Removal of textile dyes from aqueous solutions using low cost Moroccan clay

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Abstract. This study aims to evaluate the technical feasibility to apply natural clay from Fez area as a low cost alternative adsorbent to remove dyes from contaminated waters. Methylene blue (MB) and congo red (CR) are used here as representatives of cationic and anionic dyes normally present in wastewater from textile industry. This material was characterised by different physical-chemical methods, including BET, X-ray fluorescence and pH\textsubscript{pzc}. Additionally, the influence of operating conditions such as contact time, adsorbent dosages and pH were evaluated. Experimental results show that the adsorption processes takes place very rapid, reaching the equilibrium at 30 and 45 min for MB and CR, respectively. Maximum adsorption capacities result to be pH-dependents. Hence, MB adsorption is favoured under basic pH conditions, whereas CR does it at acid pH. A pseudo-second-order kinetic model provides the best fit to the experimental data of MB and CR adsorption. Adsorption data are better described by Langmuir and Toth isotherm models. Adsorption occurs with a maximum monolayer adsorption capacity of 195 and 185 mg g\textsuperscript{-1} for MB and CR, respectively. Experimental results indicate that the Moroccan clay could be used as a potential adsorbent for the elimination of dyes from contaminated waters, at a lower cost.

1. Introduction

Currently, a great number of dyes are used in paper-making, textile, food, and pharmaceutical industries [1]. The presence of synthetic dyes in the environment poses serious environmental and health problems, because most of them are toxic, mutagenic and carcinogenic [2]. Such pollutants must be removed from wastewater streams to acceptable levels by appropriate methods. Adsorption is widely used process in the removal of dyes from contaminated waters due to its low cost and operational simplicity [3–4].
Activated carbons have been a common choice as adsorbents in many industrial processes; since they exhibit great affinity toward organic compounds. However, the use of activated carbons as adsorbents is limited by their high operating costs, pore blocking and safety issues. Synthetic zeolites overcome such drawbacks but their high acquisition cost limits their application at industrial scale (10 folds more expensive than activated carbons) [5-6]. In this perspective, effective and low cost alternative adsorbents for the removal of dyes have to be found.

In this regard, natural clays could be used as low cost adsorbents to clean contaminated waters from toxic dyes. In this study, the feasibility to apply inexpensive materials like Moroccan clay as adsorbent to remove two types of dyes, methylene blue (MB) and congo red (CR), from aqueous solutions is investigated. Moroccan clay is physically and chemically characterised. Moreover, the effect of different adsorption parameters such as pH, initial dye concentration, contact time and adsorbent dosage are evaluated. Additionally, kinetic and equilibrium models are applied to experimental data and the best models are selected.

2. Materials and methods

2.1 Materials

Natural clay was obtained from an extraction site situated in the nearness to Fez city, Morocco (named here as CFS) and was used without any previous activation. It was sieved into a range of 60-100 μm and washed with deionised water. Then, it was dried at 383 K for 24 h and stored in a dessicator until further use.

Methylene blue (MB; C_{16}H_{18}ClN_{3}S; Mw = 319.85 g mol^{-1}; HiMedia Laboratories, Mumbai, India) and congo red (CR, C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}, Mw = 696.66 g mol^{-1}; Sigma-Aldrich) were chosen as model dyes for adsorption experiments. Dyes of commercial purity were used without any further purification; their chemical structures are given in Figure 1. The pH was adjusted to a given value by addition of HCl (1N) or NaOH (1N) and was measured using a JENCO – Electrocinics LTD pH-Meter.

\[(a)\]

\[
\text{(CH}_3\text{)}_2\text{N}
\]

\[
\text{S}\text{N (CH}_3\text{)}_2
\]

\[
\text{N+ Cl}^{-}
\]

\[(b)\]

\[
\text{NH}_2
\]

\[
\text{N}_2\text{N-N-}
\]

\[
\text{O=SO=O}
\]

\[
\text{ONa}
\]

\[
\text{NH}_2
\]

\[
\text{N}_2\text{N-N-}
\]

\[
\text{O=SO=O}
\]

\[
\text{ONa}
\]

\[\text{Figure 1. Chemical structures: (a) MB, and (b) CR.}\]

