Fast Removal and Recovery of Methylene Blue by Activated Carbon Modified with Magnetic Iron Oxide Nanoparticles

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A magnetic adsorbent was synthesized by modification of activated carbons with magnetic iron oxide nanoparticles (AC-MIONs). The preparation method is fast and could be carried out in an ordinary condition. The AC-MIONs were used as quite efficient adsorbents for separation of methylene blue (MB) from aqueous solution in a batch process. The effect of different parameters such as pH, temperature, electrolyte concentration, contact time and interfering ions on the removal of MB were studied. The adsorption data were analyzed by Langmuir and Freundlich isotherm models and a maximum adsorption amount of 47.62 mg g⁻¹ and a langmuir adsorption equilibrium constant of 3.0 L mg⁻¹ were obtained. The obtained results revealed that AC-MIONs were effective adsorbents for fast removal of MB from different aqueous solutions. This adsorbent was successfully used for removal of MB from Karoon River water.

**Keywords:** Magnetic separation; Activated carbon; Methylene blue; Iron oxide nano particles; Adsorbent.

INTRODUCTION

Industrial, agricultural and domestic wastes are often discharged in natural water bodies due to the rapid development of technology. Generally, this discharge is directed to the nearest water resources such as rivers, lakes and seas. One of the most important contaminating industries responsible for the continuous pollution of the environment is the textile dyeing industry. Treatment of the textile industries dyeing and finishing processes’ effluents is one of the most significant environmental problems since most synthetic dyes have complex aromatic molecular structures which make them inert and non-biodegradable when discharged into the environment. Colored wastes are harmful to aquatic life in rivers, lakes and seas where they are discharged. Colored water hinders light penetration and may consequently disturb biological processes in water-bodies. Moreover, dyes themselves are highly toxic to some organisms and hence disturb the ecosystem. Dyes may however cause allergic dermatitis, skin irritation, cancer, mutation, etc. Dyes biodegradation may sometimes produce aromatic amines which are highly carcinogenic. The continuous exposure of workers in the textile industries has been linked to higher bladder cancer risk.¹ As a result; removal of hazardous industrial effluents is one of the growing needs of the present time. Various techniques such as coagulation, adsorption, chemical oxidation and froth floatation etc. have been used for the removal of organic as well as inorganic compounds from wastewaters.² The adsorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters.

Currently, adsorption by activated carbon (AC) is one of the most widely used and effective physical methods in the industries.³ AC has been proven to be an effective adsorbent for the removal of a wide variety of pollutants dissolved in aqueous media or gaseous environments and is also used in the treatment of wastewaters due to its extended surface area, complex micro-porous structure, high adsorption capacity and high degree of surface reactivity.⁴ Several methods have been tried to remove various dyes from industrial effluents by AC.⁴⁻⁹ Unfortunately, ACs are notoriously difficult to separate from solutions.⁵

Magnetic separation is a new solid-phase extraction (SPE) method which according to the characteristics of the target systems can be employed in two different ways:

1) Separation of magnetic target by an external magnetic field; and

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2) Separation of non-magnetic target such as organic molecule through formation of a complex with magnetic particles which shall then be separated by an external magnetic field.\(^\text{10}\)

Several papers reporting the use of magnetic adsorbents for removal, separation and determination of non-magnetic targets have so far been published.\(^\text{3,5,10-19}\)

At present, considerable attention is being paid to SPE as a way to isolate and preconcentrate desired components from a sample matrix. SPE offers an excellent alternative to the conventional sample preparation methods. The separation and preconcentration of an analyte from large volume of solution by making use of standard column SPE is a time consuming process while the new SPE method which is called magnetic solid-phase extraction (MSPE) and is based on the use of magnetic or magnetizable adsorbents takes considerable shorter time to be accomplished. In this method magnetic adsorbents were added to a solution containing target analyte. The analyte was adsorbed on the magnetic adsorbents and separated, preconcentrated and recovered from the suspension using an appropriate magnetic separator such as an external magnetic field in a short time.\(^\text{13}\)

Present work describes a simple procedure for separation and removal of methylene blue (MB) dye from aqueous media, using AC-MIONs. A magnetic field is used to accelerate the separation process. Therefore, this adsorbent could adsorb dye which could then be separated in a magnetic field.\(^\text{10-19}\)

Large quantities of MB (Fig. 1) is used in some medical applications, paper coloring, cotton and wool dyeing, coating for paper stocks, etc.

