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Efficient Removal of Methyl Orange from Water onto PVC/Bentonite Membranes: Experimental Validation and COMSOL Multiphysics

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Abstract: Nowadays, the treatment of domestic and industrial wastewater is a very important topic in environmental protection. Reuse of this water is one of the possibilities already implemented. A rapidly developing process in this area is membrane filtration. Membranes based on polymer materials are generally employed in the purification of wastewater resulting from the accumulation of dyes in industries such as textiles, paper, and others. In this regard, membranes using polyvinyl chloride (PVC) added to Bentonite, which is natural clay obtained from the Roussel deposit (Maghnia, Algeria) were prepared. Bentonite was chosen for its remarkable ion adsorption properties and its incorporation at different ratios improves the membrane's efficacy for water treatment purposes. The filtrates collected were studied using UV-Vis spectroscopy. This technique allowed us to estimate the removal capacity of organic dye, methyl orange, from our membranes. The results demonstrated that our newly prepared materials with higher Bentonite content exhibited a better depollution efficiency and, consequently, higher capacity adsorption for methyl orange. This is indubitably attributed to the porous structure of Bentonite. Thus, these membranes represent the current best alternative to known separation techniques. The finite element method-based software COMSOL Multiphysics has been used to investigate filtration processes in the model system. Finally, the numerical results of the proposed model are compared with the available experimental data and that represent good agreement.

Keywords: *Membrane, Bentonite, Dye,PVC, Filtration.*

1. Introduction

Industrial waste from energy, metal production and processing sectors, as well as the paper pulp industry, textile pre-treatment and dyeing, and tanning, produce an impact on our environment in all its aspects: air, water, and soil. The effluents from these activities contain highly toxic chemicals that are generally non-biodegradable. Directives from the European Environment Agency (EEA) oblige all manufacturers to considerably reduce both atmospheric emissions and heavily loaded effluents. Therefore, each industrial operator is obliged to apply the best available techniques.

The accumulation of dyes in wastewater from the textile, paper, cosmetics, rubber and plastics industries has been identified as a major source of water pollution. Reactive dyes and anionic dyes are the most commonly used because of their resistance, bright colour and ease of application **[1].**

Methyl orange is a carcinogenic, hydro-soluble anionic azo dye that is widely employed in the textile industry, in the manufacture of printing paper and research laboratories. It is a synthetic and stable dye with low biodegradability, making it difficult to remove from aqueous solutions using traditional methods **[2-3]**.

The use of membranes in the treatment of industrial wastewater from washing operations, which is often highly polluted, emanated as a technique employed by industries. Strict regulations imposing high fees for connecting to the domestic sewer network encourage them to explore new alternatives for reducing the costs linked to wastewater purification. Membrane treatment offers them two advantages: advanced treatment of effluent that ameliorates its characteristics, and the possibility of recycling residual water **[4]**.

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In the present work, we have prepared composite membranes based on polyvinyl chloride (PVC) with the addition of Bentonite obtained from the Roussel Maghnia deposit, in Western Algeria.

Bentonite's utilization in wastewater treatment is gaining more and more attention and is now an attractive market because it is abundant, low cost and available in many countries.

Compared to other types of membranes for wastewater treatment, these membranes offer several advantages. They are relatively inexpensive and easy to produce, making them accessible to small scale wastewater treatment facilities. Additionally, they exhibit high efficiency in the removal of a wide range of colouring agents.

Clay membranes are a type of polymeric membrane containing clay, an abundant natural material available in many parts of the world. Due to their selectivity, chemical stability and relatively low cost, they are used for liquid phase separation or removal of contaminants **[5].**

Due to their hydrophobic and oleophobic properties, clay membranes can be applied to separate immiscible liquids (such as water and oil). They can also be used to separate solutes from aqueous solutions, depending on their size and charge. Clay membranes can be modified to increase their selectivity in relation to the components which are to be separated.

They can also be utilized for the removal of organic contaminants, heavy metals and nutrients from water. The selectivity of clay membranes gives the ability to focus on the contaminants to be removed. The controllable porosity of the membrane makes it possible to improve the depollution capacity.

