Removal of Malachite Green Dye from Industrial Wastewater by Using Concrete Modified with Rubber Powder

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Abstract

Background: In recent years, the need for new methods of water treatment on an industrial scale in order to compensate the shortage of water resources has become imperative. Among different methods, the use of adsorption in order to remove aqueous contaminates, including synthetic dyes, has been so effective.

Methods: In this research, removal of malachite green from aqueous solution by concrete modified with rubber powder has been studied. In order to achieve the maximum efficiency of malachite green removal, the impact of different parameters such as initial concentration of malachite green, pH, adsorbent dosage and contact time was studied using batch experimental method.

Results: According to the results, optimum conditions of MG removal were pH of 9, initial concentration of 30 ppm, rubber powder dosage of 35% of sand weight, and contact time of 90 min. Results of compressive strength test have shown that compressive strength of concrete with 35 wt.% of rubber powder reduced 84.13% compared to simple concrete. The removal percentage of MG is 98.33% when the surface of concrete is covered by rubber powder. Experimental data corresponded with pseudo-first order equation with R^2=0.93, Langmuir and Freundlich adsorption isotherms with R^2=0.85 and 0.84, respectively. Real waste sample was used to confirm the application of concrete in ordinary conditions of wastewater basin in accordance with optimum conditions of kinetics wastewater. Elimination rate of MG happened in an optimum condition with real samples taken from industrial factory.

Conclusion: Concrete modified with rubber powder has potentials for removal of MG dye from wastewater. Covering the concrete surface with rubber powder can be an innovative and useful solution for increasing the rate of elimination of pollutants and contaminants, cost reduction and accelerating the absorption process. Actually, it could be considered as one solution for managing waste rubber.

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Introduction

Water pollution is one of the most important problems in every human society. One of the water pollutants are dyes. Water reuse can be considered as an appropriate method to provide required water resources and meet the rising demand for water. The majority of dyes have synthetic sources, complex molecular structures, and aromatic properties that make them resistant and complicated in decomposition and recycle processes. Synthetic dyes are widely used in textile industry, paper, rubber, leather tanning, cosmetics, medicine and food processing.[1] Discharge of colored wastewater of these industries into surface water resources can trigger serious problems such as increase in toxins and chemical oxygen demand, decrease in sunlight penetration, and disruption in photosynthesis.[1] Malachite green dye is commonly used in textile industry and aquaculture industry as an antifungal and disinfection agent. Malachite green dye in the environment has implications such as cancer, genetic mutation, congenital disorder and respiratory disease in mammals. According to the standards of European countries, malachite green concentration in wastewater cannot exceed 100 micrograms per liter.[2] Various methods are used in the removal of MG dyes from wastewater such as coagulation, sedimentation, filtration, chemical processes, membrane separation, etc.[3-7] Most conventional methods have high operational costs and in many cases contaminants are not completely decomposed. Among them, adsorption has been introduced as an effective method with high reliability and capability to remove a wide range of contaminants. The main challenge in the adsorption process is achieving an adsorbent with high adsorption capacity, high stability in the presence of organic materials, and low costs of production and operation. In order to find low-cost alternatives as adsorbents, many researchers have reported the feasibility of using various adsorbents derived from natural materials, industrial solid waste, agricultural by-products and household waste, due to their low costs and abundance.[8] Some adsorbents such as TiO_2 nanoparticles; mesoporous Carbon; and solid agricultural waste by-products such as wheat bran, rice husk, peanut shell and leaves of the acacia tree, bagasses fly ash, rice husk activated carbon, Rattan sawdust and coffee beans have been also used as an adsorbent.[9-15]

In this study, samples of concrete modified with rubber powder were constructed and the effectiveness of this low-cost adsorbent in removal of malachite green dye under different process conditions has been investigated. In researches, several various experimental conditions have been discussed to achieve a desired separation for dyes. Experimental conditions such as pH, initial concentration of MG dye, dosage of adsorbent and contact time affect the adsorption process.

Methods

In this study, concrete mix design has been chosen according to ACI (211) standard.[16] It was obtained after correction due to moisture and weather conditions. The content of concrete has been shown in Table 1.

Rubber was 35% of the total fine aggregate weight.

The materials used in concrete construction were as follows:

● Portland cement type **II** that is most commonly used in different weather conditions.

● Rock (coarse aggregate) with a maximum grain size of 19mm

● Sand with a maximum grain size of 4.7mm

● Rubber scrap consisting of two sizes:

2.36 mm (sieve No.8)

1.18 mm (sieve No. 16)

● Rubber powder consisting of three sizes:

0.6 mm (sieve No. 30)

0.3 mm (sieve No. 50)

0.15 mm (sieve No. 100)

All chemicals including malachite green dye were of analytical reagent grade and supplied from Merck Co. Molecular structure and specifications of malachite green dye are presented in Table 2.