Although MB is not considered as a strongly hazardous agent, it can cause some harmful effects. Acute exposure to MB causes increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans\(^\text{20}\) so; there is a dire need to develop effective methods for its removal, recovery and determination in wastewater. Several reported methods have been tried to remove MB.\(^\text{19-26}\)

Introducing AC-MIONs as an efficient solid phase extractor and development of a new method for removal and determination of MB using AC-MIONs is the main objective of the present work.

**EXPERIMENTAL**

**Chemicals and reagents**

All chemicals and reagents were of analytical grade. Methylene blue, phosphoric acid (85% m/m), ammonia solution (25% m/m), hydrochloric acid (37% w/w), FeCl\(_3\) (96% w/w), FeCl\(_2\)-4H\(_2\)O (99.9% w/w), methanol (99.9% w/w), acetone (99.5% w/w), chloroform (99% w/w), and ethylene glycol monobuthyl ether (99% w/w) were purchased from Merck (Darmstadt, Germany). Phosphate buffer solution (pH 6) was prepared by adding appropriate amounts of sodium hydroxide solution (1 M) to the phosphoric acid solution (0.1 M). The activated carbon (AC) powder (< 170 \(\mu\)m) was supplied by Aldrich Co. (USA) and used after washing with 3 M nitric acid solution and drying for 1 h in 50 °C.

**Apparatus**

The spectrophotometric measurements were carried out with a Cintra 101\(^\text{21}\) spectrophotometer (GBC SCIENTIFIC EQUIPMENT, Australia). A pH-meter (632 Metrohm\(^\text{21}\), Herisau, Switzerland), super magnet (1.2 T, 10 cm × 5 cm × 2 cm) and a stirrer (E649 Metrohm\(^\text{21}\), Herisau, Switzerland) were used.

**Preparation of AC-MIONs**

Previously reported procedure for the synthesis of iron oxide nanoparticles\(^\text{27}\) was modified for the preparation of AC-MIONs. 4 mL of FeCl\(_3\) (1 M) solution was added to 1 mL of FeCl\(_2\) (2 M) solution in a beaker. Then 0.2 g of carbon powder (previously washed and activated with 0.1 M HNO\(_3\) solution to remove impurities and enhance the active surface of carbon particles, filtered and dried) was added and mixed completely using a mechanical stirrer. Ammonia (1 M) solution (50 mL) was added drop wise to the solution while stirring. Iron oxide nanoparticles were adsorbed with maximum amount of activated carbon to enhance the adsorption capacity of the particles. The beaker was then placed on the magnet and after complete settlement of AC-MIONs, the solution was decanted. AC-MIONs Particles (< 250 \(\mu\)m) were washed with water for several times to remove excess ammonia solution.

**Separation procedure**

Adsorption of MB on AC-MIONs was investigated using a 50 mL solution of MB (3 \(\mu\)g mL\(^{-1}\)) with 3 mL of
phosphate buffer (pH 6) in a beaker. Damp AC-MIONs (0.3 g) which was equivalent to 0.034 g of dry AC-MIONs was added to the beaker and the mixture was stirred by a glass rod for about 2 minutes. MB adsorbed AC-MIONs was then collected by placing the beaker on the magnet and allowing the upper solution to become colorless. Removal percentage of MB was determined by spectrophotometrically measurement of solution absorbance before and after separation process at 663 nm.

RESULTS AND DISCUSSION

Effect of the amount of activated carbons

The amount of activated carbon which was used for the preparation of AC-MIONs by the above mentioned procedure was optimized. As it is shown in Fig. 2, the optimum amount of activated carbon coated with the magnetic iron oxide nanoparticles is 0.2 g. Above this value the excess of carbons were remain floated on the solution when applying a magnetic field. Without using activated carbon there was no significant adsorption and hence removing of the dye.