2.2 Physical-chemical characterisation of the Moroccan clay

Specific surface area and pore volume of the CFS clay were obtained from N\textsubscript{2} adsorption isotherms at 77 K, using a Micromeritics Asap 2010 (Micromeritics Corporate Headquarters, U.S.A). Mineralogical composition was determined by X-ray diffraction analysis using X'Pert PRO Philips diffractometer (Phillips Japan, Ltd, Japan), equipped with CuK\textsubscript{α} radiation (\(\lambda=1.5406\ \text{Å}\)). Bulk chemical composition was determined using a X-ray fluorescence (XRF) in a Bruker S4 Pioneer spectrometer (Bruker AXS GmbH Karlsruhe, Germany).
Basic and acid surface sites were determined by the titration method [7]. A mass of 1.5 g CFS sample was placed into vials and 40 mL of solutions of NaOH (0.1N) and HCl (0.1 N) were poured. Vials were sealed and stirred during 72 h and then filtered. A volume of 10 mL of each filtrate was back-titrated using HCl (0.1 N) or NaOH (0.1 N), respectively. The number of acidic sites was determined under the assumption that NaOH neutralises acid sites. The number of basic sites was calculated from the amount of HCl that reacted with basic surface sites of present on CFS.

The pH of the point of zero charge (pH$_{pzc}$), was determined using the acidimetric–alkalimetric titration method [8]. Vials were filled with 20 mL of NaCl (0.1 N) and 0.1 g of CFS was placed into each vial. Different amount of NaOH (0.1N) and HCl (0.1 N) were added to each vial, varying the pH range and one was kept without any base or acid. Then, the suspensions were shaken and the equilibrium pH was measured by using a pH-meter (JENCO – Electrocinics LTD).

2.3 Adsorption experiments

Dye adsorption experiments were carried out using the batch method. A mass of 10 mg of CFS was dispersed in 20 mL solution with an initial dye concentration in the range from 0 to 1000 mg L$^{-1}$ at pH= 7. The mixture was shaken (~200 rpm) until the equilibrium was reached using a water shaker bath. After that, the solid phase was separated from the liquid phase by centrifugation (5000 rpm during 10 min). Finally, the remaining concentration of MB and CR were determined by measuring the absorbance at 664 nm and at 500 nm, respectively by using a spectrophotometer (UV 1600PC).

The quantity of adsorbed dye at the equilibrium per gram of CFS $(q_e, \text{mg g}^{-1})$ and the amount of dye adsorbed per gram of CFS at specific contact time $(q_t, \text{mg g}^{-1})$ were calculated using Eq. (1):

$$q_{e} = \frac{(C_{0} - C_{e})V}{m} \tag{1}$$

where $C_{0}$ (mg L$^{-1}$) and $C_{e}$ (mg L$^{-1}$) are the dye concentration at the beginning and at equilibrium or specific time, respectively. $m$ is the mass of adsorbent (g), and $V$ is the total volume of liquid (L).

The influence of operating conditions on the adsorption of dye onto CFS clay was studied in a batch system by varying the CFS dosage from 1 to 35 g.L$^{-1}$, the initial dye concentration from 10 to 1000 mg L$^{-1}$ and the pH of the dye solution in the range of 2-12. The pH was adjusted to a given value by the addition of HCl or NaOH.

3. Results and discussion

3.1. Characterisation of CFS clay

Figure 1 displays N$_2$ adsorption-desorption data of CFS clay. Results show a type IV isotherm according to the IUPAC classification. The initial part of the isotherm (P/P$_0$<0.4) could be attributed to physical adsorption. At a high relative pressure range, a clear hysteresis loop is observed that could be related to capillary condensation, taking place in mesopores structures formed between the elementary clay particles named tactoids.

The CFS clay used in this study has a specific surface area of 29 m$^2$ g$^{-1}$, with a highly developed microporous structure. Average pore diameter is around 2.1 nm. A summary of physical-chemical properties of CFS are listed in Table 1.
It can be observed that the amount of basic sites is significantly higher than the amount of acidic sites. These results suggest that CFS clay has a basic character. These results are in agreement with the measured value of pHpzc. When the pH of the solution is higher than the pHpzc, CFS surface will be negatively charged. In the pH region below pHpzc, positive charges will dominated on CFS surface.

