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Freeze–dried agarose gels: A cheap, simple and recyclable adsorbent for the purification of methylene blue from industrial wastewater

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ABSTRACT

Dye colourants are being produced yearly on the kilotonne-scale and a significant percentage end up as highly-polluting industrial effluents. Freeze–dried agarose gels are demonstrated here to be efficient adsorbents for the removal of methylene blue, an important industrial dye. A hydrogel adsorbent offers advantages over powdered formulations, which can be difficult to handle. Freeze-drying further allows the adsorbent to be packaged, transported and stored in a dry format, thus conferring cost savings. Parameters such as the volume or concentration of agarose or dye, exposure time, pH and gel/water contact area influenced adsorption capacity and kinetics. Salt inhibited adsorption in a dose-dependent manner and this was exploited for the recycling of adsorbent and dye. Langmuir and Freundlich isotherms were also applied to model the adsorption process. The freeze–dried agarose gel achieved an adsorption capacity of 10.4 ± 0.2 mg/g, which was comparable to commercial activated carbon assessed under similar conditions. Additionally, unlike most activated carbon, agarose is derived from a renewable source. Since agarose is cheaply available commercially, this method can enjoy rapid industrial translation.

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1. Introduction

A huge worldwide demand for dyes as colourants has resulted in more than 700 kilotonnes of dye compounds being produced annually [1]. Among various sectors such as the paper, leather, food and plastic industry, the textile industry is the biggest consumer and alone accounts for more than two-thirds of the dye trade [2]. However, out of the total amount of dye used, an estimated 15% are lost during the dyeing process, resulting in highly coloured wastewaters [3]. If released untreated, such coloured wastewaters pollute our water sources and are highly deleterious to marine animals either through direct toxicity, or indirectly from the impedance of sunlight penetration necessary for photosynthesis by aquatic plants. In line with increasingly stringent environmental regulations and rising public awareness, companies are therefore keenly aware of the need for cheap, simple and sustainable methods to remove dye contaminants from wastewaters before disposal.

Methylene blue (MB) is the most frequently used colourant for cotton, silk and wood [4]. It is a heterocyclic aromatic thiazine dye first synthesized in 1876 by BASF primarily for staining cotton [5]. Since then, MB has found use in microbiology, as a redox indicator and also as a drug to treat a range of diseases including malaria [6].

Due to their complex chemical structures, conventional wastewater treatment regimes are less able to efficiently remove purpose-designed synthetic dyes such as MB [4]. Therefore, alternative methods are being explored and can be either biological, physical, chemical or a mixture in nature. For instance, bacterial cells were used to decolourize textile wastewaters [1]. Membrane-based technologies such as vacuum distillation [7], ultrafiltration [8] and cation exchange [9] were also studied for the removal of dye contaminants from wastewaters. On the other hand, chemical methods mainly involve advanced oxidation processes (AOPs). AOPs refer to the oxidative breakdown of dye (most likely due to the generation of reactive hydroxyl radicals) in the presence or absence of a catalyst (usually titania, TiO_2), ultrasonic agitation or photoillumination. Combinations include TiO_2/H_2O_2/ultrasonic [10], Fe/H_2O_2 (Fenton) [11], H_2O_2/UV followed by microbial biofilm treatment [2] and TiO_2/Ti/visible light [12]. Although effective to varying degrees, limitations faced by the above methods include the need for a complicated set-up or synthesis (e.g., bioreactors, vacuum, high temperature, etc.) and a

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large initial investment. Furthermore, the use of certain materials and catalysts can create secondary pollution. To address these concerns, the physical method of adsorption has been proposed and is generally well-received by the industry.

Adsorptive removal refers to the transfer of dye contaminants from the liquid phase onto a solid support for easy disposal. It is conceptually simple and a wide spectrum of adsorbents ranging from agricultural waste to graphene oxide [13] and zirconia-cobalt oxide composites [14] has been investigated. The reader is referred to an informative review on the different types of adsorbents explored for the removal of MB from wastewaters [4]. Some of the adsorbent raw materials such as rice husk [3], natural clay [15], castor seed pod husk [16] and almond shell [17] are cheaply, or even freely available. However, these materials usually require significant processing (high temperature, pressure, strong acid treatment, intensive physical grinding) before becoming suitable for use and the cost associated must be considered before industrial production. Similarly, activated carbon is now one of the most efficient and widely-accepted adsorbent. However, it is commonly derived from coal [4], which is a non-renewable resource. The conversion from coal to activated carbon is also extremely energy and time intensive. Furthermore, coal is chemically heterogeneous and the adsorption property will depend strongly on its source and treatment history. Cost is another issue as commercially available activated carbon is priced ~US$20/kg [4].