As they are relatively inexpensive and readily available, clay membranes have the potential to provide an economical and performing solution for liquid phase separation or dewatering processes.

Some examples of studies on the use of clay membranes in these areas are described in the section below.

To begin with, industrial wastewater decontamination: One study involved the use of clay membranes to remove dyes from industrial effluents. Membranes based on montmorillonite-type clay were found to have a high capacity for adsorbing dyes, leading to a significant reduction in the concentration of dyes in the wastewater **[6]**.

In addition, oil/water separation: Clay membranes have also been successfully employed to separate oil and water in industrial wastewater. Membranes that contain kaolinite-type clay have proven to be highly selective for oils, thus providing an efficient method of separating oil from water.

Furthermore, nanoparticle filtration: Clay-based membranes were also used in nanoparticle filtration. Membranes prepared with montmorillonite-type clay showed a high nanoparticle filtration capacity, resulting in efficient separation of nanoparticles in liquid phases. And lastly, groundwater decontamination: The clay membranes use the PVC/Bentonite membrane technique developed to decontaminate groundwater. It consists of creating a watertight barrier from PVC sheets and Bentonite, a clay material. This is intended to prevent the spreading of contaminants into the groundwater.

Currently, scientific research cannot do without digital solutions which allow us to model the various problems posed and thus optimize the parameters and settings of the proposed models. On the other hand, the very great evolution of the performance of modern computers in terms of computing power and the extent of central memory, have allowed researchers to take advantage of this benefits offered to find numerical solutions to their scientific problems without recourse to very expensive mainframe computers. The great advantages and the different models that computer aided design (CAD) software can provide us guarantee that we no longer have to worry about writing tedious and complex codes concerning the different mathematical equations that define physicochemical phenomena of the real-world. The user's task is thus made very easy thanks to an interactive graphical interface presented by this software. Among several CAD software which utilize the finite element method (FEM) in their resolver kernel, we found that COMSOL Multiphysics fulfills the simulation task well and can give us very precise results [7].

2. Materials and methods

2.1 Materials

2.1.1 Polymer

The polyvinyl chloride is supplied by the national petrochemical company TINDAL (M'sila). (Algéria). It is a thermoplastic polymer produced using the suspension polymerizing method. It is a white powder.

2.1.2 Bentonite

The clay used is a natural montmorillonite extracted from the Roussel deposit (Maghnia-Algeria). The chemical composition is listed in Table 1.

Table 1: Chemical composition of natural Bentonite from Maghnia (% by weight).

Compound	Percentage (%)	Compound	Percentage (%)
SiO_2	59.52	K_2O	1.84
Al_2O_3	17.6	TiO_2	0.79
Fe_2O_3	8.72	P_2O_5	0.19
CaO	4.56	Na_2O	0.14
MgO	1.56	Other compounds (SO_3, Mn_3O_4, Cl…)	<0.08

2.1.3 The Dye

The dye is helianthine, also known as Methyl Orange or Orange III, with a molecular weight of 327.33 g/mol and a molecular formula of $C_{14}H_{14}N_3NaO_3S$. Obtained from Asia Pacific Specialty Chemicals was provided by Sigma-Aldrich. It is a coloured indicator used in chemistry to indicate the presence of an acidic or basic medium. The acid form is called 4-benzenesulphonic acid and the basic form (as the sodium salt) is sodium 4-benzenesulphonate. The chemical structure is illustrated in Figure 1.

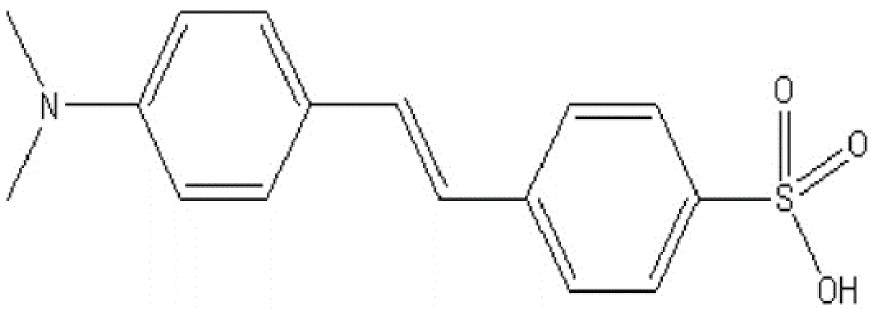


Figure 1: Chemical Structure of Methyl Orange

2.1.4 The solvent

The choice of solvent plays an essential role in membrane synthesis as the polymer must be soluble in the solvent. Tetrahydrofuran (THF) with a molecular weight of 72.11 g/mol and a molecular formula of C_4H_8O provided by Sigma-Aldrich serves as the the most suitable solvent for PVC. It was used without any further purification.

