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Removal of Malachite Green from Wastewaters Using Modified Sand Filtering

***Mansour Aslani**

Department of Chemistry, Faculty of science, Islamic Azad University, Omidiyeh branch, Omidiyeh, Iran

***Corres.author:= m_aslani89@yahoo.com**

Abstract: This study present separation and removal of malachite green from wastewaters by sand filtering modified with sulfur nanoparticles as adsorbent. Different parameters were optimized. The concentration of malachite green in the dilute phase was determined by measuring the absorbance at 633 nm. Maximum removal efficiencies were obtained at pH=5 by using 5g of absorbent. The method showed good linearity for determination of malachite green in range of 1-10 mg L^{-1} with a regression coefficient 0.9991. The effect of some interfering ions on the removal process was also investigated. The relative standard deviation (RSD) for 4 and 6 mg L^{-1} of real sample of malachite green dye were 3.77% and 5.27%, respectively.

Key words: Suphur nano particles,malachite green, removal.

Introduction

Malachite green (MG) is traditionally used as a dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose[1]. MG is active against the oomycete Saprolegnia, which infects fish eggs in commercial aquaculture, and other fungi. Furthermore, MG is also used as a parasiticide and antibacterial[2]. It is a very popular treatment against ichthyophthirius in freshwater aquaria.

Malachite is a copper carbonate hydroxide mineral, with the formula $Cu_2CO_3(OH)_2$. This opaque, green banded mineral crystallizes in the monoclinic crystal system, and most often forms botryoidal, fibrous, or stalagmitic masses, in fractures and spaces, deep underground, where the water table and hydrothermal fluids provide the means for chemical precipitation. Individual crystals are rare but do occur as slender to acicular prisms. Pseudomorphs after more tabular or blocky azurite crystals also occur. Typical malachite is laminated and whether or not microbes intervene in its formation is unknown[2].

Malachite green (MG) is a metallic-looking crystal. It dissolves in water easily as a blue-green solution. It is a toxic chemical primarily used as a dye and has been found very effective in treating parasites, fungal infections, and bacterial infections in fish and fish eggs[3]. On uptake, MG is rapidly reduced into leucomalachite green (LMG) and deposited in the fatty tissue of the fish with little MG remaining.

MG can cause significant health risk for humans who eat contaminated fish. For example, it can cause liver tumor formation and is suspected of carcinogenesis. have already banned MG in fishery. Due to its low cost and

antifungal effectiveness, MG is still being used illegally as indicated in the European Rapid Alert System for Food and Feed[4]. Therefore determination and removal of MG in real sample especial water sample by simple and reliable method is very important[5-7].

This study present separation and removal of malachite green from wastewaters by sand filtering modified with sulfur nanoparticles as adsorbent. The present method was applied to some waste waters sample which gave satisfactory results.

Experimental

Material and apparatus

All reagents were of analytical grade purity and all solutions were prepared with doubly distilled water. Malachite Green (Fluka), ammonia (25%), hydrochloric acid (37% m/m), sodium hydroxide, Nitric acid, Acetic acid, Boric acid, and sodium thiosulfate were purchased from Merck (Darmstadt, Germany). The spectrophotometric measurements were carried out with a Perkin-Elmer UV-Vis Lambada 25 at λ=633 nm. A pH-meter (632 Metrohm, Herisau, Swizerland) and super magnet (1.4 Tesla, 10cm× 5cm× 2cm) were used.

Procedure

1 Kg sand after preparation with mesh 60 purred in 1 Lit HNO_3 0.1 M for 24 hour. Sodium thiosulfate 0.1 M added to hydrochloric acid 0.1 M which produces sulfur nanaoparticles as bellow reaction. Then nanoparticles added to sand and put in oven to cause dry adsorbent.

$$Na_2S_2O_3 + 2HCl \leftrightarrow 2NaCl + SO_2 + S\downarrow + H_2O$$

This adsorbent was palced in column then the solution containing malachite green passed through this column and the removal was determined spectrophotometrically by bellow equation.

$$\text{Removal \%} = A_i - A_f / A_i \text{ X100}$$

Where A_i and A_f are initial and final absorbance at 633 nm.

Results and discussion

Effect of pH

The pH value of solution is an important process controlling parameter in the adsorption study since it determines the surface charged of sorbent. The effect of pH was studied at pH range of 3-9. The result was shown in Fig. 1. pH 5 was chosen for sorption of MG in the experiment.

