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Mathematical Modelling of the Removal of Basic Blue Dye from Effluent by a Mineral Membrane

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Abstract: Water contamination is a major challenge due to the discharging of wastes into the natural resources. In this study, a novel branched pore adsorption model was developed by utilizing external mass transfer coefficients, K_f, effective diffusivity, and lumped microspore diffusion rate parameters. This describes sorption kinetics from long-term adsorption that occurs between an adsorbent and an adsorbate. An investigation of the effects of dye concentration on Basic Blue 9 removal was conducted. Then by considering of initial and boundary conditions the government equations were solved. Using this model, the Basic Blue 9 (or methylene blue is an industrial inhibitor) was removed from a bentonite sample polluted by Basic Blue 9. The maximum adsorption capacity was achieved by using of Freundlich analysis. Based on the experimental data, theoretical concentration - time adjusted models were developed using a FORTRAN computer program to fit the experimental data more precisely and confirm the precision and accuracy of this research.

Keywords: Effluent, Adsorption, Dye, Basic Blue 9, Freundlich analysis, Isotherms.

1. INTRODUCTION

Textiles, rubber, paint, tanneries, leather, laundry, etc., production processes contribute significantly to coloured effluent pollution [1-4]. Due to colours from various dyes used in textile-making procedures, textile wastewater poses problems when released into the environment. Dye-containing wastewater discharged into natural streams and rivers can cause severe problems since dyes are toxic to aquatic life [5]. It is dangerous for marine so that disposed of untreated liquid into water resources causes serious health problems for humans.

However, treating wastewater containing dyes is challenging since the organic molecules have a high resistance to aerobic absorption and heat, light, and oxidation. Several methods, such as precipitation, oxidation, coagulation, electrolysis, flotation, and adsorption, are generally used to treat colour contaminated effluents. Selection of the treatment method for any situation mainly depends on the concentration of colour and the cost of treatment. In addition, the adsorption method of removing dyes, pigments, and other dyes and pigments is highly effective and economical [6].

Activated carbons with high surface area are the most famous adsorbent and have shown high adsorption capacities for a lot of adsorbents containing dyes. However, it has several disadvantages, including excessive regeneration costs [7]. In place of activated carbon, alternative low-cost, new, domestically available adsorbents are currently being used to remove dye effluents from aqueous solutions in textile dye production. Bentonite and Montmorillonite are clays with high chemical and mechanical properties and are low in cost.

Several studies have been on removing of basic dye from effluent. According to Shawabkeh *et al*. [8], diatomaceous earth adsorbed methylene blue from a aqueous solution. They also investigated how adsorption is affected by particle size and concentration of adsorbents, initial dye concentrations, and agitation speed. De Souza *et al*. [9] modelled an adsorption process for textile dyes using fixed bed columns. Several extensive tests were conducted to study the aqueous adsorption isotherms of Basic Green 4 over activated carbon granules. Among the different adsorption isotherm models, Langmuir and Radke-Prausnitz performed best. In an investigation by Abidi *et al*. [10], dyes, salts, and auxiliary chemicals were combined to treat dye-containing effluents by adsorption onto natural clay. Real and synthetic effluents were used in the adsorption experiments, including dyes (Reactive Orange 84, Reactive Red

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120, and Reactive Blue 160) and natural clays (Fouchana and Tabarka). A promising adsorbent alternative to dyeing effluents is clay, which is inexpensive and effective. Dave *et al*. [11] investigated how sewage sludge could be used to remove basic dye basic red-12 from an aqueous solution.

Various parameters were investigated, including temperature, initial pH, initial adsorbent dosage, contact time, and initial dye concentration. Adsorption isotherms were analyzed using the Langmuir and Freundlich equations. Saibaba and King used a green carbon bio-sorbent derived from plant biowaste to tackle the problem of aqueous solutions containing a basic Methylene Blue (MB). Several experimental runs were performed to assess the influence of pH, temperature, initial dye absorption, and bio-sorbent dosage on dye removal. Abdelmajid Regti *et al*. [12] examined the effects of phosphoric acid on activated carbon derived from Persea Americana nuts on the absorption of Basic Blue 41 dye. To determine the adsorption capacity, pH, the amount of adsorbent, dye concentration, temperature, operating parameters, and contact time were tested. The adsorption behaviour of cationic surfactant-modified bentonite clay was studied systematically by Anirudhan and Ramachandran [13]. They demonstrated that it was effective by removing the basic dyes from aqueous phase, such as methylene blue (MB), rhodamine B (RB), and crystal violet (CV). Shakoor and Nasar [14] examined the effectiveness of an adsorbent derived from citrus limetta peel (CLP) for removing Methylene blue dye (MB).