2.2 Methods

2.2.1 Membrane preparation

The PVC/Bentonite composite membranes have been produced using a sol-gel method following a procedure reported by Sugiura, and al. **[8]**. They were prepared by mixing PVC/Bentonite in different ratios (10%, 25%, 50% and 100%). These two materials were dissolved separately in 15ml of THF under constant mechanical stirring (3000 rpm) for t = 45 minutes at T = 25°C. The solution obtained was then poured into a glass Petri dish with a diameter of 9.5 cm. After evaporation of the solvent in the open air, a film was formed which was easily peeled from the glass surface.

2.2.2 Filtration test

The test's objective is to estimate the membrane's filtration capacity and retention of the organic pollutant Methyl Orange. We have proceeded as follows. The filtration device in which the membrane is placed is shown in Figure 2. The contaminated water was introduced over the top, passed through the membrane and the filtrate collected in an Erlenmeyer flask. Pressure was applied to facilitate diffusion of the water through the membrane and filtration was continued until the membrane pores were saturated. Samples were taken before and after filtration for UV-Vis analysis to determine filtration efficiency. The calibration curve relating the absorbance to the concentration of Methyl Orange was used to determine the concentration of the contaminant after filtration **[9]**.

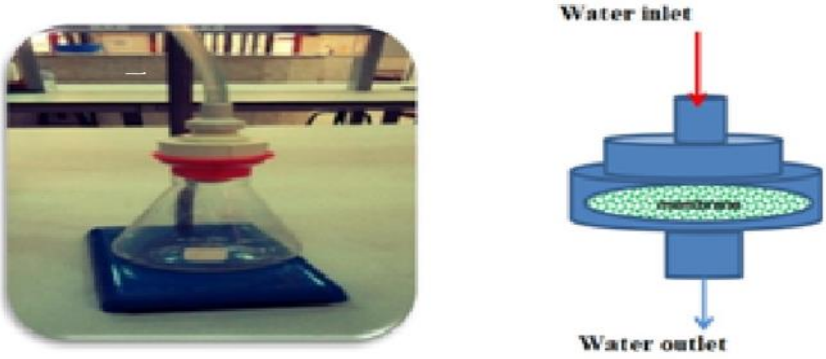


Figure 2: Image of the filtration device

2.2.3 Calibration curve

It was performed using UV/VIS-1700 spectrophotometer (Shanghai Phoenix). The wavelength has been set at 465 nm. The calibration curve is given in Figure 3. The study was carried out in distilled water at T = 21°C.

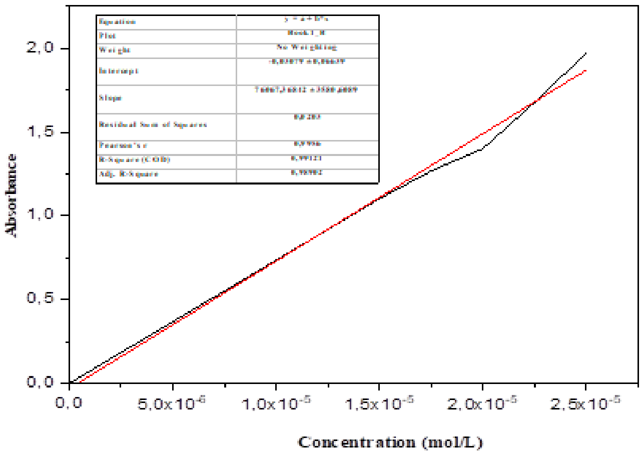


Figure 3: Methyl Orange calibration curve at λ_{max} = 465 nm

2.2.4 Membrane treatment

As it has been described by Tahani-Achouak Chinar and al.**[10]** the procedure followed for the adsorption of the dye is as follows. The stock standard solution was prepared with an initial concentration of Methyl Orange equal to 2.5x 10^{-5}mol/L. A volume of 30 ml was filtered through the prepared membranes. Filtration was performed at T = 21°C. The filtrates were then analysed in the visible light at 465nm.