Table 1: Physical–chemical properties of CFS clay.

| Property                              | CFS clay          |
|---------------------------------------|-------------------|
| Origin                                | Fez area (Morocco)|
| Colour                                | grey              |
| Apparent density (g dm\(^{-3}\))      | 700               |
| Specific surface area \(S_{BET}\) (m\(^2\) g\(^{-1}\)) | 29                |
| Total pore volume \(V_T\) (cm\(^3\) g\(^{-1}\)) | 0.03              |
| Mesopore volume \(V_{meso}\) (cm\(^3\) g\(^{-1}\)) | 0.025             |
| Micropore volume \(V_{micro}\) (cm\(^3\) g\(^{-1}\)) | 0.005             |
| Average pore diameter \(D_p\) (nm)    | 2.1               |
| SiO\(_2\)/Al\(_2\)O\(_3\) (mol mol\(^{-1}\)) | 5.71              |
| pH\(_{PZC}\)                           | 9.4               |
| Total acidic sites (mmol g\(^{-1}\))  | 0.32              |
| Total basic sites (mmol g\(^{-1}\))   | 2.67              |

Figure 3 shows the mineralogical composition of CFS clay. On one hand, results reveal a complex heterogeneous structure, mainly composed of quartz (Q) combined with calcite (C). On the other hand, X-ray fluorescence (XRF) results reveal its chemical composition, being mainly composed by SiO\(_2\) (41.28 %), Al\(_2\)O\(_3\) (12.29 %), CaO (14.23%), Fe\(_2\)O\(_3\) (4.13 %) and by traces of other oxides such as MgO, K\(_2\)O, Na\(_2\)O, P\(_2\)O\(_5\), TiO\(_2\). with a SiO\(_2\)/Al\(_2\)O\(_3\) of 3.4.
3.2. Effect of adsorbent dosage

Figure 4 shows the results of the influence of different dosage of CFS clay (0-20 g.L\(^{-1}\)) on the removal of MB and CR dyes, using 20 mL of dye solution (500 mg L\(^{-1}\)) at 25 °C during 1.5 h.

![Diagram showing adsorption and removal percentages.](image)

**Figure 4.** Effect of adsorbent dosage on MB and CR removal. Experimental conditions: 500 mg L\(^{-1}\) of initial concentration of MB or CR, 0–40 g.L\(^{-1}\) of CFS, 24 h of contact time, 200 rpm at 25 °C.

As it can be seen in Figure 4, dye removal efficiencies increase as the adsorbent dosage increases, which is related to the increase on the availability of adsorption sites on CFS surface. The optimum adsorbent dosages toward MB and CR result to be 7.5 g.L\(^{-1}\) and 5 g.L\(^{-1}\), respectively. Removal efficiencies for MB and CR reach values up to 99.9% and 98.6%, respectively.
3.3 Effect of pH

Results of the effect of pH values (2-12) on the adsorption of MB and CR are illustrated in Figure 5. The initial solution pH was adjusted by the addition of HCl or NaOH solutions. Results show that MB adsorption onto CFS clay is clearly pH-dependant. MB adsorption increases at pH conditions higher than the pHPZC. Maximum adsorption capacity toward MB, \( q_e \), increases from 88 to 119.9 mg g\(^{-1}\), when the solution pH increases from 2 to 12. Such results may be due to the fact that at \( pH > pHPZC \) CFS surface becomes negative charged, enhancing electrostatic attractions with positively charged MB cations [9].

![Figure 5. Effect of pH on the adsorption of MB and CR onto CFS: Initial conc.: 500 mg L\(^{-1}\), contact time= 6 h, R= 5 g L\(^{-1}\) for MB and CR, agitation speed= 200 rpm and \( T = 25^\circ C \).](image)

However, as pH decreases, CFS surface increases its number of sites positively charged; leading to a decrease on the adsorption capacity toward MB. Repulsion forces among a positively charged surface and MB cationic molecules could be responsible of such results. In the case of the adsorption of CR, adsorption capacities shows a maximum in the pH range between 2 and 4 that could be related to an increase on electrostatic attraction forces among positively charged sites of CFS surface and CR anionic molecules.

