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Research paper

Extraction of malachite green from wastewater by using polymer inclusion membrane

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ABSTRACT

An extraction of a basic dye, Malachite Green (MG) from synthetic and real wastewaters solution was carried out by using polymer inclusion membrane (PIM). The PIM consists of poly(vinyl) chloride (PVC) as base polymer, bis-(2-ethylhexyl) phosphate (B2EHP) as extractant and dioctyl phthalate (DOP) as plasticizer. The composition of the components were varied to determine the optimum composition of the membrane with better extraction ability. After optimization the composition of PIM, the average extraction efficiency achieved was >98% for MG concentration of 20–80 mg L^{-1}. The PIM was characterized by Fourier Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) methods PIM produced in this study is mechanical and chemically stable. Finally, the PIM was applied to remove MG in the wastewater samples. Results showed that average percent extraction achieved for MG were >98% and >96%, for both wastewater samples of 50 and 100 mg L^{-1} respectively.

1. Introduction

In 21st century, numbers of synthetic dyes are used in many industries, for example paper, rubber, textile, cosmetic, plastic, food pesticide and leather for colouring their product or other different purpose due to their ease and cost effectiveness in synthesis, firmness, stability in light and resistance to aerobic bio-oxidation compared to natural dyes [1,2]. Among various pollutants of aquatic ecosystem, dyes are of a vital group of chemicals [3]. It is known that public perception of water is hugely affected by colour. Colour from dyes is the first contaminant to be recognized in wastewater due to the fact that these dyes are invariably left as industrial waste and consequently discharged mostly to surface water resources [1,3]. Once the water is polluted by dyes, its removal by conventional wastewater treatment method is particularly difficult because many dyes are stable to light and oxidizing agent and are resistant to aerobic bio-oxidation. In addition, dyes even in low concentration are easily detected and can affect the aquatic life and food web.

As a dye, malachite green (MG) is commonly used in the production of textiles materials and paper products [4]. The dye is also used extensively for dyeing wool, leather, and cotton and to treat fungal and protozoan infection due to its effectiveness, availability and relatively low cost compare to the other anti-fungi agents [4,5]. However, due to the risks, MG poses to the consumers including its effect on immune system, reproductive system and its genotoxic and carcinogenic properties, MG has become a highly controversial compound [2]. Moreover, surface and ground water was contaminated with dyes due to untreated waste of dyes from industries. Presence of MG in water causes serious health effects such as mutagenesis, teratogenecity, chromosomal, respiratory toxicity, fractures, and carcinogenesis which heavily depend on exposure time, temperature and concentration of dye [6].

Thus, it is environmentally crucial to remove the colour synthetic organic dyestuff from waste effluents. It is rather difficult to treat dye effluents because of their synthetic origins and their mainly aromatic structures, which are biologically non-degradable [3]. For example, MG which is a triphenylmethane dyes, biodegradation due to presence of nitrogen in their back bone is a difficult task [2]. Therefore, the decolorization of wastewaters containing these dyes prior to discharge is mandatory by environmental regulations in most countries [3].

In recent studies, several method of physio-chemical decolorization have been developed, for instance membrane separation, electrochemical, flocculation–coagulation, reverse osmosis, chemical oxidation and photocatalytic processes, adsorption and liquid-liquid extraction [1–4].

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Among membrane technologies, liquid membranes have acquired a prominent role for their use in separation, purification or other analytical applications such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy [1]. The application of liquid membrane in separation processes has increase significantly in recent years [3]. The big importance in membrane separation technology lies essentially in the fact that it is potentially energy-efficient and the membranes are highly permeable and highly selective [7]. Separation systems have recently received much attention because of their lower costs and greater flexibility.

There are several main types of liquid membrane, namely bulk liquid membranes (BLM), emulsion liquid membranes (ELM), supported liquid membranes (SLM) and polymer inclusion membranes (PIM). SLM extractions process can selective removes the selected analyte in single step and hence, it has great potential for large scale application [1]. Also, it is an alternative to the conventional solvent extraction because of its high selectivity, operational simplicity, low solvent inventory, low energy consumption and zero effluent discharge [8]. Although SLM is an attractive alternative to liquid-liquid extraction due to its combination of extraction and stripping processes in single step which especially works for dilute solutions, it has a main drawback which is lack of long-term stability [7].