Desorption of MB from AC-MIONs surface and Recovery calculation

Desorption of MB from AC-MIONs was performed by a solution of sodium dodecyl sulfate (SDS) (0.5% w/v) in ethylene glycol monobuthyl ether. The desorbent solution was added to the particles and after stirring for 60 s, the magnetic adsorbents were collected and separated using a magnet. The amount of eluted dye to the organic solvent was measured spectrophotometrically at 663 nm and was used to calculate the recovery percentage. The recovery rate of more than 98% was obtained.

Effect of pH

The effect of pH was examined by varying the pH of the test solution in the range of 3-10. The pH of 50 mL of MB solution (3 μg mL⁻¹) was adjusted to the desired value using HCl and/or NaOH solution (0.1 M), and 0.50 g of AC-MIONs was added as the adsorbing agent. In low pH values, the solution became dark brown due to dissolution of iron oxide nanoparticles. On the other hand in solutions with high pH values, the particles were converted to colloidal form and did not settle by the applied magnetic field. The obtained results showed that the dye removal was practically constant (more than 99.6%) in the studied pH range. Therefore, it was found that pH is not a critical limiting factor on the proposed removal process. In further experiments however, the pH of the solutions was adjusted to 6 by adding 3 mL of phosphate buffer (pH 6).

Effect of the AC-MIONs amount

The adsorption of MB by AC-MIONs was studied by using varying quantities of damp AC-MIONs from 0.10 g to 0.50 g for removal of the dye from 50 mL of the test solution (3 μg mL⁻¹), while other variables were kept constant. The obtained results showed that removal percentage was constant for different amounts of adsorbent, and therefore 0.3 g of damp AC-MIONs (equivalent to 0.034 g of dry AC-MIONs) was used for further experiments.

Effect of electrolyte concentration

The effect of electrolyte concentration on the removal of MB by magnetic adsorbent was investigated. The results showed that the concentration of electrolyte has no effective influence on the removal percentage of MB in the range of 0.01 to 0.50 M of NaCl as an electrolyte. It seems
that interaction of MB with AC-MIONs was basically on scraping of MB in the pores of AC-MIONs and was not influenced by electrostatic forces; because various concentrations of NaCl showed no effective influence. However at higher concentrations of NaCl, the removal percentage decreased slightly, which can be attributed to the competition of electrolyte ions with dye ions for the occupation of AC-MIONs pores.

**Effect of Stirring Time**

The effect of stirring time of the MB solution after addition of AC-MIONs on the removal is shown in Fig. 3. As can be seen the removal increases with increasing the stirring time.

Very fast adsorption rate was indicated by the removal of more than 85% of MB in the first 30 s. The adsorption rate decreased gradually until equilibrium was attained in about 2 min. The results show that the removal process is very fast and this is an important advantage of such a separation method.

**Effect of Temperature**

It was shown that the adsorption of MB was decreased as a result of an increase in the solution temperature (Fig. 4) which is in agreement with the obtained results for the adsorption of MB on other adsorbents.\(^{24}\)

This can be explained by the exothermic adsorption process and the weakening of bonds between dye molecules and active sites of adsorbents at high temperatures. Adsorption of MB was decreased as the solution temperature decreased which could be related to the kinetic of the adsorption process.

**Effect of Co-existing Ions**

Effects of co-existing ions and compounds including four organic dyes were investigated using optimum experimental conditions. To this end separation and determination of MB was performed in the presence of co-existing ions. The maximum acceptable error was ±5%. The obtained results are shown in Table 1.

The table shows that Rose Bengal strongly interfered even in the same concentration with MB.