In this paper a novel model has been developed that using practical data consider removing of dye from water. Therefore, a key objective of this research is to investigate the isotherm and kinetic models that mimic the experimental results for the adsorption of a basic dye, Basic Blue 9, from water using bentonite clay.

2. EXPERIMENTAL METHOD

Bentonite is a clay primarily comprised of montmorillonite that forms when volcanic ash is altered. As an adsorbent, bentonite is ideal for removing several ionic impurities from wastewater due to its excess negative charge [15]. Clay minerals, like bentonite, consist of units composed of two sheets of silica tetrahedra and a sheet of aluminium octahedrons. An isomorph creates a negative charge by substituting Al^{3+} in the tetrahedral layer along with Mg^{2+} in the octahedral layer.

Bentonite used in this research is provided by ARAK Powder Company in Iran. The characteristics of used Bentonite have been shown in Table **1**. The dye used in the research is Basic Blue 9 - a cationic thiazine dye supplied by Sigma Chemical Company®, with Colour Index Number (C.I No.) 52015. Figure **1** gives the structures of this dye.

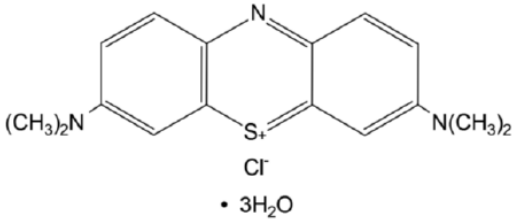

Figure 1: Basic Blue 9 Chemical Structure (in accordance with Color Index).

An absorption spectrophotometer device (made by Varian Company® brand Cary 100 – Australia manufacturer) was used along with a solution (concentration 0.01 gr/lit), and the relevant spectrum UV-VIS is shown in Figure **2**. According to this, the maximum Wavelength of Basic Blue 9 was achieved as 608 nm and has been used on mathematical modelling and practical experiments [12].

Table 1: Bentonite Characteristics (According to Manufacturer Data Sheet)

Composition	Value	Composition	Value
SiO_2	61.4%	CaO	0.6%
Al_2O_3	18.1%	K_2O	0.4%
Fe_2O_3	3.2%	Na_2O	2.2%
TiO_2	0.1%	H_2O	5.0%
MgO	2.3%	Hg	<2.5ppm
Cation exchange capacity (meqs/100gr)		80–85	

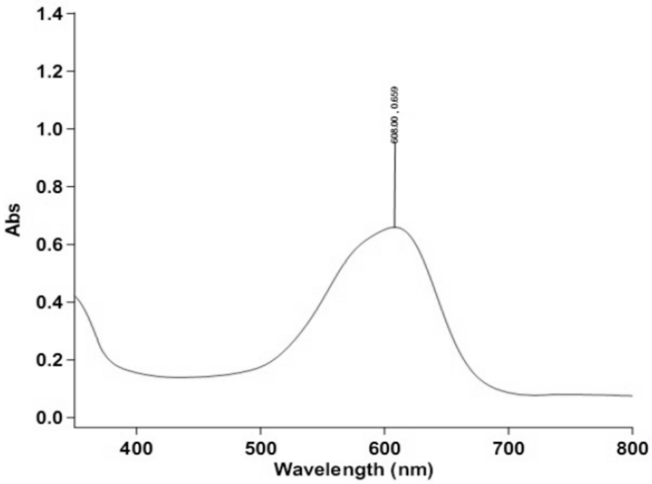

Figure 2: Maximum Wavelength of Basic Blue 9 (extracted from spectrophotometry device).

A calibration graph is necessary to evaluate remain colour concentration during an experiment. Each concentration was measured for its absorbance value by sequentially diluting the solutions to a concentration range of 0.01 to 0.05 gr/lit. The absorbance values were plotted against the concentrations to construct a calibration graph and then interpolated the measured absorbance values to obtain the subsequent dye concentrations (Table **2**, Figures **3** and **4**) [12].

