Preparation of corn cob based bioadsorbent as an effective adsorbent

Rahmatollah Rahimi, Sina Parvaz, Mahboubeh Rabbani*

Department of Chemistry, Iran University of Science and Technology, Tehran
16846-13114, Iran

Rahimi_rah@iust.ac.ir

Abstract
The high level of production and use of dyes due to industrialization has created a great global environmental concern. These pollutants are non-biodegradable and stable to light, heat, and moderate oxidizing agents which create the serious threats to human health and marine. Hence, removal of these pollutants from discharged wastewater is a very challenging task. The aim of this present study was to utilize the residual biomass of corn for eco-friendly bioadsorbent preparation and eliminating the methyl orange (MO) from aqueous solution. The effects of initial dye concentration, bioadsorbent dosage and contact time on the adsorption capacity of the bioadsorbent were investigated. The maximum adsorption capacities of the bioadsorbent for methyl orange was 350 mg.g$^{-1}$ at initial concentration of 500 mg.L$^{-1}$. Moreover, the recyclability experiments demonstrated that the bioadsorbent could be reused for at least four cycles with stable adsorption capacity. These results provide that corn cob based bioadsorbent can be utilize as an effective adsorbent for practical wastewater treatment.

Introduction
Currently, synthetic dye becomes one of the major pollutants in the industrial effluents [1]. Among the organic pollutants, color effluents were considered to be more harmful substances due to their serious toxic outcome to the plants, aquatic organisms, animals and human because Most of dyes in the effluents contain nondegradable aromatic structure, and are considered to be toxic and even carcinogenic, which results in negative influences on human health and ecological security [2,3]. Therefore, the dyes must be efficiently removed from the wastewater. So far, some alternative methods, such as chemical precipitation, ion exchange, membrane filtration, physical adsorption, chemical oxidation/reduction, and bioremoval have been developed [4-9]. Among those, the adsorption process was one of the most effective and promising method and development of economical, eco-friendly and more efficient adsorbent is an important subject. Biomass is a carbon raw material for synthesis of valuable carbonaceous materials because it is available in huge amount [10]. Corncob is one of the biomass which is the byproduct of corn production. In this paper, we convert corncob to useful bioadsorbent for eliminating the pollutants from aqueous solution. The main purpose of this work is to investigate the removal of MO from solution. Furthermore, the reusability of the bioadsorbent was evaluated.

**Materials and methods**

All chemicals used in this study were analytical grade and were used without further purification. The biomass sample used in this study was corn cob. The corncob was collected from a local farm (Tabriz, Iran).

**Preparation of bioadsorbent**
In order to preparation of bioadsorbent, biomass cut into small pieces, washed severally with distilled water to remove surface-adhered particulate matter and water soluble impurities and dried to constant weight in an oven at 70 °C. The dried samples were ground and sieved to particle size of 600-850 μm and further dried in the oven. Here, sulfuric acid (98 wt%) was used as catalyst to hydrolyze the corn cob. The ratio of corn cob to 98 wt% sulfuric acid was 2:5 (g.mL⁻¹). Hydrolysis reaction was conducted at 80°C for 40 min. Then the acid concentration of hydrolyate was diluted to 68 wt%. The liquid product was separated from solid by filtration. After washing several times with distilled water, the solid bioadsorbent was obtained.

Characterization of bioadsorbent

Scanning electron microscopy (SEM) analysis of as-prepared sample was carried out using Tescan MIRA3 scanning electron microscope to examine the surface morphology. X-ray diffraction patterns for bioadsorbent was obtained using Philips X'pert Pro diffractometer with 2θ range of 10 to 60 and step size of 0.05. The amount of residual dye in the solution was traced by UV-vis spectra (ShimadzuUV-1700), and the dye concentration was calculated by the absorbance at the maximum absorption.

Batch adsorption studies

The effect of initial dye concentration on the adsorption capacity was investigated in a range from 50 to 500mg L⁻¹ of MO with bioadsorbent dosage of 1 g.L⁻¹ at 25 °C. The effect of bioadsorbent dosage on the dye removal efficiency was evaluated in a range from 50 to 400 mg at 100 mL of MO (200 mg.L⁻¹) at 25°C. The effects of contact time was also investigated with 1 g.L⁻¹ of bioadsorbent and dye initial concentration of 200 mg.L⁻¹. The recyclability of the sample was
conducted in the 10 mL of 50 mg.L⁻¹ MO solution with 0.01 g of as-prepares sample at room temperature. The dye removal and adsorbed amount were determined according to the following:

\[
\text{Dye removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100
\]

\[
Q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(Q_e\) is the adsorbed amount of MB per unit weight of adsorbent (mg.g⁻¹), \(C_0\) and \(C_e\) (mg.L⁻¹) are the initial and equilibrium concentration of MB, respectively; \(V\) (L) is the volume of the dye solution and \(m\) (g) is the dry mass of the adsorbent.

**Results and discussion**

**Characterization**

The representative SEM (Fig. 1) image revealed that sample has cottony structures in the surface and was porous.
For as-prepared samples, X-ray diffraction pattern (Fig. 2) shows a broad diffraction peak in a 2θ range of 10–30° which matches well with that previously reported for non-graphitic carbon [11].
Effect of initial dye concentration on MO adsorption

The dye adsorption capacities onto bioadsorbent increased with the increase of the concentration of dye solutions (Fig. 3). The maximum adsorption capacities for MO reached to 350 mg g\(^{-1}\) at initial concentration of 500 mg L\(^{-1}\). The removal efficiencies for MO initially increased and then decreased which might be due to the fact that large numbers of vacant active sites were available for the adsorption at a lower initial concentration, and then saturated sites were difficult to capture the dye molecules [12].

![Graph showing the effect of initial dye concentration on MO adsorption.](image)

**Fig. 3.** Effect of initial dye concentration on MO adsorption.

Effect of bioadsorbent dosage

Fig. 4 show the effect of bioadsorbents on the percentage of removal and specific uptake of dye with respect to time. The dye removal efficiency increased dramatically with increasing the bioadsorbent dosage, which was due to the increase of available adsorption sites in bioadsorbent [13].
Effect of Contact Time

The contact time between adsorbate and the adsorbent is of significant importance in the wastewater treatment by adsorption. The obtained results (Fig. 5) for as-prepared sample show that the dye could be removed rapidly, 95% of maximum adsorption was done at short time (in the first 30 min).

Fig. 5. Effect of Contact Time.
The reusability of bioadsorbent

The reusability of the adsorbent is important for their economic feasibility and applicability. Therefore, the desorption-adsorption cycles were performed. Desorption studies were carried out using distilled water and ethanol solution, and the dye removed for each cycle were shown in Fig. 6. It can be seen that sample still retained adsorption capacity for MO even after four cycles of reuse.

![Fig. 6. Reusability of bioadsorbent.](image)

Conclusion

We investigated the adsorption of MO Dye on corn cob derived bioadsorbent as a function of initial dye concentration, contact time, adsorbent dosage and recyclability; and found that the bioadsorbent could be successfully used for the removal of dyes from aqueous solutions.