**Equilibrium Isotherm**

Equilibrium relationships between adsorbent and solute are mostly described by Langmuir and Freundlich adsorption isotherm models. The theoretical Langmuir sorption isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of solute in the plane of the surface. The adsorption behavior of MB on AC-MIONs can be described by Langmuir isotherm model (Fig. 5) with an equation of:\(^{23}\)

\[
\frac{C_s}{q_s} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

where \(C_s\) is the equilibrium concentration of dye (mg L\(^{-1}\)) and \(q_s\) is the amount of the dye adsorbed (mg) by the unit mass of AC-MIONs (mg) and \(q_m\) and \(K_L\) are the Langmuir constants related to the adsorption capacity (mg mg\(^{-1}\)) and the equilibrium constant (L mg\(^{-1}\)), respectively. The Langmuir

![Fig. 4. Effect of temperature on the MB adsorption (conditions: 50 mL of 3 µg mL\(^{-1}\) solution of MB; 0.3 g of AC-MIONs; pH 6; contact time 120 s). The presented data were average of three replicated analysis.](image)
monolayer adsorption capacity \((q_m)\) gives the amount of the dye required to occupy all the available sites per unit mass of the sample. The Langmuir monolayer adsorption capacity of MB dye was estimated to be \((47.62) \text{ mg g}^{-1}\).

The Freundlich adsorption equation was also applied to the equilibrium data for adsorption of MB on AC-MIONs adsorbent:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}
\]

where \(K_f\) and \(n\) are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Freundlich parameters \((K_f \text{ and } n)\) indicate whether the nature of adsorption is either favorable or unfavorable. The intercept and slope are indicators of adsorption capacity and intensity, respectively. A relatively slight slope \(n < 1\) indicates that adsorption intensity is good (or favorable) over the entire range of studied concentrations. Adsorption intensity is good (or favorable) at high concentrations with a steep slope \((n > 1)\), but much less at lower concentrations.

Freundlich constants of \(K_f = 1.5\) and \(n = 2.6\) were obtained for adsorption of MB on AC-MIONs adsorbent based on Freundlich adsorption isotherm model with a correlation coefficient of \(R^2 = 0.9801\) (Fig. 6).

**Reusability of the AC-MIONs**

The ability of reusing the adsorbents in several successive adsorption and desorption processes was tested. The obtained results showed that the modified magnetic particles can be reused for six times without a considerable loss in their adsorption efficiency (> 96%).

**Analysis in real water samples**

To determine the ability of the proposed method for the removal of MB in a real sample, Karoon River water was spiked. The spiked levels were \(3 \mu\text{g mL}^{-1}\) and \(4 \mu\text{g mL}^{-1}\) of MB. The removal of MB from spiked solutions was successfully performed in two different river water samples and removal percentages up to 99.38% could be obtained. Excellent removing percentage (more than 99%) indicates that the complex matrix of river water samples does not interfere with the removal of MB.

**CONCLUSION**

A fast, simple and new magnetic removal of MB from aqueous solution has been successfully developed using AC-MIONs as adsorbent. The AC-MIONs can be well dispersed in the water and can be easily separated by a magnet from the medium after adsorption of the dye in a 3 min period.

The adsorption capacities of MB were in the range of \((47.62 \text{ mg g}^{-1})\). Removal of MB by AC-MIONs has a great advantage of independence of process against a wide range of pH values. Considering the amount of adsorbent (low adsorbent dosage, \(0.3 \text{ g}\) of damp AC-MIONs), it was shown that by increasing the adsorbent dosage, better removal percentage is achieved which can be attributed to increased surface area and the activated nano-carbon adsorbent sites available. The whole adsorption–removal processes can be completed within 5 min. Last but not least, the proposed procedure offers higher removal percentages and also shorter adsorption–removal times of the dye compared with most of the previously reported methods (Table 2).
ACKNOWLEDGMENT

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REFERENCES


Table 2. Comparison of the presented method with some previously reported works

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<th>Reference no.</th>
<th>Removal %</th>
<th>removal time</th>
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<td>30 min</td>
<td>-</td>
<td>4-7</td>
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<td>-</td>
<td>2 min</td>
<td>KCl, 0.05 M</td>
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<td>30 min</td>
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