2.2.5 Methods of characterization

2.2.5.1 Fourier-transformed Infrared Spectroscopy (FTIR)

The FTIR spectra were obtained using a PerkinElmer Spectrum 1000 FT-IR spectrometer (China). The recording area ranges from 4000 cm^{-1} to 600 cm^{-1}. The number of scans was set to 15. The resolution was adjusted to 5 cm^{-1}. The samples were analysed as a 1 mm thick film or as a 3 % solid solution in KBr.

2.2.5.2 Scanning electron microscope (SEM)

Scanning electron microscopy of the prepared membranes was carried out using a NeoScope, JEOL, JCM-5000 Sétif Algeria with an applied voltage of 2 kV (for powdered Bentonite) and 1.50 kV (for the PVC/Bentonite mixture). The photomicrographs were taken at distances of 1 µm and 10 µm respectively.

3. Results and discussion

3.1 FTIR

The IR spectrum of PVC is shown in Figure 4. It reveals the characteristic bands of the polymer, specifically the broad bands at 2989 cm^{-1} and 2864 cm^{-1}, which are due to the asymmetric and symmetric stretching vibrations of the methylene groups CH_2, and others about 748 cm-

[1], 845 cm^{-1} and 629 cm^{-1}, which are the vibrations of the C-Cl bonds. As for the peak at 971 cm^{-1}, that corresponds to the skeletal vibrations of PVC. It should be noted that the absorptions at different wave numbers (from 3450 cm^{-1} to 3632 cm^{-1}, and 1738 cm^{-1}) are caused by the secondary compounds present in PVC, such as Dioctyl Phtalates (DOP) **[11].**

The spectrum of Bentonite is shown in the same Figure 4. A sharp absorption peak at 3624 cm^{-1} is attributed to the stretching of Al_2OH **[12]**, followed by a broad band at 3436 cm^{-1} corresponding to stretching vibrations of the OH of the water present in the mineral **[13]**. The band at 2368 cm^{-1} is assigned to vibrations of SiO_4 bonds. The deformation of water OH is responsible for the absorption at 1641 cm^{-1}. The Si-O-Si and Al-O-Al stretching bands of the tetrahedral layer were detected at 1034 cm^{-1} and 523 cm^{-1} respectively **[14]**. The bending vibrations of OH in the octahedral layer were at 915 cm^{-1}, while the deformation vibrations of Al-Al-OH and Al-Mg-OH were both observed at 845 cm^{-1}. The absorption at 796 cm^{-1} is attributable to the deformation vibration of Si-O **[15]**. Finally, the peak at 468 cm^{-1} corresponds to Si-O-Si deformation.

The spectra of the different membranes exhibited new peaks. These include a new band at about 3440cm^{-1}, which decreases in intensity with increasing Bentonite content. In addition, two bands at 2360 cm^{-1} and 2337 cm^{-1} appeared in the spectrum of PVC/Bentonite 10**%** and disappeared in PVC/Bentonite 25**%** and PVC/Bentonite 50**%**. These bands were assigned to SiO_4 vibrations. In general, we observed a decreasing band intensity with increasing Bentonite content.

