Removal of Methyl Orange from aqueous solution by Saffron leaves waste as a low-cost adsorbent

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Abstract
The ability of Saffron leaves to remove methyl orange (MO) from aqueous solutions has been examined in this work. Batch adsorption studies were carried out at different contact times, initial concentrations (50–150 mg/L) and adsorbent doses (0.02–0.10 g) on the removal of methyl orange (MO) at the temperature of 25 ◦C.The results indicated that percentage of dye removal increased with increasing contact time as well as the adsorbent dose. The results also indicated that increasing the initial concentration of methyl orange resulted in a gradual decrease in the percentage of dye removal. The optimum adsorbent dose was determined 0.06 gr. The low-cost Saffron leaves waste was shown to be a high-efficient adsorbent for MO removal from aqueous solution.

Keywords: dye removal, Methyl Orange, Adsorption, Wastewater.

Introduction
Dyes are mostly used in many industries such as printing, leather tanning, paper production, textile, food technology, which are the main sources of environmental pollution [1,2,3]. Therefore, removing dyes from wastewater before they are released to the environment is a necessary operation [2,4]. Various treatment processes including physical separation, chemical oxidation, and biological degradation have been mostly examined to remove dyes from the water industry [6,3]. Among several chemical and physical methods, the adsorption process is one of the effective techniques that have been successfully employed to remove dye from wastewater [7]. Activated carbon is widely used as an adsorbent but the production of activated carbon is so expensive that makes this technology economically non-efficient [5]. Many natural adsorbents have been examined to reduce dye concentrations from aqueous solutions. Between the natural materials used as adsorbents for artificial dyes, agricultural by-products are considered to be low-cost products [3,8].
Chen et al [9] examined the removal of methyl orange (MO) and methyl violet (MV) from aqueous by *Phragmites Australis* activated carbon (PAAC) through an adsorption system. They investigated the effect of parameters such as initial concentration, adsorbent dose, pH and contact time. The results demonstrated the PAAC as low-cost adsorbent is very effective to remove MO and MV from wastewater.

Jiang et al [10] investigated the adsorption of methyl orange by a magnetic adsorbent from an aqueous solution. They synthesized AC/$NiFe_2O_4$ magnetic composite by a facile hydrothermal synthesis method. MO was selected as a model of azo dyes to examine the adsorption property of AC/$NiFe_2O_4$ composite. They investigated pH and concentration of MO solution, contact time, temperature, adsorbent dosage, and ionic strength were systematically examined by batch adsorption experiments. The MO removal efficiencies could reach 93% in the first 2 min and 99% within 30 min at the temperature of 303 K.The equilibrium adsorption of MO onto AC/$NiFe_2O_4$ composite was suitably described by the Langmuir model with a monolayer adsorption capacity of 182.82 (mg/g) at 303 K. the results showed AC/$NiFe_2O_4$ composite could be used as a promising and effective adsorbent for the removal of MO from dye wastewater.
In this study, the leaf of Saffron has been used as a low-cost adsorbent to separate methyl orange as a toxic substance from aqueous solution. The effects of contact time, initial contraction, and adsorbent dose on the removal of MO from wastewater were investigated.

Experimental

1. Adsorbate

Methyl orange (MO), obtained from Merk Co. was used without any further purification. The chemical structure of MO is shown in Figure 1. The initial pH was neutral. All of the reagents were used in analytical grade. A stock solution of 2000 mg/L was prepared by dissolving accurate amounts of MO separate doses of 1000 mL distilled water. The desirable experimental concentrations of solutions were prepared by diluting the stock solution with distilled water.

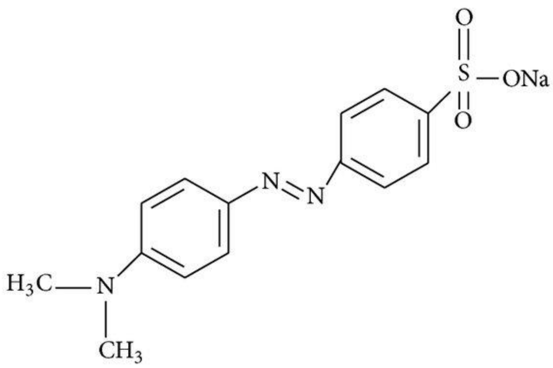

Figure 1. The chemical structure of methyl orange dye.

