

UTILIZAÇÃO DA ARGILA MONTMORILONITA PARA ADSORÇÃO DO CORANTE VERDE MALAQUITA

USE OF MONTMORILLONITE CLAY FOR ADSORPTION MALACHITE GREEN DYE

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RESUMO

A remoção por adsorção do corante verde de malaquita em solução aquosa usando a argila montmorilonita é relatada neste trabalho. O verde malaquita é um corante catiônico amplamente utilizado na indústria têxtil. Devido à sua persistência no meio aquática, torna-se um problema ambiental para organismos aquáticos e terrestres. Este corante pode ser adsorvido através de várias técnicas, mas os altos custos de aquisição e de operação impede a ampla utilização. Diversos adsorventes estão disponíveis no mercado, mas o mais se destaca são as argilas, em especial, as montmorilonitas. Estas argilas são material finamente divididos (< 0,002mm) e suas propriedades de adsorção estão continuamente investigadas. As argilas 2:1 (duas tetraédricas para uma octaédrica) são chamados de expansíveis. A montmorilonita ter um potencial de remoção de corantes e contaminantes químicos de águas residuais devido à alta área superficial, porosidade com excelente capacidade de troca catiônica conferindo sua propriedade adsorvente. Este trabalho tem como objetivo utilizar a montmorilonita, em um sistema de adsorção em estágios, para descolorir um efluente têxtil, composto do corante verde malaquita, reproduzido em laboratório. A caracterização da argila confere alta pureza sendo utilizada como adsorvente de boa qualidade e eficiência. O sistema de retenção do corante composto de montmorilonita disposto em estágios de separação se mostrou eficiente. O efeito da concentração do corante e o tempo de retenção são os parâmetros mais importantes utilizados neste estudo. Altas concentrações e tempo de retenção abaixo de 24 horas resultou em níveis de remoção de 25%. Por outro lado, o baixo nível de concentração inicial aumenta a eficiência de remoção (57%), Deste modo, os resultados obtidos neste trabalho permite concluir que a montmorilonita é capaz de remover o corante verde malaquita.

Palavras-chave: *Difração de Raio-X, Indústria Têxtil, Adsorventes de baixo-custo.*

ABSTRACT

Removal of malachite green dye by adsorption from aqueous solution using montmorillonite clay is reported in this work. A malachite green dye is a cationic widely used in textile industries. Due to its persistence in the aquatic environment, it becomes a problem for aquatic and terrestrial organisms. This dye can be adsorbed through various techniques, but high acquisition and operating costs preclude widespread use. Several adsorbents are available in the market, but the most outstanding are the clays, especially the montmorillonites. These clays are finely divided material (< 0.002 mm), and its adsorption properties are continuously investigated. Types of clays 2:1 (two tetrahedral to one octahedral) are called expandables. The montmorillonite has a potential for dyes removal in wastewater due to the high surface area, porosity with excellent cation exchange capacity conferring its adsorbent property. This work aims to use the montmorillonite as an adsorption system in stages to textile decolorization effluent, composed of malachite green dye, reproduced in the laboratory. The characterization of the clay gives high purity and is used as adsorbent of good quality and efficiency. The retention of dyes in the system composed of montmorillonite arranged in separation stages was efficient. The effect of dye concentration and retention time are the most important parameters used in this study. High concentrations and retention time below 24 hours resulted in low levels of removal (25%). On the other hand, the low level of initial concentration increases removal efficiency (57%). Thus, the results obtained in this work allow concluding that montmorillonite is able to removal malachite green dye.