3.4 Adsorption kinetics

Adsorption kinetics provides important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. The effect of contact time on the adsorption of dyes using CFS clay is shown in Fig. 6. The rate of MB and CR adsorption onto CFS clay was studied by measuring the adsorbed amount as a function of time, keeping constant the volume (\( V = 200 \text{ mL} \)), the initial concentration (\( C_0 = 200 \text{ mg L}^{-1} \)) and the mass of adsorbent per liter of aqueous solution (\( R = 7.5 \text{ g L}^{-1} \) for MB and \( R = 5 \text{ g L}^{-1} \) for CR).
Experimental data show that the adsorption capacity of CFS toward MB and CR increases sharply during the first minutes of the process. Then, it increases slower over time, until equilibrium is reached at 120 min. These results suggest that the adsorption CR and MB onto CFS clay is a fast process. The fast adsorption rates imply strong interactions among the active adsorption sites of CFS surface and the dye molecules. Adsorption data fit very well pseudo-first-order (Eq. 2) and pseudo-second-order (Eq. 3) kinetic models, representing the kinetic and mechanism of solid-liquid adsorption interactions [10-11].

\[
q_t = q_e (1 - e^{-k_1t}) \\
q_e = \frac{k_2 q_i^2 t}{1 + k_2 q_i t}
\]

where \(q_t\) and \(q_e\) (mg g\(^{-1}\)) are the adsorption capacity at any time \(t\) and at the equilibrium, respectively. \(k_1\) (min\(^{-1}\)) and \(k_2\) (g. mg\(^{-1}\).min\(^{-1}\)) are the adsorption rate constants for the pseudo-first-order and pseudo-second-order kinetic models, respectively.

Kinetic parameters are summarised in Table 2. Pseudo-second-order kinetic model gives a better fit to the adsorption data of MB and CR onto CFS clay, with higher values of the correlation coefficient \(R^2\)\(^{>0.98}\). Additionally, \(q_e\) values determined using the pseudo-second-order kinetic model are more in agreement with the experimentally values \(q_{exp}\) than those obtained with the pseudo-first-order model. Such results suggest that chemical interactions are responsible for the adsorption of MB and CR onto CFS clay [12].

| Dyes | \(q_{exp}\) (mg g\(^{-1}\)) | Pseudo-first-order | Pseudo-second-order |
|------|-----------------|-------------------|--------------------|
|      | \(q_{cal}\) (mg g\(^{-1}\)) | \(k_1\) (min\(^{-1}\)) | \(R^2\) | \(q_{cal}\) (mg g\(^{-1}\)) | \(k_2\) (g mg\(^{-1}\).min\(^{-1}\)) | \(R^2\) |
| MB   | 49              | 42.24             | 0.036             | 0.96 | 49.21              | 0.0008         | 0.98 |
| CR   | 57              | 54.73             | 0.432             | 0.99 | 56.4               | 0.015          | 0.99 |

3.5 Adsorption isotherm

Adsorption isotherms indicate how adsorbate molecules are distributed between the liquid and solid phases when the equilibrium is reached [13]. Experimental data fit to different adsorption isotherm models is an important step to determine the most suitable model.
Figure 7 represents the total amount of adsorbed dyes onto CFS clay at the equilibrium \(q_e\). Three adsorption isotherms are fitted to the experimental data, including Langmuir (Eq. 4), Freundlich (Eq. 5) and Toth (Eq. 6) isotherms [14-16], as follows:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{(4)}
\]

\[
q_e = K_F C_e^{-\frac{1}{n}} \quad \text{(5)}
\]

\[
q_e = \frac{q_m K_T C_e}{(1+(K_T C_e)^t)} \quad \text{(6)}
\]

where \(K_L\) (L.mg\(^{-1}\)) is the Langmuir equilibrium constant related to the energy of adsorption. \(q_m\) and \(q_e\) (mg.g\(^{-1}\)) are the maximum and the equilibrium adsorption capacities of the Langmuir model, respectively. \(C_e\) (mg. L\(^{-1}\)) is the equilibrium concentration of the adsorbate. \(K_F\) (L.mg\(^{-1}\)) is the Freundlich constant and \(1/n\) is the heterogeneity factor. \(q_mT\) (mg.g\(^{-1}\)) is the Toth maximum adsorption capacity. \(K_T\) is the Toth equilibrium constant, and \(t\) is the Toth model exponent.