Beer – Lambert Equation equable coefficient was extracted from above mentioned results as shown in following:

$$A=\epsilon bC$$

that A, ϵ, b and C are absorbance, molar absorptivity, length of light pad, concentration, respectively. Using

Table 2: Extracted Data for Calibration Graph of Basic Blue 9

C.	0.01	0.02	0.04	0.06	0.08
A.	0.1497	0.1663	0.2431	0.2700	0.3440

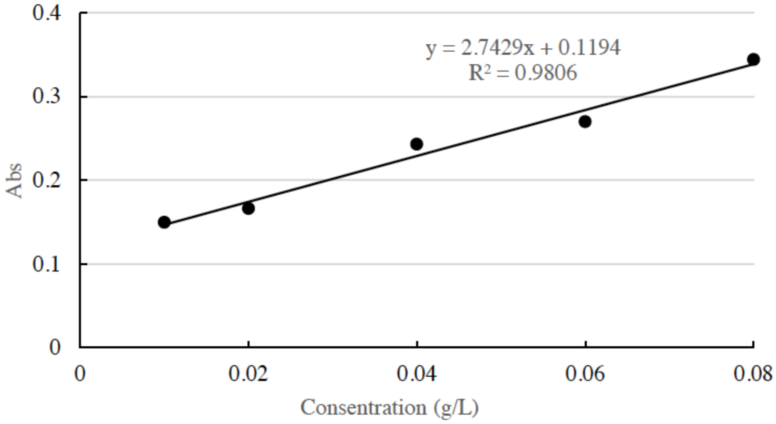

Figure 3: Basic Blue 9 Calibration Graph (extracted from spectrophotometry device).

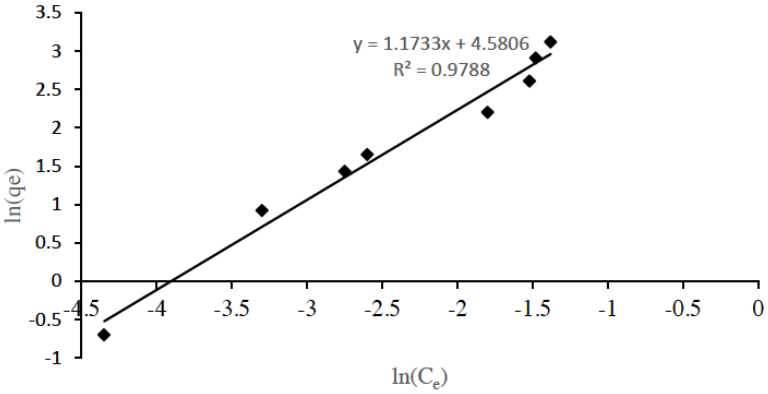

Figure 4: Freundlich Isotherm, Linear Shape (the graph has been originated based on the change in Ln of adsorption quantity "q_e" at the equilibrium point against with Ln of concentration of basic blue 9 at the same point).

Table **2** data, ϵ achieved equal to 4.8 M^{-1}cm^{-1}, accordingly.

2.1. Adsorption Isotherm

Below equation is applicable for adsorption of solutions on the solid adsorbent:

$$-V\frac{dC}{dt}=M\frac{dq_e}{dt} \tag{1}$$

And consequently, below equation is applicable:

$$C(\tau_1)=C_0-(\frac{M}{V})\bar{q}(\tau_1) \tag{2}$$

The solution under mass transfer process reaches the external surface of the absorbent, and then in line with relevant constants coefficients will infiltrate into the adsorbent particles. To find adsorption isotherm, various concentrations of colour were prepared, and 0.1 gr of Bentonite was added to the solutions. On the regular periodic time, the absorption number was recorded.

2.2. Mathematical Model

The mathematical model was designed on FORTRAN, and inputs data were defined as follows:

1-The average diameter of adsorption particles as per the manufacturer catalogue: 22.44 µm

2-Porosity coefficient of used Bentonite: 0.398

3-The density of used Bentonite: 1.261gr/cm^3

Considering the quantity of bentonite particles equal to *1.61 ×,10-9.*, the external surface area of bentonite particles for 12 gr is: S_f = *1.58 ×,10-9.* cm^2.

The mathematical model has been designed in accordance with FPSD (Film Pore Surface Diffusion) type [16]. At the first step, Basic Blue 9 molecules in the solution under K_f effects are moving to Bentonite particles' external surface. Then diffusion into the solution between particle pores is affected by D_p coefficient. After this stage, adsorption of colour molecules to Bentonite porosity will occur. The mentioned process is going onward repeatedly.