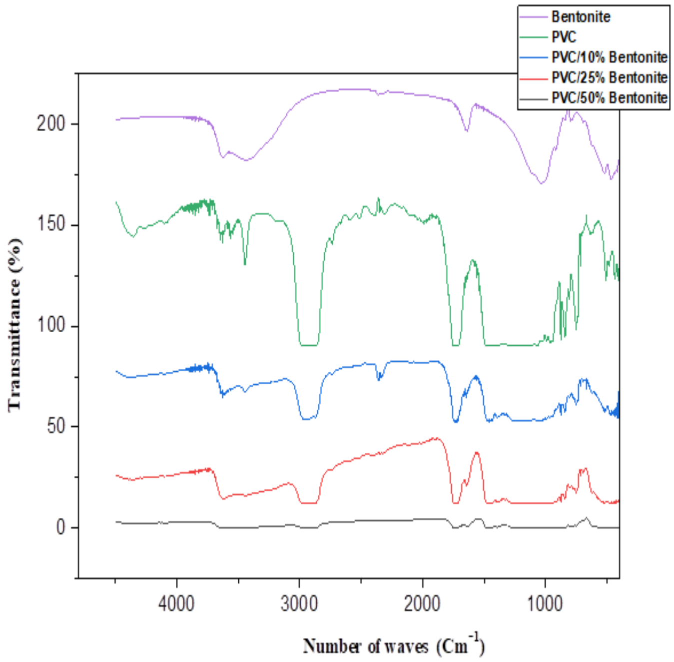


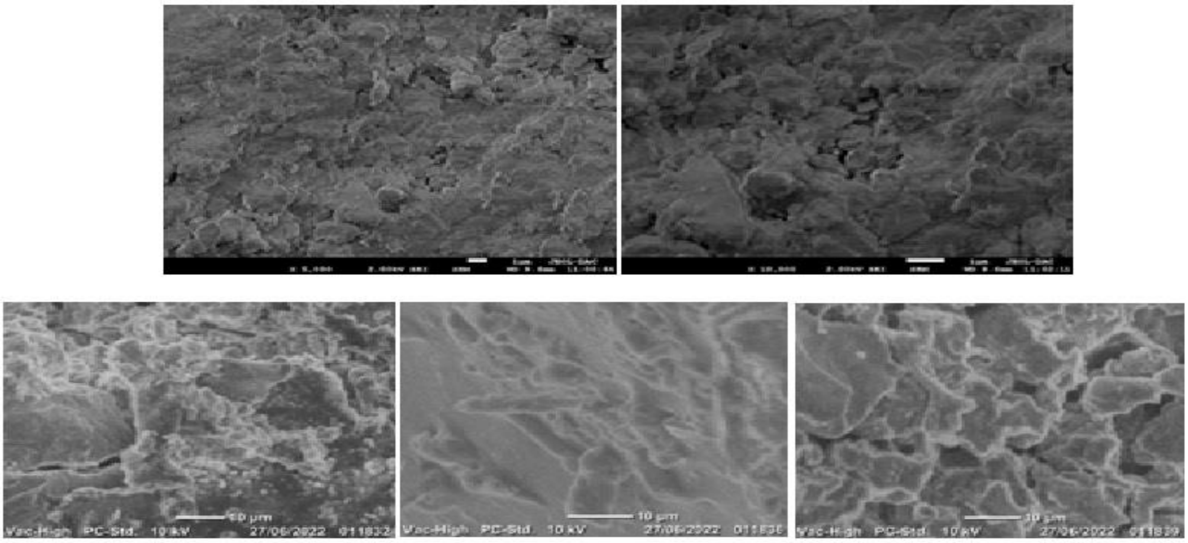
Figure 4: FTIR spectra of PVC, Bentonite, PVC/Bentonite 10%, PVC/Bentonite 25% and PVC/Bentonite 50%.

3.2 Scanning electron microscope (SEM)

From Figure 5, the raw Bentonite shows a broad distribution of grain sizes. Also, we note the arrangement in the form of sheets in a particle, when enlarged to 1 µm and a considerable presence of macropores **[16]**.

Otherwise, about the SEM of the PVC/Bentonite matrices, it appears that the predominant shape of the pores has become circular. Furthermore, the increase in the proportion of Bentonite is favourable to the regular appearance of a large number of pores **[17]**.

a) b)



b) d) e)

Figure 5 : SEM images of Bentonite in powder form (a-b), PVC/Bentonite 10% (c); PVC/Bentonite 25% (d); PVC/Bentonite 50% (e)

3.3 Membrane treatment

According to the obtained results Table 2, it is evident that the retention percentage increases with the concentration of Bentonite. This can be explained by the porous structure that promotes this inclusion.