Agarose is a natural polysaccharide derived from seaweeds and is the purified fraction of agar: a mixture of agarose and agaropectin. Agarose powder becomes soluble in near-boiling water. Upon cooling, the polymeric chains self-assemble into helical fibers that ultimately aggregate to form a hydrogel. Agarose gels are routinely used in molecular biology to separate nucleic acids. We now introduce freeze–dried agarose hydrogels as a recyclable adsorbent, using MB as the industrially-relevant model dye. In another publication, agar had been primarily evaluated as a powdered adsorbent for MB [18]. Grain or mesh size is an important parameter for powdered adsorbent as dye molecules will need access to the inner surfaces for efficient loading. Powers can also be difficult to handle. For example, during actual industrial use, either a second filtering step or a device to immobilise the powder is needed in order to isolate the saturated adsorbent for disposal. This adds to operational cost. Here, we investigated agarose, which is more chemically defined than agar and less susceptible to batch variation. Usefully, the hydrogel formulation removes the dependence on grain or mesh size as hydrogels consist of a network of interconnected pores that are permeable to the diffusion of dye molecules. Bulk agarose hydrogel can also be easily removed from the wastewater without the need for a fine filtering step. Additionally, agarose is already commercially produced in tonnes quantity. Hence, the cost associated with the development of novel materials (e.g., scaling up for industrial production) is avoided. Agarose can also be cheaper than commercial activated carbon. Finally, supplying the adsorbent as freeze–dried pellets allows the dry shipment and long-term storage of products, thus conferring cost savings. This method can potentially have rapid translation into the industry.

2. Experimental

2.1. Preparation of agarose gel

Agarose (Invitrogen, Singapore) was completely dissolved in water to the desired concentration in a microwave oven. 200 μL of agarose solution was transferred to a custom-made hollow ring cast (internal diameter 0.8 cm) and allowed to cool. The resulting gel disc was then placed in either a 6-, 12- or 24-well plate (Nunc, Singapore) for further testing.

2.2. Adsorption studies with MB

Depending on the experiment, MB (Sigma–Aldrich, Singapore) was dissolved in various aqueous formulations to the desired concentration. Where pH adjustments were needed, 100 mM solutions of NaOH or HCl was added to achieve pH levels of 4.2, 5.4, 6.2 and 8.0. Acidity was measured with a Accumet™ AB150 pH meter (Fisher Scientific, Singapore). Various volume of the MB solution was then filled into the wells ($n = 4–5$) to completely submerge the gel discs. At appropriate time points (3, 20, 24, 48 and 72 h), 100 μL of the MB solution was sampled for absorbance measurements at 610 nm with a FlexStation® 3 microplate reader (Molecular Devices LLC, CA, USA). The aliquot was later returned to the wells so that volume remained unchanged. Prior to this, a wavelength sweep was performed to determine the optimum value for sensitive detection of MB within the relevant concentration range. For quantification of concentration, a calibration curve ($R^2 \geq 0.99$) was obtained with MB dissolved in the corresponding aqueous formulation. The amount of dye adsorbed was obtained by subtracting the amount of dye remaining from the amount present at the start of experiment. Consequently, adsorption capacity (mg/g), defined as mg of dye adsorbed per g of adsorbent was calculated. All experiments were conducted at room temperature. For experiments involving commercial activated carbon, 6.0 mg of IPG 12 × 40 (a kind gift from Calgon Carbon Corporation, Singapore) was added to each well instead of agarose. This amount of carbon was chosen based on the amount of agarose (200 μL of 30 mg/mL) present in each freeze–dried pellet.

2.3. Field emission scanning electron microscope (FESEM)

Agarose gels were prepared as above, freeze–dried, sputtered with platinum and then observed with a JSM-7400F FESEM (Joel, Tokyo, Japan) at 30,000 × magnification.

2.4. Degree of swelling of freeze–dried hydrogel

Agarose pellets were prepared as before and lyophilized. The mass of each freeze–dried adsorbent was then recorded before being submerged in 3 mL of deionized water (in the absence of MB) at room temperature. After 24 h, each pellet was removed and excess surface water was carefully wicked away before recording the hydrated mass. The degree of swelling was expressed in terms of folds increase in hydrated mass with respect to freeze–dried mass (average ± standard deviation, $n = 8$).

3. Results and discussion

Agarose is a natural polysaccharide derived from seaweeds while MB is one of the most frequently used synthetic cationic dye in the textile industry. Their chemical structures are shown in Fig. 1a,b. A glycosidic bond connects D-galactose (left) with 3,6-anhydro-L-galactose (right) to form the alternating disaccharide repeat unit in agarose. The pendant hydroxyl groups on D-galactose are believed to be responsible for the binding and adsorption of cationic MB molecules [18].

Agarose becomes soluble in heated water and spontaneously forms a hydrogel upon cooling. Fig. 1c shows circular agarose gels of diameter ~1 cm prepared at varying concentration. Scanning electron microscopy revealed that the microstructure of agarose gels consisted of a dense interwoven network of fibres and pores (Fig. 1d). It was reported that an individual MB molecule has a molecular cross-section of 0.8 nm and can pass freely through

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