontaneous reaction. The positive values of enthalpy change confirm the endothermic nature of the adsorption process and the positive values of ΔS° reflect an increase in randomness at the solid-solution interface during the adsorption of MB.

Table 2: Thermodynamic parameters calculated for the adsorption of MB dye by HA-coating Alumina

T(K)	Q_{ads} (mg/g)	KD	ΔG° (J/mol)	ΔH° (kJ/mol)	ΔS° (J/K.mol)
298	24.58	-0.033	-188.44	12.411	42.28
303	27.38	0.19098	-399.84		
313	29.11	0.33181	-822.64		
323	30.45	0.44311	-1245.44		

Adsorption modeling

The adsorption isotherms of MB basic dye onto the HA-coating Alumina were fitted to the various theoretical models such as Langmuir, Freundlich and Dubinin-Radushkevich. The obtained results of these analyzes are represented in Table 3.

Table 3: Isotherm models constants for MB adsorption onto HA-coating Alumina

		Langmuir			Freundlich			D-R		
		q_{max}	K_L	r	K_F	n	r	q_{max}	B	r
pH	4	114.41	6.10×10^{-3}	0.994	1.518	0.712	0.973	40.20	3.41×10^{-3}	0.988
	6	100.3	1.36×10^{-2}	0.997	2.887	0.656	0.971	51.34	3.47×10^{-3}	0.992
	8	105.93	2.16×10^{-2}	0.995	4.899	0.600	0.976	68.34	2.13×10^{-3}	0.989
	10	142.24	2.54×10^{-2}	0.994	6.239	0.659	0.969	78.96	1.40×10^{-3}	0.994
I(M)	10^{-1}	114.41	6.10×10^{-3}	0.994	1.518	0.712	0.973	40.20	3.41×10^{-3}	0.988
	10^{-2}	100.30	1.36×10^{-2}	0.997	2.887	0.656	0.971	51.34	3.47×10^{-3}	0.992
	10^{-3}	88.18	2.70×10^{-2}	0.995	5.569	0.544	0.972	60.89	1.96×10^{-3}	0.988
Me ²⁺	Ca ²⁺	87.64	1.24×10^{-2}	0.995	5.132	0.465	0.962	46.02	2.82×10^{-3}	0.993
	Ba ²⁺	157.72	4.20×10^{-3}	0.990	3.479	0.516	0.981	41.38	3.52×10^{-3}	0.995
	Cu ²⁺	68.92	8.3×10^{-3}	0.997	1.789	0.610	0.969	29.58	3.10×10^{-3}	0.988

where q_{max} : the maximum adsorption capacity (mg/g), K_L : Langmuir equilibrium constant (L/mg), K_F : Freundlich constant ($mg^{1-1/n}/L^{1/n}$ /g), B: constant related to the adsorption energy (mol/J), n: heterogeneity factor, r: correlation coefficient.

From the Table 3, we can note that the best fit is observed with the Dubinin-Radushkevich model as shown by the high correlation coefficient ($r=0.99$). Moreover, the calculated amount of dye adsorbed at equilibrium was very close to the experimentally obtained value.

Conclusions

The HA-coating Alumina exhibited good adsorption capacity for the removal of MB from aqueous solutions. The adsorption was depending on initial solution pH, ionic strength, temperature, and nature of divalent cation. In fact, the MB adsorbed amount onto the ALHUM was found to increase by increasing either the aqueous phase pH or the temperature of the adsorption medium. However, decreases in the MB adsorbed amount were observed upon the increase of the divalent cation (Ca^{2+} , Ba^{2+} and Cu^{2+}) affinity toward the ALHUM and/or the aqueous solution ionic strength. These results suggested that ALHUM is a potential adsorbent for the reduction of dye accumulations normally found in the effluent of various industries.

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