Table 2: Results of dye adsorption on membranes

Membrane	Number of filtrations	Methyl orange absorbance	Final concentration of methyl orange (mol/l)	Percentage of adsorbed methyl orange (%)	Retention percentage (%)
PVC	5	1.764	$2.321*10^{-5}$	11	7.16
PVC/Bentonite (10%)	5	1.523	$2.113*10^{-5}$	23	15.48
PVC/ Bentonite (25%)	3	1.358	$1.916*10^{-5}$	31	23.36
PVC/ Bentonite (50%)	1	0.964	$1.326*10^{-5}$	51	46.96

The retention increases with Bentonite concentration, and the highest retention was obtained in the PVC polymer-based Bentonite, with a retention of about 50% **[10]**.

This study aims to valorize natural clay (Bentonite) by using it in the fabrication of biodegradable polymeric matrices-based membranes for the removal of dye from aqueous solutions **[18-19]**.

3.4 Membrane modelling and simulation

The traditional design approach is to use the zero-dimensional description of a simulated entity which is less computationally demanding. In many areas and during the design steps, in order to estimate key and relevant variables of any process, e.g. pressures, temperatures, flow rates, concentrations, etc. such as the data presented in Table 3, the latter approach is often used. On the other hand, due to the dizzying evolution of computers which have become very powerful and to the perfection of software and advanced programs, modeling based on three-dimensional geometries has become a very widespread practice **[20]**.

The basic mode commonly used when considering the flows arrangement, is the cross-flow setup Figure 6.

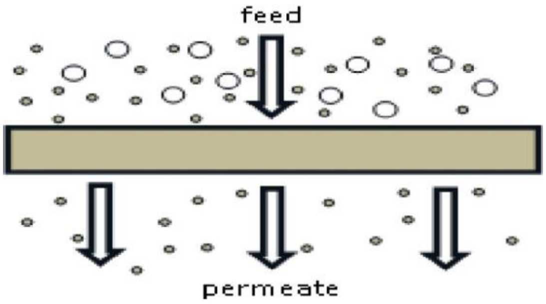


Figure 6 : the cross-flow mode of the membrane filtration.

The physicochemical model with a fouling limitation applied is given in the following form :

$$R_f = R^*(1 - pe^{-qx}) \quad (1)$$

where R is the long-term fouling resistance, p and q are specific constants.

The variable p is responsible for the very large increase in resistance at the initial moment, this phenomenon is due to the adsorption of the substance at the membrane, thus causing the blocking of the pores. The concentration of the wastewater across the membrane follows the same form as equation 1 but in a descending manner which can be written as follows:

$$C_m = C_i e^{-qx} \quad (2)$$

where C_m is the concentration in the membrane and C_i is inlet flow concentration shown in Figure .

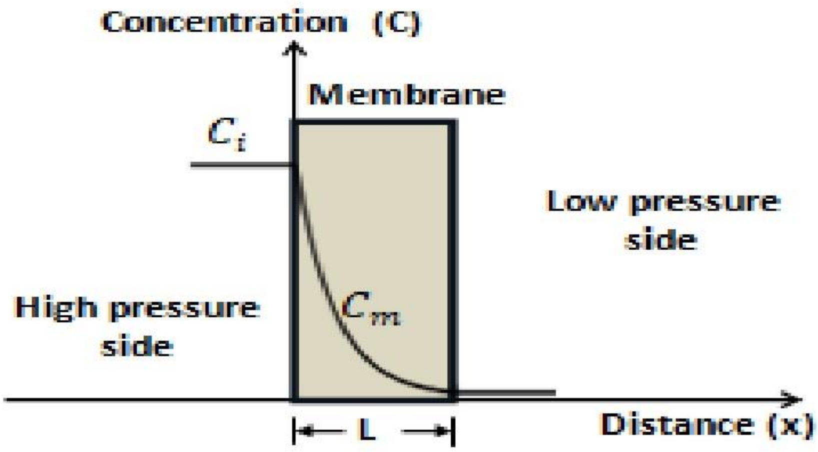


Figure 7 : Membrane under permeation solute concentrations.