The main equation for model is:

$$\frac{dC_t}{dt}=-K_fS_A\left(C_t-C_s\right) \tag{3}$$

In order to extract K_f the proposed method has been used [14].

$$\frac{dC_t}{dt}=-K_fS_A\left(C_t-C_s\right) \tag{4}$$

$$\left.\frac{dC_t}{dt}\right|_{t=0}=\frac{C_t-C_0}{t-0} \tag{5}$$

D_p has been calculated in accordance with PDSMATB (Pore Diffusion Sorption Model applied to the Batch Test) method that in spherical system below equation is applicable:

$$\frac{\partial q_p}{\partial t}=D_A(\frac{\partial^2 q_p}{\partial r^2}+\frac{2}{r}\frac{\partial q_p}{\partial r}) \tag{6}$$

And D_A is extracted with below equation:

$$D_A=\frac{D_P}{1+\frac{(10-\varepsilon_p)}{\varepsilon_p}.K_l} \tag{7}$$

$$D_A=1.19297e-10 \quad \Rightarrow \quad D_P=1.98802e-6(cm^2/s)$$

To calculate Molecular Mass Transfer (D$_s$) for a sphere material, below equation has been considered [17]:

$$\begin{gathered}\frac{q_t}{q_\infty}=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2D_st}{r^2}\right)\Rightarrow\\ \frac{q_t}{q_\infty}=6\left(\frac{D_st}{r^2}\right)^{0.5}\left[\frac{1}{\sqrt{\pi}}+2\sum_{n=1}^{\infty}erfc\left(\frac{nr}{\sqrt{D_st}}\right)\right]-\frac{3D_st}{r^2}\end{gathered} \tag{8}$$

In equation (8), the erfs is the complementary error function.

3. RESULTS AND DISCUSSION

Adsorption Kinetics

To study the adsorption kinetics, the data extracted from spectrophotometry device were simulated with mentioned model.

The graph for q_e against C_e has been shown in Figures **3** to **5**. In accordance with these graphs, q_m and k_1 were extracted.

Considering regression coefficients for both graphs, in this paper was established that the firm isotherm is

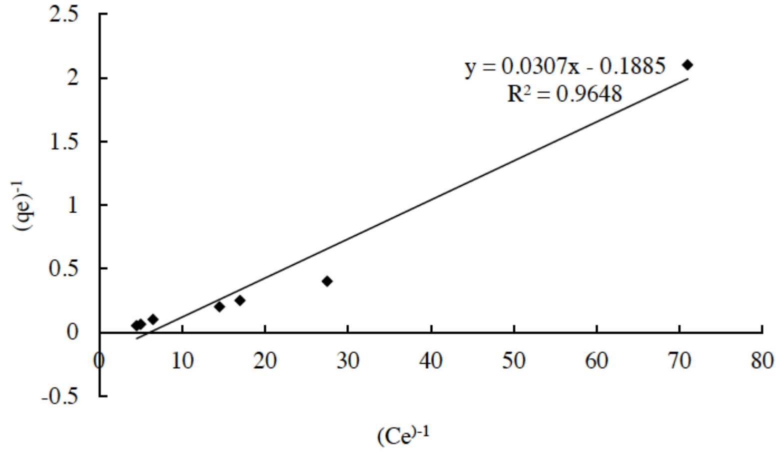

Figure 5: Langmuir Isotherm, Linear Shape (the graph has been originated based on the change in Ln of adsorption quantity "q_e" at the equilibrium point against with Ln of concentration of basic blue 9 at the same point).

Freundlich. With consideration in Table **3**, Ln K_f, 1/n and saturated concentration of bentonite have been shown in Figure **6**.

The Ln K_f, 1/n and saturated capacity of adsorption particles are shown on Table **3**.

The mentioned concentration, have been extracted from Beer – Lambert Equation as mentioned previously.