Keywords: *X-Ray Diffraction, Textile Industries, Low-Cost Adsorbents.*

1. INTRODUCTION

Clay minerals refer to a group of hydrated aluminosilicates that predominate the fraction of the clay size (< 0.002 mm) alone (Jia *et al.*, 2019; Sadri *et al.*, 2018). These minerals are similar in chemical and structural products. Composition of primary minerals originating from the earth's crust; however, transformations in the geometric arrangement of atoms and ions within their structures occur due to weathering (Chang *et al.*, 2014; Gemeay *et al.*, 2002; Krupskaya *et al.*, 2019; Komadel, 2016). Clays are of great importance in geological prospecting, in agriculture, soil mechanics and in a large number of industries due to their absorbent properties for problems of contamination by agricultural products, decolorization of textile effluents, among others (Raval *et al.*, 2016; Timofeeva *et al.*, 2015). Its structural units are silicon tetrahedra (SiO_4) and aluminum octahedra (AlO_6). The silicon units unite to form tetrahedral sheets, and hexagons are formed every six units oriented in the same direction (Timofeeva *et al.*, 2017). The same happens for aluminum or magnesium units, which form the octahedral sheet. The formation of the lamellar structure of the clays occurs with the overlap of the tetrahedral and octahedral leaves (Cygan *et al.*, 2019). The overlap ratio gives them two distinct classes. When the composition occurs in the ratio of 1:1 (a tetrahedral to an octahedral), the materials are classified as non-expandable. Already when the 2:1 overlap occurs (two tetrahedrons for an octahedron) are called expandables (Zheng and Zaoui, 2018; Zheng *et al.*, 2011; Cadene *et al.*, 2005). This denomination is due to the possibility that clays with 2: 1 composition receive in their interlamellar spaces cations and water molecules, and in the minerals of the group 1:1 hydrogen bonds between the oxygen atoms of the hydroxyl groups of the octahedral layers and the hydrogens of the tetrahedral leaves that prevent the entry of these species (Zheng and Zaoui, 2018). In this way, the materials of this class have a low surface area, being restricted to the external surface. Montmorillonite is a smectite-type clay, so it is a 2: 1 material (Zheng *et al.*, 2011). These clays have three structures, primary, secondary, and tertiary (Krupskaya *et al.*, 2019). The primary structure is of the lamellar type, with two tetrahedral silicon (IV) sheets intercalated by an aluminum (III) octahedral sheet (Komadel, 2016). The secondary structure is the formation of the layer; that is, it results from valence deficiencies (Timofeeva *et al.*, 2015).

The silicon atoms (IV) of the tetrahedral sheets may undergo an isomorphic substitution by aluminum (III) atoms, and the aluminum positions of the octahedral sheets may be completely filled, called trioctahedral, or only two thirds may be filled, dioctahedral. The two facts together provoke an excess of negative charges that are scattered on the surface of the oxygens of the octahedral and tetrahedral leaves (Marsh *et al.*, 2018).

The tertiary structure occurs because of the excess of negative charges. This excess is compensated by cations, which are trapped between the layers and with free movement in them (Na^+ , K^+ , Ca^{2+} , etc.) (Fernandez *et al.*, 2011). These cations can be replaced by more acidic or complex catalytic activity or, depending on their size, increase the interlamellar distance of the clay, allowing larger molecules to diffuse between the lamellae. The structure of these minerals gives Brønsted acidity, due to the interaction of the hydration waters present in the lamellae with the compensating and formation cations of hydroxyl groups, and of Lewis, associated to the cations of compensation of the interlayers. In view of these properties, this work aims to use montmorillonite clay as adsorber of malachite green dye (MG) widely used in the textile industry (Raval *et al.*, 2016). Dyes are being produced on a large scale and used in various industries. Whether they are textiles, pharmaceuticals, printing, cellulose, plastics, among others. Dyes are organic compounds of high toxicity and considered carcinogenic (Monteiro *et al.*, 2014). Due to the chemical structure, the dyes are resistant to decolorization, being difficult to be degraded and released to the aquatic without damaging the existing flora and fauna (Raval *et al.*, 2016). Given this scenario, there are many methods for the removal of these effluents such as oxidation, biodegradation, ion exchange, ozonation, reverse osmosis and adsorption, especially the use of montmorillonite as an efficient and promising method of low cost and ease of operation (Hajira *et al.*, 2010).

The montmorillonite is a material with a large surface area, presence of porosity, high surface charge, and cation exchange capacity that make it an excellent adsorbent (Raval *et al.*, 2016).

2. MATERIALS AND METHODS

2.1. Raw materials

The chemical composition of montmorillonite clay is given in Table 1. In order

to simulate dye contaminated effluent, an aqueous solution of malachite green (MG) was used (Merck™). The properties of the MG is cationic classification, with molecular formula $C_{23}H_{25}N_2Cl$, molecular weight $364.91 \text{ g}\cdot\text{mol}^{-1}$, and visible region exhibit the main peak with a maximum absorbance at λ_{max} at 620 nm (Qu *et al.*, 2013). Dye concentrations (100, 75, 50, 25, 10, 5 e 1 $\text{mg}\cdot\text{L}^{-1}$) were determined by UV-visible spectrophotometry (Ultra-Fast Scan UV-1900 – SHIMADZU™).