The dimensionless constant of Langmuir isotherm model (equilibrium parameter, \(R_L\)) for the adsorption process of MB and CR dyes is calculated from Eq (7). \(R_L\) values are useful to understand the nature of the adsorption process. All the calculated \(R_L\) values are higher than zero and lower than the unity (0<\(R_L<1\)) which reflects favourable adsorption of MB and CR onto CFS clay.

\[
R_L = \frac{1}{(1+K_L C_o)} \quad \text{(7)}
\]

![Figure 7](image_url)

**Figure 7.** Equilibrium data and non-linear fitted curves isotherms: (A) MB and (B) CR onto CFS adsorbent at 25°C.

Parameters of Langmuir, Freundlich and Toth isotherm models and their respective correlation coefficients are listed in Table 3. As it can be seen, the obtained values of \(R^2\) of the Toth and Langmuir isotherm models (\(R^2\sim0.98\)) indicate a better fit to the experimental data. Toth isotherm model has been developed from the potential theory in order to enhance the outcomes of Langmuir isotherm and be able to be used in heterogeneous adsorption systems. The adsorption of CR dye is well represented by the Langmuir isotherm model, followed by Toth isotherm model. Such results could indicate that the adsorption of CR onto CFS clay could occur forming a monolayer. On the other hand, the adsorption of MB is very well fitted to Toth isotherm model, indicating that different kind of interactions take places.
Table 3: Langmuir, Freundlich and Toth parameters for MB and RC adsorption onto CFS clay.

| Models   | Isotherm parameters | Dyes |
|----------|---------------------|------|
|          |                     | MB   | CR   |
| Langmuir |                     |      |      |
|          | $q_m$ (mg g$^{-1}$) | 117.65 | 181.8 |
|          | $K_L$ (L mg$^{-1}$) | 0.093 | 0.093 |
|          | $R^2$               | 0.90  | 0.99  |
|          | $R_L$               | 0.007-0.26 | 0.01-0.3 |
| Freundlich | $K_F$ (mg g$^{-1}$) (L mg$^{-1}$)$^1/n$ | 53.11 | 90.01 |
|          | $n$                 | 7.73  | 8     |
|          | $R^2$               | 0.89  | 0.96  |
| Toth     |                     |      |      |
|          | $q_{mT}$ (mg g$^{-1}$) | 195  | 185   |
|          | $K_T$ (L mg$^{-1}$) | 414   | 0.056 |
|          | $t$                 | 0.19  | 1.12  |
|          | $R^2$               | 0.98  | 0.99  |

Maximum adsorption capacities predicted by Toth isotherm for MB and CR onto CFS clay are 195 and 185 mg g$^{-1}$, respectively and are compared here to maximum monolayer adsorption capacities of different types of adsorbents used in the removal of such dyes (see data presented in Table 4). It can be observed that the obtained values of $q_m$ in the present study are higher than those reported in the literature using different kind of adsorbents.

Table 4: Comparison of the values of maximum adsorption capacity of different kinds of adsorbents toward MB and CR.

| Adsorbent          | Adsorption capacity (mg g$^{-1}$) | References |
|--------------------|-----------------------------------|------------|
|                    | MB   | CR   |               |
| CFS clay           | 195  | 185  | Present work  |
| Banana peel        | 20.80| --   | [17]         |
| Rice husk          | 40.60| --   | [17]         |
| D. harra           | 185.59| -- | [18]         |
| G. coronaria L.    | 258.76| -- | [18]         |
| Natural ilittic clay | 24.87 | -- | [19]         |
| Kaolin             | --   | 5.44 | [20]         |
| Bagasse fly ash    | --   | 11.89| [21]         |
| Montmorillonite    | --   | 12.70| [22]         |
| Ca-bentonite       | --   | 107.41| [23]        |
| Mesoporous activated carbon | -- | 189 | [24] |