Effect of Dye Adsorption Concentration

Effect of dye absorption versus time at various preliminary dye concentration and constant absorbent was compared between experimental and model results (model results have been achieved from Mathematical Model. Figure **7** shows dye absorption at dye concentration of 0.01 gr/lit and 0.1 gr bentonite. Increasing time by 60 minutes decreased the dye concentration ratio (C_t/C_0) up to 0.75 as an

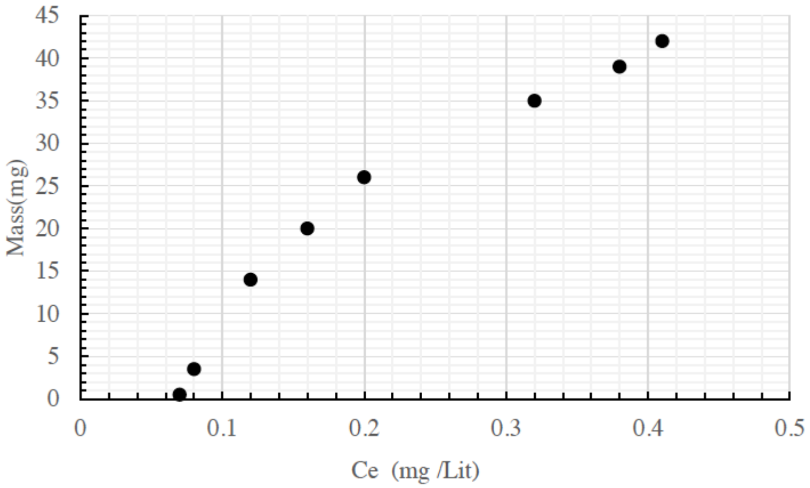

Figure 6: Freundlich Isotherm (has been drawn for adsorption of Basic Blue 9 into bentonite).

Table 3: Raw Calculated Data for Bentonite (These Data are Necessary for the Mathematical Modeling)

K_f **[(mg/gr).(l/mg)^1/n)]**	**1/n**	q_m **(mg/g)Saturated Capacity**
43.669	0.180	56.338

experimental result. The developed model shows ratio of 0.7 after this time. Also, Figure **8** shows absorption ratio at same bentonite concentration and 0.03 gr/lit dye. After passing time of 60 min the concentration ratio reached around 0.75. It can be seen in Figure **9** too. It is concluded from Figures **7**-**9**: First, there is a good agreement between practice and simulated data. Second, after 60 min the various concentration reached into same ratio. This is showing that absorbent can absorb the dye in an appropriate time at various concentration. So, the time is important factor for absorption. To demonstrate effect of time on absorption better, Figure **10** shows effects of time versus concentration ratio at various bentonite concentrations and constant dye concentration. This figure represents in the first times, increasing bentonite concentration increases the absorption ratio; however, after passing the time the absorption ratio reached to same value (about 0.75). This shows the time has a important effect on the dye absorption, so that, at different dye and bentonite concentrations after 60 min the concentration ratio has reached around 0.75.

CONCLUSION

This study analysed, a new branched - pore adsorption model. An investigation was conducted into how initial dye concentration and bentonite mass affect Basic Blue 9 removal rates. We determined the maximum adsorption capacities using Freundlich analysis. According to mathematical model output, adsorption quantity will decrease with an increase in the volume of adsorbent particles which was estimated because of decreasing on special surface area. On the other hand, the adsorption increases significantly under

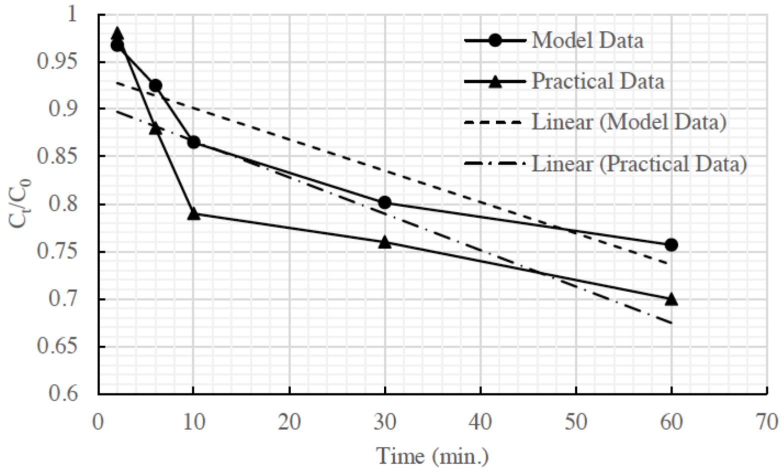

Figure 7: Effect of dye absorption versus time at preliminary dye concentration of 0.01 gr/lit and 0.1 gr bentonite.