Table 1: Chemical composition of montmorillonite clay (wt%).

Oxides	Montmorillonite
SiO ₂	49.92
Al ₂ O ₃	15.81
CaO	8.03
Fe ₂ O ₃	7.11
MgO	3.72
K ₂ O	2.27
Na ₂ O	2.08
TiO ₂	0.74
Others	10.32

The adsorption tests were performed according to figure 1. In 25 mL of the MG solutions, the dye was left in contact with the montmorillonite at time intervals of 3, 6, 12, 24, 48 and 72 hours (Klunk *et al.*, 2019).

3. RESULTS AND DISCUSSION

3.1. Characterization of montmorillonite

The surface area (BET) for montmorillonite is $40.52 \text{ m}^2/\text{g}$ and cation exchange capacity (CEC) of the montmorillonite is 89 meq/100 g. The mineral composition of montmorillonite was determined via powder XRD using a Philips X'pert APD diffractometer with PW3020 goniometer, Cu lamp, and graphite monochromator. Diffraction data were processed by Philips X'Pert and ClayLab ver. 1.0 software. The obtained diffractograms are shown in figure 2. The presence of sharp peaks indicates high crystalline structures of montmorillonite. The characteristic diffraction peaks at 2θ of 6.75° ; 10.83° ; 19.78° ; 22.65° ; 27.54° and 34.93° which were earlier reported by Zhao *et al.*, 2019, suggesting good crystallinity (Ahmed *et al.*, 2018). These results were identified based on the International Union Database Crystallography's Joint Committee on Powder Diffraction Standards (JCPDS) (Scapin, 2003; Atkins and Jones, 2001).

Thermogravimetric analysis is a method in which the mass loss of the sample is measured over time (Ma *et al.*, 2019; Hojiyev *et al.*, 2017). TG/DTA curves of montmorillonite are shown in Figure 3. As observed, the curve of montmorillonite revealed a two-step mass loss in the ranges of $50\text{--}250^\circ\text{C}$ and $500\text{--}700^\circ\text{C}$. The first and dominant endothermic peak between 50 and 250°C was due to the removal of physically adsorbed water with a maximum loss of 8.95% observed at 160°C . The second endothermic peak between 500 and 700°C might be attributed to dehydroxylation of the aluminosilicate layers with a maximum loss of 14.73% observed at 650°C .

FTIR spectra of montmorillonite (Figure 4) show absorption bands in the region at 3630 and 1635 cm^{-1} can be assigned to stretching and bending vibrations of OH groups of crystal and adsorbed water molecules, respectively, and the band at 3629 cm^{-1} to the stretching vibration of the OH groups in the silicate layer. The band at 1050 cm^{-1} corresponded to the stretching vibration of Si-O. The bands at 920 and 750 cm^{-1} can be assigned to the OH bending modes of AlOH groups, respectively. The vibrational band at 620 cm^{-1} , 525 cm^{-1} and 485 cm^{-1} resulted from Si-O-Si, and these are the internal asymmetric stretching vibration, coupling vibration of Al-O and Si-O bending vibrations respectively (Zhao *et al.*, 2019; Zhang *et al.*, 2017). The adsorption-desorption hysteresis loops for the montmorillonite is shown in Figure 5 and correspond to Type H3, which is commonly ascribed to layered materials. In $P/P_0 = 0.4\text{--}0.6$ point of hysteresis loops formed during rapid desorption of N_2 molecules from the surface also corresponds to the layered materials (Ma *et al.*, 2019; Hojiyev *et al.*, 2017).

3.2. Adsorption study of dye in montmorillonite

The adsorption process of the dye was investigated in concentrations of 100, 75, 50, 25, 10, 5 and 1 mg/L and the results (removal percentage of dye) are in Figures 6. In high concentration of the dye, 100, 75 and 50 mg/L, the percentage of dye removal has an efficiency of 2.0, 2.5 and 5.5%, respectively, for 3 hours of contact with the adsorbent (clay material). Therefore, at low concentrations, 25, 10, 5 and 1 mg/L, the decolorization system had an efficiency of 12, 17, 19 and 25%, respectively, in 3 hours in the adsorption system. The highest adsorbent performance is recorded at the contact time of 72 hours where the removal percentage reaches values of 31, 38, 49 and 57% at low

concentrations of 25, 10, 5 and 1 mg/L, respectively. According to the schematic representation of Figure 1, we can see that the performance of the system becomes more efficient for high retention times (24, 48, and 72 hours). This is due to the removal capacity of the built system because as the dye goes through the withdrawal stages (1 - 6), the concentration decreases. Montmorillonite plays its role in retaining the chromophoric groups efficiently.