2. Preparation of the adsorbent

Saffron leaves were obtained from the farmlands of Jouvin, Sabzevar city, Iran, and then were washed with distilled water to remove dust and other pollutions, then Saffron was treated with hydrochloric acid (0.1M) solutions. The acidized Saffron was mixed for 24 h under continuous agitation (200 rpm). Sample was washed several times with distilled water. The washing and filtration steps were repeated until the filtrate became neutral.

3. Adsorption studies

batch experiments were performed in a set of 250 mL stoppered flasks (Erlenmeyer flasks). In each experiment, the specific amount of adsorbent was added to the desired volume (25 mL in each flask) of certain concentration and pH at 25C^o. The Erlenmeyer flasks were kept in a shaker at a constant speed of 200 rpm for a definite time. The sample solutions were filtered at equilibrium using filter paper to determine the final concentrations. The percent of the dye removal at equilibrium condition (Removal %) was calculated by the following equations:

$$\mathrm{Re}\% = \frac{(C_o - Ce)}{C_0} \times 100$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), respectively.

3.1. Effect of adsorbent dose

To examine the effect of adsorbent dose on the dye removal, different amounts of adsorbent (varying from 0.02 to 0.1 g) were respectively added into initial MO solution of 50 mg/L concentration. The mixtures were shaken in 250 ml flasks at 25 °C at neutral pH until the equilibrium time was gained.

3.3. Effect of contact time

Time is one of the most important parameters in design of economical adsorption systems. The adsorption of dyes onto Saffron during various times (5-240min) was studied in order to determine the required equilibrium time. Rapid uptake and quick establishment of equilibrium imply the efficiency of particular adsorbent in terms of usage in wastewater treatment.

3.2. Effect of initial concentration

In this step, the effect of MO concentration in dye solution on the amount of adsorption were studied in the range of 50 to 150 mg/L, at natural pH, certain dose of adsorbent and constant temperature (25 °C).

Results and discussion

3.1. Effect of adsorbent dose

As illustrated in Figure 2, at first, the removal percent increased rapidly with an increase in the amount of adsorbent and in a certain dose, the removal percentage nearly reached a constant value. The MO removal percentage increased from 31% to 92% with the increase of adsorbent dose from 0.02 to 0.1 g. The increase in dye removal percentage was due to the increased sorption surface and hence, the availability of more adsorption sites.

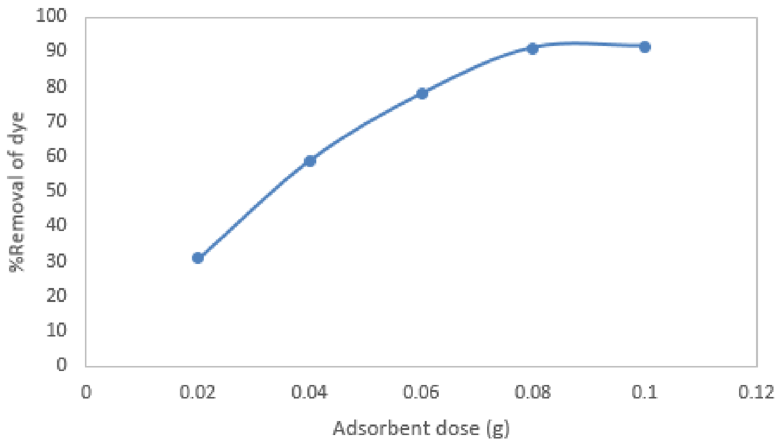

Figure 2- the effect of adsorbent dose on the dye removal (initial concentration=50 ppm, contact time=240min)

3.3. Effect of contact time

Figure 3 shows the effects of contact time on the adsorption of dyes by Saffron. As illustrated. the removal percentage was increased rapidly with the progress of adsorption time and then gradually increased until the equilibrium was reached. A sharp increase in adsorption during the initial stage may presumably be due to the availability of vacant active sites on the surface of the dye. The slow increase at the later stage may be related to the diffusion of dye into the pores of the adsorbent since the external sites are assumed to be completely occupied.