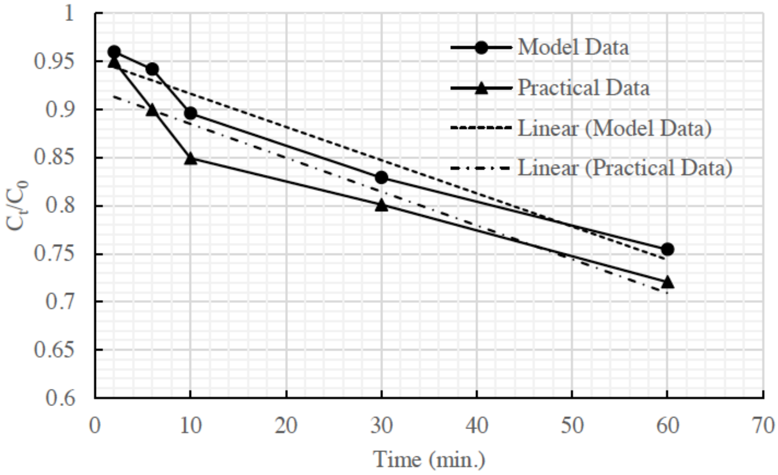

Figure 8: Effect of dye absorption versus time at preliminary dye concentration of 0.03 gr/lit and 0.1 gr bentonite.

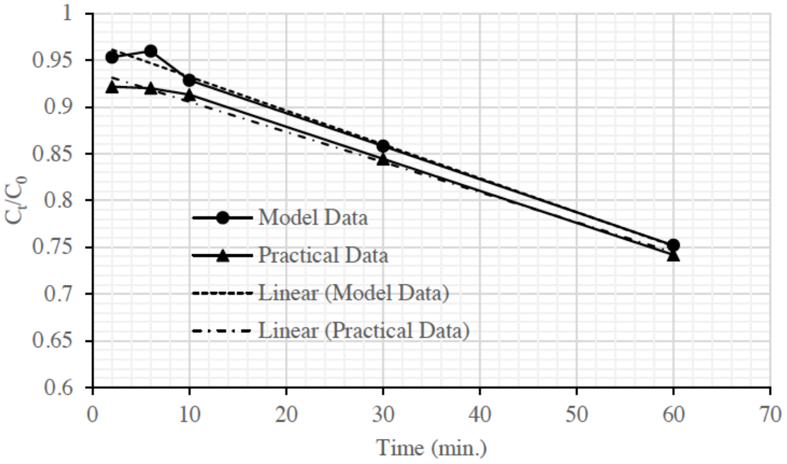

Figure 9: Effect of dye absorption versus time at preliminary dye concentration of 0.05 gr/lit and 0.1 gr.

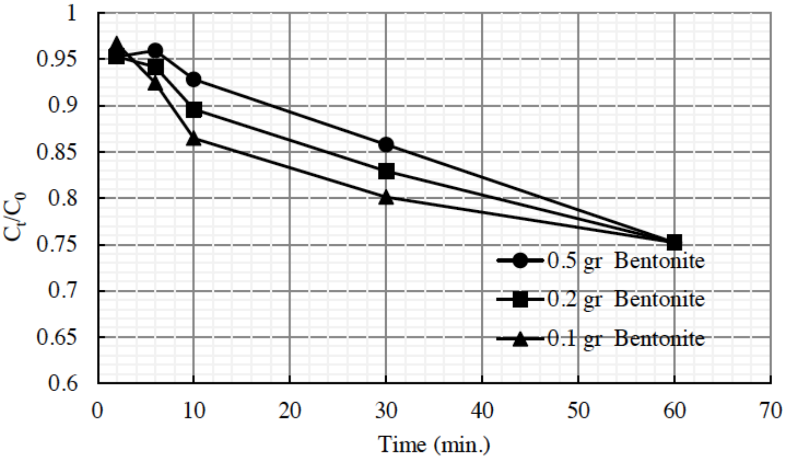

Figure 10: Effect of dye absorption versus time at constant preliminary dye concentration of 0.03 gr/lit.

the less preliminary concentration of colour. Meanwhile, an increase in the Bentonite mass has a few positive effects on adsorption, because after passage of time the concentration ratio reached to an approximately constant value.

ARTICLE HIGHLIGHTS

- The modelling of an adsorption process applied.
- Removing of basic dye from water.
- This study aims to use bentonite clay for adsorption of basic dyes.

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