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Use of beach bivalve shells located at Port Said coast (Egypt) as a green approach for methylene blue removal

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ABSTRACT

Bivalve shells of *Anadara uropigimelana* were firstly tested as a potential biosorbent for methylene blue (MB) recovery from an aqueous solution, Scanning electron microscopy (SEM), energy dispersive X-Ray analysis (EDX), Fourier-transform infrared (FTIR) and zeta potential measurements were used to characterize bivalve shells sorbent. The influence of variables including pH, amount of sorbent, contact time, concentration of the dye and temperature on MB sorption has been investigated. Percentage removal of 93.6% were obtained under optimum conditions of variables (initial pH of 10.4, sorbent dose of 1 g L^{-1}, initial MB concentration of 20 mg L^{-1}, and temperature of 25 ± 1 °C). The sorption of MB dye onto the sorbent could reach equilibrium after 10 min. Equilibrium data were well fitted to the Langmuir model. Sorption isotherm results showed that the maximum sorption capacity of MB by bivalve shells was 1000 μg g^{-1}. Thermodynamic analysis showed that the sorption of MB onto bivalve shells increased with increasing temperature from 25 to 55 °C, indicating the endothermic nature of the sorption process. Meanwhile, the positive values of ΔS^{o} suggest the increased randomness at the solid/solution interface during the MB sorption. The sorbent was successfully tested for color removal from dyeing facility. This work shows that the bivalve shells hold promises acting as effective sorbent to remove dyes in the wastewater.

1. Introduction

The industries textile, paper, paint, food, pharmaceutical and cosmetic industries consume enormous volumes of water, and their effluents severely impact the environment because of the toxic nature of their residues [1]. The widely released dyes from these industries are the major polluter of both groundwater and surface water [2]. Dyes presence in water is undesirable due to the lasting color, the increase in the chemical oxygen demand and the effect in the microorganisms present in the water streams [3]. Synthetic dyes are difficult to degrade and generally stable to light, heat and oxidizing agents due to their complex aromatic structure [4]. Once these dyes degrade into toxic, they could generate mutagenic or carcinogenic byproducts which are even more toxic than the dyes themselves [5]. Methylene blue (MB) (3,7-bis (dimethylamino)-phenazathionium chloride) is commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools and so on [6]. MB is a good choice for testing the performance of sorbents whose mesoporosity suggests their application for sorption of liquid pollutants [7].

Although MB is not considered to be a very toxic dye, it can reveal very harmful effects on living things such as difficulties in breathing, vomiting, diarrhea and nausea [8], Hence, removal of the dye contaminants prior to their discharge into the environment is necessary [9]. Textile effluents are usually treated by several physicochemical decolourisation processes, such as coagulation/flocculation [10], adsorption [11], membrane filtration [12], photocatalytic degradation [13] irradiation [14], micellar-enhanced ultrafiltration [15] and Biological Treatment [16].

Biosorption has been proved as an efficient process to remove a multiplicity of solutes from aqueous solution [17]. Various biosorbents have found promising applications in wastewater treatment that is, nowadays, the spotlight due to the promotion of environmental sustainability [18]. Due to the increasing consciousnesses of cost effectiveness and public environmental protection, lower-cost, more efficient and safer sorbents for the treatment of

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contaminated wastewater are now in demand. To date, many such sorbents have been studied, including chitosan [18], zeolites [19], clay [20], agricultural wastes [21], and waste products from industrial operations such as fly ash, coal and oxides [22].

Bivalves shells which are typically a calcareous exoskeleton which encloses supports and protects the soft parts of an animal in the phylum Mollusca, which includes snails, clams, tusk shells, and several other classes. Bivalves by definition possess two shells or valves, a "right valve" and a "left valve", that are joined by a ligament. The bivalve shells of *Anadara uropigimelana* are located in huge amounts (tons) in Port Said coast, Egypt. These materials are not only thrown away without any commercial return and a lot of money is being spent for its disposal but also causing pollution and environmental problems. With the rapid increase in demand for balance between natural phenomena and ecology in bio-environment, there is a significant need for continuous development of new technologies that consume these abandoned shell husks.

In view of that, in this work we used the bivalve shells of *Anadara uropigimelana* located at Port Said coast, Egypt, as a potential sorbent of MB from aqueous solution. The aim of this study is trying to take advantage of wastes of some marine organisms to get materials which will be used later in water treatment applications. The ability of bivalve shells to remove dyes aqueous solution was characterized. The effect of several parameters, including the pH of the solution, concentration of the dye, temperature, the sorbent dose, and ionic strength were studied.