4. CONCLUSIONS

The adsorption of malachite green onto montmorillonite proved to be efficient. According to the characterization results, clay has excellent crystallinity, high adsorption, and desorption capacity, large surface area (40.52 m²/g) and high cation exchange capacity of 89 meq/100 g. The FTIR shows that the montmorillonite used in this study has high purity. The dye retention system composed of montmorillonite arranged in separation stages was efficient. The effect of dye concentration and retention time are the most important parameters used in this study. High concentrations and retention time below 24 hours resulted in levels of removal (25%). On the other hand, the low level of initial concentration increases removal efficiency (57%). Thus, the results obtained in this work allow concluding that montmorillonite is able to removal malachite green dye.

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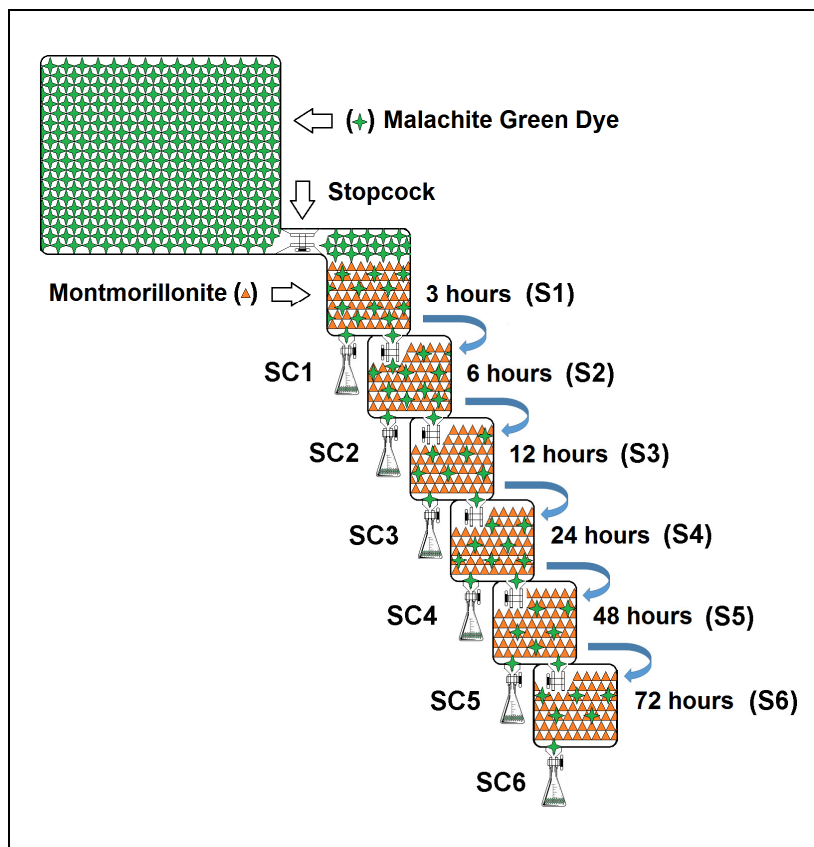


Figure 1: Schematic decolorization system (DS) of the dye with montmorillonite in stage 1 (S1) to stage 6 (S6) and sample collection (SC1 to SC6).