In recent years, PIM has proved to have properties making them extremely attractive for application to a wide range of separation problems [9]. This method receives high attention for its high stability compared to that of SLM [7]. Besides retaining most advantages of SLM, PIM contains effective carrier, it is easy to prepare, versatile, stable, has a good chemical and mechanical properties compared to SLM [8]. The lower diffusion coefficients often encountered in PIM can be easily offset by creating a much thinner membrane in comparison to its traditional SLM [10]. PIM can be prepared easily and has an excellent mechanical properties [7]. PIM are formed by casting a solution containing a base polymer, an extractant and a plasticizer. The base polymer such as poly(vinyl chloride) (PVC) or cellulose triacetate (CTA) forms a thin, flexible and stable film providing the mechanical strength, the extractant effectively transports and binds the ion across the membrane and lastly plasticizers are additives that increase the plasticity or fluidity of the materials. It also provides elasticity and constitutes the liquid phase in which the carrier molecule can diffuse. The resulting self-supporting membrane can selectively separate the solutes of interest in similar fashion to that of SLM [7–11].

In addition, PIM is better than SLM because it incorporates a liquid extractant which acts as a carrier but differ in that the carrier is held within the membrane polymeric structure instead of being dissolved in a diluent and held by capillary forces within the relatively large pores of a polymeric support. This proves that PIM has a longer lifetime and greater stability with respect to the loss of the membrane liquid phase to the aqueous phase than SLM [9]. There is also a large number of reference devoted to PIM during the last decades, reveals the great interest for their membranes. A general review concerning extraction and transport of metal ions and small organic molecules using PIM has been published, pointing out their better mechanical properties and chemical resistance compared to the traditional SLM. The transport mechanism in PIM depends on factors like membrane composition, homogeneity and surface morphology [7].

The objective of this study is to investigate the PIM consisting of PVC as base polymer, bis-(2-ethylhexyl) phosphate (B2EHP) as extractant and ioctyl phthalate (DOP) as plasticizer for extracting the basic cationic dye MG from wastewater solution. The composition of the PIM and the initial dye concentration have been optimized.

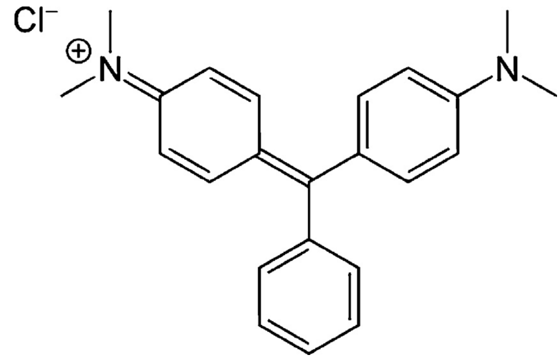

Fig. 1. Structure of malachite green (MG).

2. Experimental

2.1. Materials and chemicals

Poly(vinyl) chloride (PVC), bis-(2-ethylhexyl) phosphate (B2EHP), dioctyl phthalate (DOP), nitric acid (65%) were obtained from Aldrich. Tetrahydrofuran (THF) and Malachite green (MG) were obtained from QRëC. The structure of MG is given in Fig. 1.

2.2. Preparation of polymer inclusion membrane (PIM)

The PIM prepared in this study is similar to that prepared by Suah et al. [12] as shown in Fig. 2. PVC, B2EHP and DOP were weighted separately in 50 mL beaker. The solution of PVC was prepared by dissolving 250 mg of PVC in 10 mL of THF. Another two separate solutions containing 200 mg of B2EHP and 50 mg of DOP were prepared in 5 mL of THF respectively. Then, three solutions were mixed and stirred for at least 4 h to form a homogenous casting solution.

Next, the casting solution was spread evenly on a 9 cm diameter flat bottom petri dish which was kept on a leveled surface for uniform PIM formation. The petri dish was covered with filter paper to allow gradual evaporation of THF. The evaporation process was carried in fume hood at room temperature overnight. On the

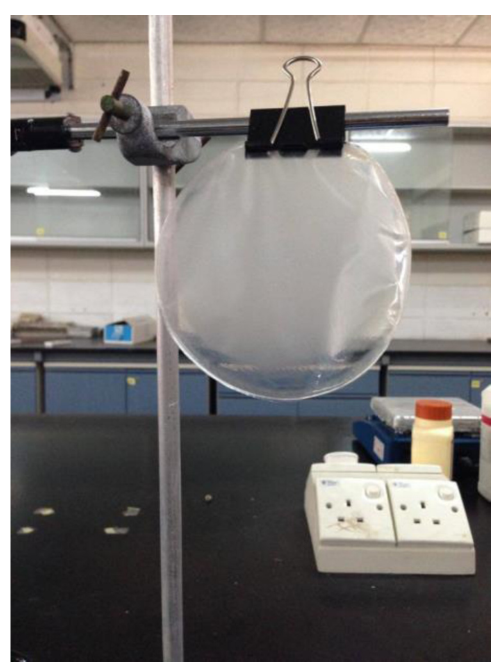

Fig. 2. Polymer inclusion membrane (PIM) prepared in this study.