2. Materials and method

2.1. Chemicals and reagents

Bivalve shells of *Anadara uropigimelana* were collected from the beach of Port Said coast, Egypt. All chemicals used were of analytical grade and demineralized water was used for the preparation of all aqueous solutions. Methylene blue (MB) was supplied by Sigma-Aldrich (Switzerland). All other chemicals were Prolabo products and were used as received.

2.2. Biosorbent preparation

Bivalve shells samples were initially washed with tap water to remove surface impurities then the shells were decolorized by soaking the shells in acetone for 10 min and dried for 2 h at ambient temperature followed by bleaching step by soaking the shells in sodium hypochlorite solution for 3 h. Samples were then washed with tap water, followed washing by distilled water and dried again in oven for 3 h at 110 °C. Pestle instrument was used for converting shells to small pieces. Mortar and grinder instrument was used for converting small pieces to powder. The obtained $CaCO_3$ powder was dried in oven for one hour at 110 °C to remove any moisture may be found in it. The product was finally sieved and the fraction below 1 mm was retained for experiments.

2.3. Characterization of the sorbent

FT-IR of bivalve shells was examined in dried KBr powder by recording the infrared spectra over the range of 4000–400 cm^{-1} using a Fourier transform infrared (FTIR) spectrophotometer (FT/IR4100 Jasco-Japan). The morphology the bivalve shells sorbent was analyzed with Scanning Electron Microscope coupled with an Energy Dispersive X-ray analysis system (Jeol (JSM-6510LV)). The zeta potential of the sorbent particles was measured using a Nano Zeta Sizer (Malvern Zetasize Nano-zs90, Malvern Instruments Ltd.) at various pHs from 6 to 11 in 0.01 M NaCl solution at 25 °C.

The surface area of the bivalve shells sorbent was measured by MB adsorption as this material is known to be adsorbed as a monolayer only on solid sorbents. To calculate the surface area, 1.0 g of bivalve shells sorbent was treated with 25 mL of MB of concentration 20 mg L^{-1}. The treatment lasted until reaching saturation capacity of the sorbent. The amount of MB adsorbed was calculated based on concentration difference between the initial and equilibrium values, which analyzed by the spectrophotometry method at 664.5 nm using photometer 7100, Palintest, USA. The surface area of the sorbent was calculated using the following equation:

$$As = \frac{G\ N_{Av} Ø 10^{-20}}{M M_W} \quad (1)$$

where A_s is the sorbent surface area in m^2/g, G the amount of methylene blue adsorbed (g), N_{Av} the Avogadro's number (6.02×10^{23}), Ø the methylene blue molecular cross-section (197.2 $Å^2$), MW the molecular weight of MB (319.85 g/mol) and M is the mass of adsorbent (g).

2.4. Preparation of solutions

Stock solution (100 mg L^{-1}) of methylene blue (MB) was prepared in distilled water. The other solutions were obtained by dilution of the stock solution with distilled water just prior experiments. HCl (0.01–0.5 M) and NaOH (0.01–0.5 M) were used to change the acidity of the medium. MB concentration of all samples was analyzed by the spectrophotometry method at 664.5 nm using photometer 7100, Palintest, USA. Aqueous solutions of the dye within the concentration range 0–30 mg L^{-1} were used for calibration curve. Plot of absorbance against concentration was linear with correlation coefficient (R^2) = 0.996.

2.5. Sorption experiments

For the study of pH effect 20 mL of 20 mg L^{-1} of MB solution at different pH values (in the range 1.7–11.6) was mixed with 1.0 g of sorbent (dried weight) for 3 h, and the stirring speed was maintained at 40 rpm using a reciprocal agitator, Rota bit, J.P. Selecta (Spain). The pH values were adjusted by addition of 0.01–0.5 M HCl and 0.01–0.5 M NaOH solutions and measured by using a pH meter (Aqualytic AL15). Samples were collected and filtrated. The filtrate was analyzed for residual MB concentration. The pH was not controlled during the sorption but the final pH was systematically recorded.

For sorption isotherms 1.0 g of sorbent (m) was mixed with 20 mL of MB at different initial concentrations (C_0, ranging between 5.0 and 50.0 mg/L) for 3 h. The pH of the solutions was initially set at 5.32. After solid/liquid separation, the residual concentration of MB was determined and the sorption capacity (q_e, mg g^{-1}) and % removal were determined by the following mass balance equations, respectively:

$$q_{eq} = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Where C_0 and C_e is the initial and equilibrium concentration of dye in solution (M), respectively, V is the volume of solution (L) and m the mass of sorbent (g).

For uptake kinetics 9.0 g of sorbent was mixed with 180 mL of MB solution (C_0: 20 mg L^{-1}) at pH 5.32. Samples (5 mL) were collected at fixed times and the residual concentrations were