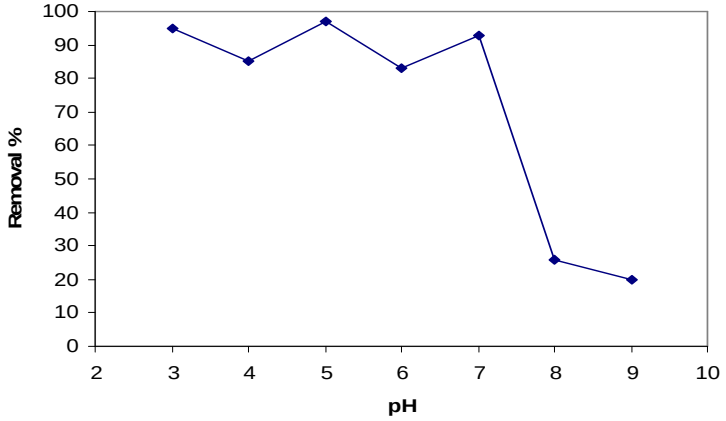

Fig. 1. Effect of pH on the removal of MG

Effect of adsorbent

The amount of nano sorbent investigated to 1-7 gr. Dye removal increased with increasing nanosorbent. An adsorbent content of 5 g was enough for more than 97 % dye removal. The result showed that 5 g was optimum of sorbent (Fig 2).

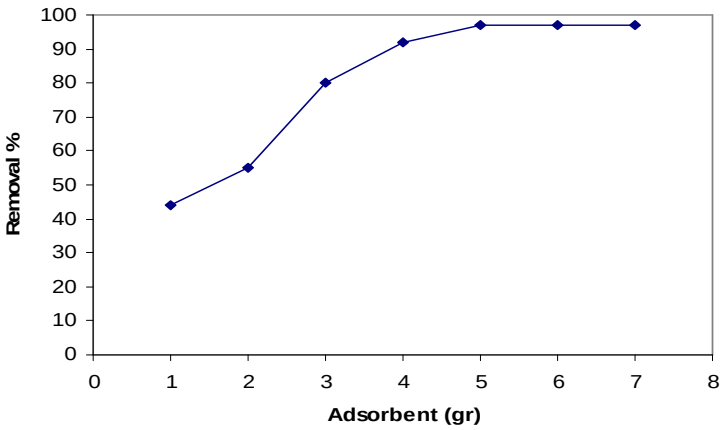

Fig. 2. Effect of amount of nanosorbent on removal of MG

Figures of merit

In order to show the validation of the proposed method, the analytical features of the method such as linear range of the calibration curve, accuracy and precision were examined. The calibration graphs were linear in the ranges of 1.0-10.0 mg L^{-1} of MG dye. The equations for this calibration graphs were $Y=0.0332\ C_{MG} + 0.0069$ (r^2 =0.9991).

The relative standard deviation (RSD) for 4 and 6 mg L^{-1} of real sample of malachite green dye were 3.77% and 5.27%, respectively.

Determination of MG in fresh aquarium water and laboratory samples

In order to test the reliability of the proposed methodology the assaying were done for determination of MG in Persian gulf water at two different concentration of MG by perposed method. The results are shown in Table 1 which gave satisfactory results.

Table 1. Determination of Cu MG in fresh aquarium water and laboratory samples.

Sample	**MG(mg L^{-1})**		**% Recovery**
	Added	**Found**	
No. 1	0.00	ND[a]	-
	4.00	4.05	101
No. 2	0.00	ND	-
	4.00	3.85	96
No. 3	0.00	ND	-
	4.00	4.00	100
No. 4	0.00	ND	-
	6.00	6.10	102
No. 5	0.00	ND	-
	6.00	5.85	98
No. 6	0.00	ND	-
	6.00	6.15	103

[a]: Not Detection

Conclusion

In this paper, the adsorption behavior of MG on sand which modied br nanosulfur was investigated. The main advantages of the procedure are simplicity, good linearity of calibration graph in ranges of 1.0-10.0 mg L^{-1}, viable and high efficient. The sulfur NPs are synthesized easily and can be regenerated. The purposed method was applied to water sample which gave satisfactory results.

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