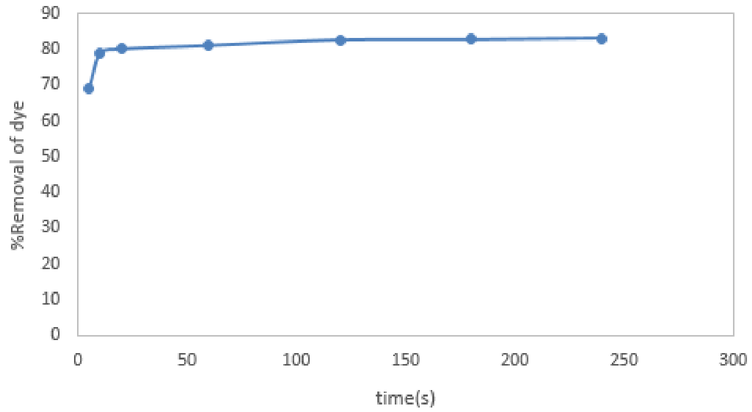

Figure 3- the effect of contact time on the dye removal (initial concentration=50 ppm, adsorbent dose=0.06gr)

3.2. Effect of initial concentration

In this part, the effect of MO concentration on the amount of adsorption were studied in the range of 50 to 150 mg/L, at natural pH, certain dose of adsorbent and constant temperature (25 °C). The reduction of removal percentage of MO with the increase of its initial concentration can be explained as follows: Since the mass of Saffron was constant in all solutions, the MO molecules had to compete for sites onto which they could adsorb. In fact, lower concentration of MO in initial solution, greater ratio of MO to Saffron and hence, lower percentage of removed MO.

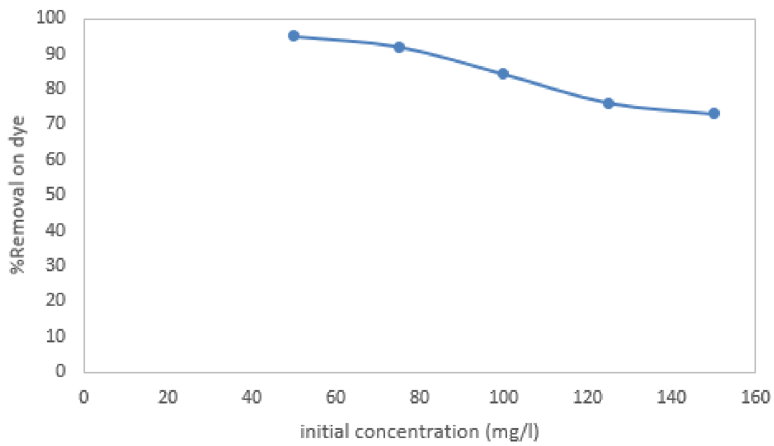

Figure 4- the effect of initial concentration on removal percentage of MO (adsorbent dose= 0.06gr, time contact=120min)

Conclusions

The removal of MO from aqueous solution using Saffron leaf as low-cost adsorbent was examined under different conditions in a batch system. The results indicated that the percentage of dye removal increased up to a maximum amount with increasing contact time as well as the adsorbent dose. The results also indicated that increasing the initial concentration of methyl orange in the initial solution resulted in a gradual decrease in the percentage of dye removal. A maximum percentage of methyl orange removal (95.13%) was obtained for an initial concentration of 50 ppm, a contact time of 120 min and a dose of 0.06 g adsorbent. The results of the present investigation showed that Saffron, a low-cost adsorbent could be efficiently employed as an adsorbent for the removal of MO from aqueous solutions.

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