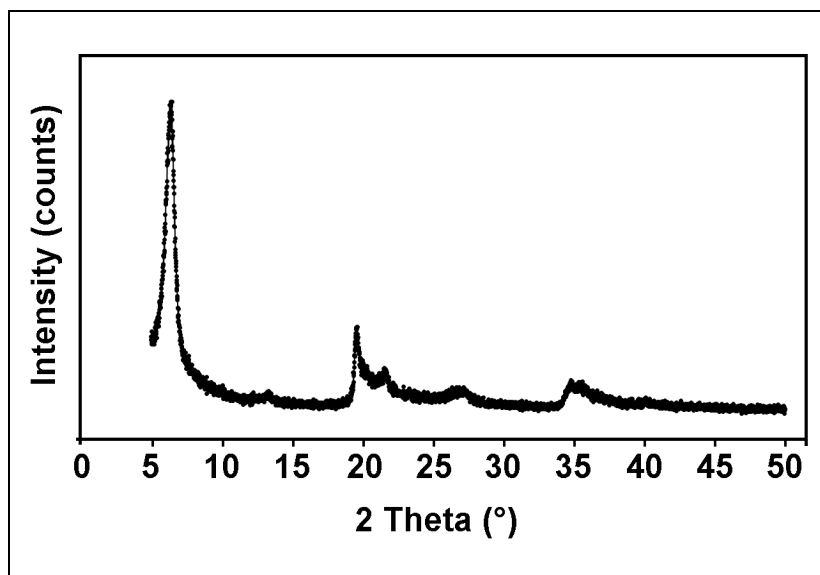


Figure 2: XRD of Montmorillonite.

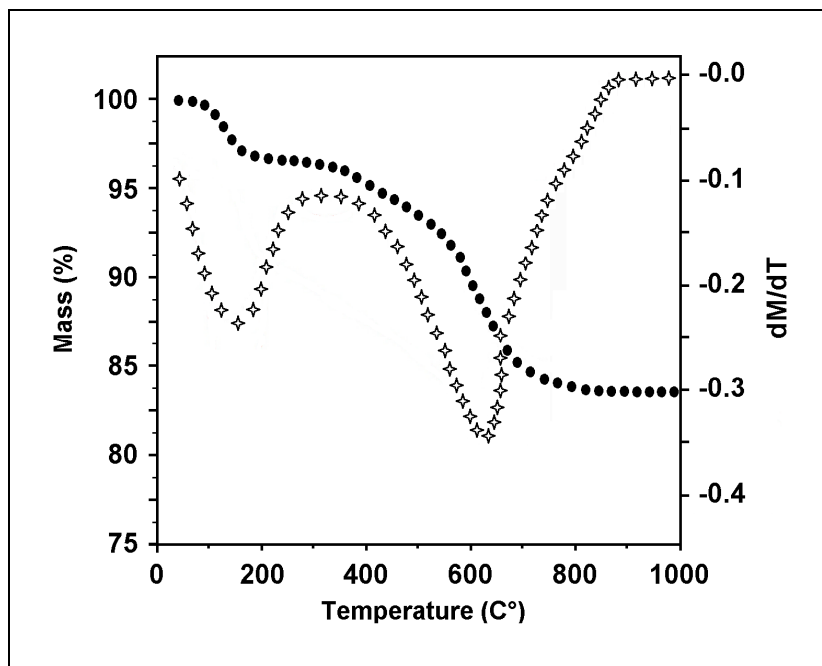


Figure 3: TG/DTA curves of montmorillonite.

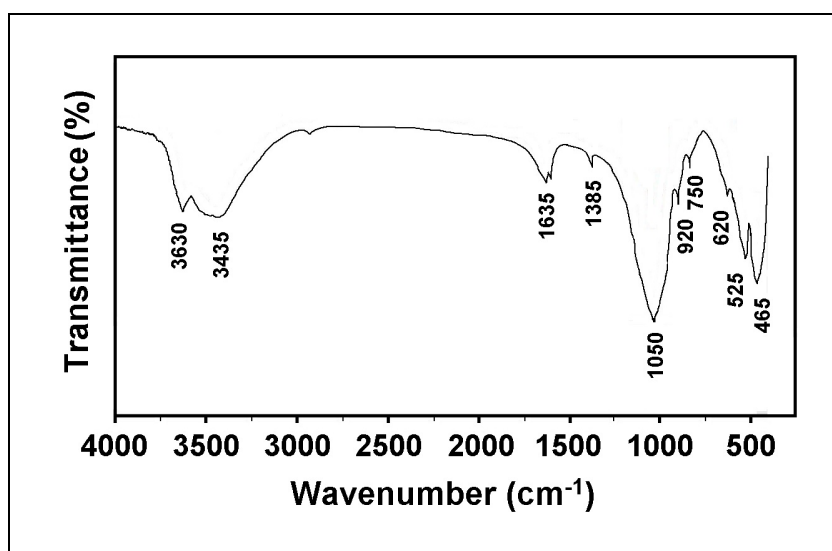


Figure 4: Fourier Transform Infrared Spectroscopy of montmorillonite.