The numerical model was conducted by 3D-simulation using COMSOL Multiphysics. The simulation process begins with designing a filtration device as shown in Figure 8. This is intended to determine the dye concentration across the membrane.

Using COMSOL Multiphysics, we have solved the problem of membrane filtration, taking into account all above mentioned membrane geometry dimensions, and compared simulations to experimental results.

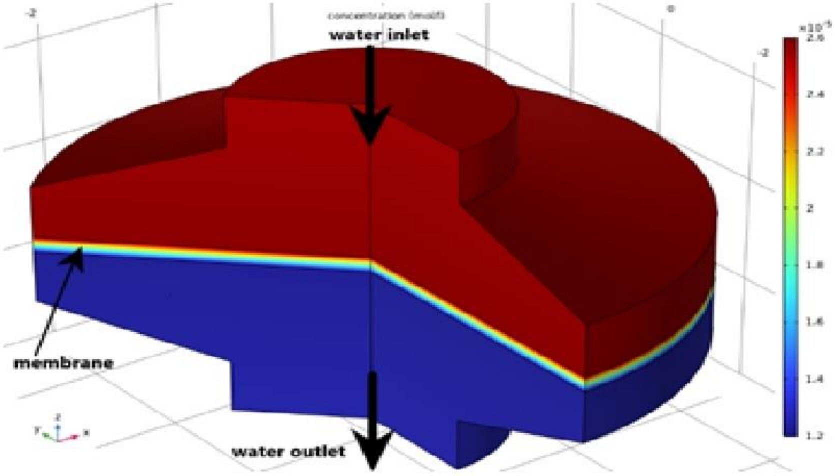


Figure 8 : Model simulation of the membrane filtration.

Figure 9 presents the simulation results of the filtration model which shows the variation of the methyl orange concentration across the membrane. As can be seen, increasing the Bentonite content of the polymer membrane allows an improvement in the filtration power of the dye.

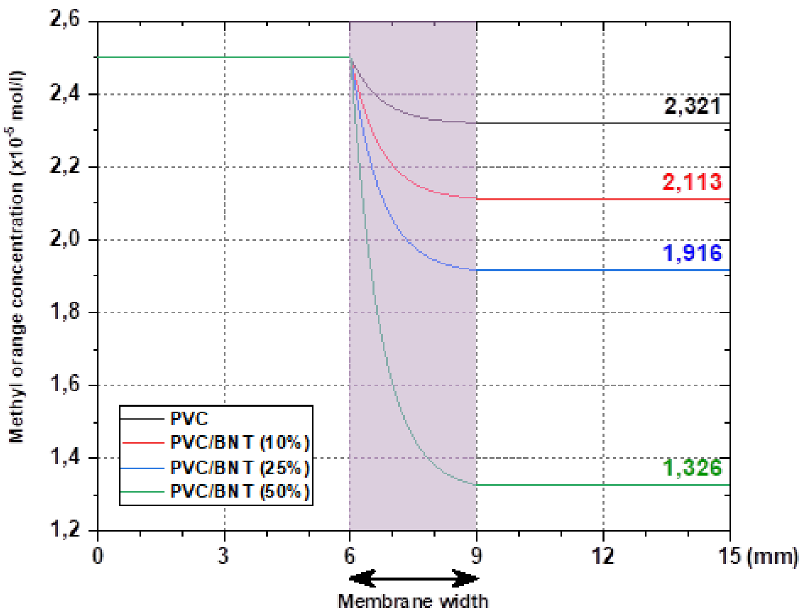


Figure 9 : Methyl Orange concentration during the filtration process.

Conclusion

The utilization of PVC/Bentonite membranes represents a significant advancement in wastewater treatment technology. Their ability to efficiently remove Methyl Orange underscores their potential for addressing water pollution challenges. Through experimental validation and computational simulations, we have demonstrated the effectiveness of these membranes and it appears also that the membrane retention is proportional to the Bentonite concentration. This efficiency is related to the ability of Bentonite to adsorb pollutants.. With further optimization and scale-up, PVC/Bentonite membranes hold promise for widespread application in industrial wastewater treatment, contributing to environmental sustainability and resource conservation.

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