4. Conclusions

Results obtained in this study show that natural clay from Fez area (CFS) can be used as a low cost adsorbent to remove cationic and anionic dyes from polluted waters. Kinetic studies reveal that an equilibrium time of 120 min is achieved in the adsorption of methylene blue and Congo red dyes. The adsorption processes are very well represented by a pseudo-second-order kinetic model. Congo red adsorption equilibrium data are better described by Langmuir model, suggesting the formation of a monolayer onto the surface of CFS clay; whereas methylene blue adsorption data are depicted by Toth model, indicating that different kinds of interactions are involved. Results also show that the adsorption capacity of CFS clay is highly controlled by the pH values. Maximum removal efficiency toward MB is obtained at alkaline conditions; while better performances for CR uptake are attained at acidic conditions. Natural clays seem to be promising candidates for fast removal of ionic pollutants.
References

[1] Pokhrel D and Viraraghavan T 2004 *Sci. Total Environ.* **333** 37–58.

[2] O’Neill C, Hawkes F, Hawkes D, Lourenco N, Pinheiro H and Delee W 1999 *J. Chem. Tech. Biotech.* **74** 1009-1018.

[3] Jain A K, Gupta V K, Bhatnagar A and Suhas 2003 *J. Hazard. Mater.* **101** 31–42.

[4] Ho Y S and McKay G 2003 *Process Biochem.* **38**(7) 1047–1061.

[5] Elmoubarki R, Mahjoubi FZ, Tounsadi H, Moustadraf J, Abdennouri M, Zouhri A, El Albani A and Barka N 2015 *Wat. Resour. Ind.* **9** 16–29.

[6] Hadri M, Chaouki Z, Draouli K, Nawdali M, Barhoun A, Valdés H, Drouiche N and Zaitan H 2017 *Desal. Water Treat.* **75** 213–224

[7] Boehm HP 1994 *Carbon* **32** 759-764.

[8] Noh JS and Schwarz JA 1989 *J. Colloid Interface Sci.* **130** 157–164.

[9] Ozcan A, Omeroğlu C, Erdoğan Y, Ozcan AS 2007 *J. Hazard. Mater.* **140** 173–179.

[10] S. Lagergren 1898 *Kungliga Svenska Vetenskapsakademiens Handlingar* **24**(4) 1–39.

[11] Ho YS, McKay G, Wase D A J and Forster CF 2000 *Adsorp. Sci. Technol.* **18** 639–650.

[12] Malash GF and E K Mie 2010 *J Colloid Interf Sci.* **348**(2) 537–545.

[13] Fu J, Chen Z, Wang M, Liu S, Zhang J, Zhang J, Han R and Xu Q 2015 *Chem Eng J.* **259** 53–61.

[14] Langmuir I 1918 *J. Am. Chem. Soc.* **40**(9) 1361-1403.

[15] Freundlich H M F 1906 *Z. Phys. Chem.* **57** 385-470.

[16] Toth J 1971 *Acta Chem. Acad. Hung.* **69** 311–317.

[17] Annadurai G, Juang R and Lee D 2002 *J. Hazard. Mater.* **92** 263–274.

[18] Tounsadi H, Khalidi A, Abdennouri M and Barka N 2016 *Desal. Water Treat.* **57** 16633–16642.

[19] Ozdes D, Duran C, Senturk H. B, Avan H and Bicer B 2014 *Desal. Water Treat.* **52** (1-3) 208-218.

[20] Vimonses V, Lei S, Jin B, Chow C, and Saint C 2009 *Chem. Eng. J.* **148** 354–364.

[21] Mall I, Srivastava V, Agarwal N and Mishra I 2005 *Chemosphere* **61** 492–501.

[22] Wang L and Wang A 2007 *J. Hazard. Mater.* **147** 979–985.

[23] Lian L, Guo L and Guo C 2009 *J. Hazard. Mater* **161** 126–131

[24] Grabowska E and Gryglewicz G 2007 *Dyes Pigments* **74** 34–40.

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