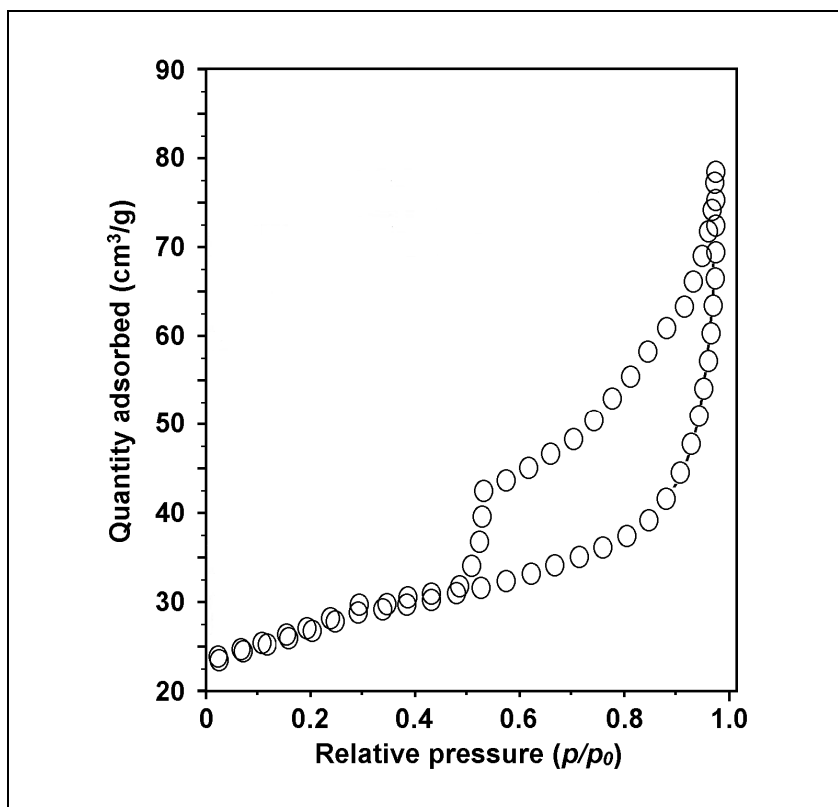


Figure 5: N_2 adsorption and desorption isotherms at montmorillonite

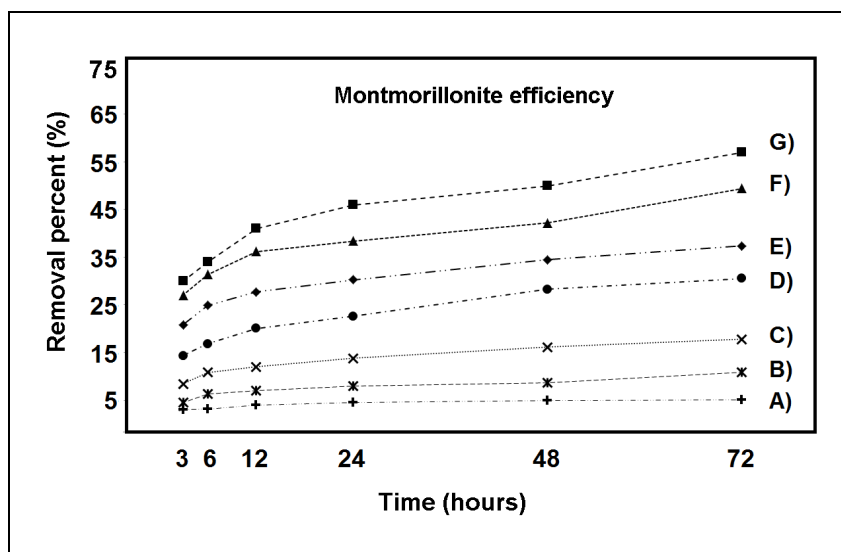


Figure 6: Percentage of removal dye in montmorillonite. (A), (B), (C), (D), (E), (F) and (G) represent concentration of the dye 100, 75, 50, 25, 10, 5 and 1 mg/L, respectively.