The equipment used in the experiments was as follows:

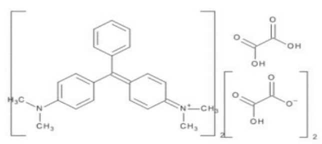
● pH Meter Model pHS-3F

● Magnetic Stirrer Model BH-1200, manufactured by Behdad Company.

Table 1: Concrete Mix Design

Sand (kg/m^3)	Coarse aggregate (kg/m^3)	Cement (kg/m^3)	Concrete Density (kg/m^3)	Water (L/m^3)	Rubber (kg/m^3)
587	1012	312	2345	190	315

Table 2: Specification of Malachite Green Dye

Molecular Formula	Molecular Mass	Molecular Structure
$C_{52}H_{54}N_4O_{12}$	927.01 g/mol	

● Digital Mass Balance Model ED2242, made in Germany.

● Spectrophotometer Model JENWAY 6310, made in England.

To construct the concrete samples, we used a plastic cylindrical mould with a diameter of 16 cm, concrete height of 3 cm, and total volume of 0.0006 m^3.

At first, concrete samples containing adsorbent of rubber powder were prepared based on mix design. Then, 250 ml of MG solutions with specified concentration were contacted with concrete samples to achieve the equilibrium time. Adsorption of malachite green dye was measured by a spectrophotometer at the maximum wavelength of 619 nm. After a specified period of time, the dye removal efficiency was obtained based on the following equation:

$$E\% = \frac{C_1 - C_2}{C_1} \times 100 \quad (1)$$

Where, E% is the efficiency of MG removal from aqueous solution, C_1 is the initial concentration of MG dye and C_2 is the concentration of MG dye after contact with the concrete sample.

Results

In this research, MG dyes removal from wastewater by using concrete modified with rubber powder has been investigated. All experiments has been carried out under laboratory conditions; the optimum conditions for the adsorption of MG by using adsorbent have been examined and determined. The parameters involved were pH, time, initial concentration of MG and adsorbent dose. In each step, to determine the optimal conditions, we considered one of the parameters as the variable and the other parameters were kept constant.

Effect of pH: To investigate the effect of pH on the adsorption of MG dye onto concrete modified with rubber powder, we prepared a set of similar solutions with the volume of 250 ml and concentration of 10 ppm at the pH of 1-11. The samples were contacted with the modified concrete for 120 minutes. In all cases, the pH was adjusted by 0.1 molar solutions of HCl and NaOH. pH of the solution plays an important role in determining the concentration of anions and cations of solution. The most favorable adsorption was seen at pH=9 with 99.4% removal of MG dye.

Effect of contact time: Time is one of the important parameters that affects the dye adsorption and kinetics of the process. The optimum time was studied with a 250 ml of the sample with initial concentration of 10 ppm at optimum pH. The sample was contacted with the modified concrete for 120 minutes. The measurement of color absorbance was done with spectrophotometer every 30 minutes. The equilibrium time and adsorption efficiency as economic factors make a serious impact on science development and technology of water treatment based on natural adsorbent. The relative increase in the removal of dye after contact time of 90 min was not significant; hence, it was fixed as the optimum contact time. The maximum efficiency reached 99.4% after 90 minutes.

Effect of initial concentration: Dye adsorption on various adsorbents is a function of initial concentration of the dye. To determine the influence of initial concentration on the adsorption rate, we carried out a set of similar experiments on 250 ml samples at the optimum pH and contact time with initial concentration of 10 to 100 ppm. The maximum efficiency of 99.7% was obtained at the initial dye concentration of 30 ppm.

Effect of adsorbent: The amount of adsorbent and number of active sites on the surface are so effective in the adsorption rate of MG dye. To investigate the effect of rubber powder, three concrete samples were prepared with rubber powder to the 30, 35 and 40% of the sand weight. The absorption rate was obtained for 250ml samples at optimum value of initial concentration, pH, and contact time. The results showed an increase in the adsorbent amount to 35% of fine aggregate weight and increase in the removal efficiency of MG dye to 99.7%. Actually, the optimum value of the variable parameters has been shown in Table 3.

Compressive Strength Test: To study the effect of rubber powder on the strength of modified concrete, the compressive strength test was applied based on ACI standard. Some cubic moulds were constructed with dimensions of 15*15*15cm. The concrete samples were made based on the mentioned mix design with different weight percentages of the rubber. These specimens were kept under saturation condition in water for curing. After 28 days, they were tested by compression testing machine (hydraulic jack). Load should be applied gradually till the specimens fail. Loads at the failure were measured. Compressive strength was calculated based on the following formula:

$$\sigma = \frac{N}{A}\left(\frac{kg}{cm^2}\right) \quad (2)$$

Where N is the the load in Kg, A is area of cube in cm^2 and σ is the compressive strength.

As seen in Table 4, the results illustrated an increase in the content of rubber powder from 5-35% of the sand weight led to a decrease in compressive strength from 271.6 to 43.11 kg/cm^2.

Comparison removal percentage of MG with plain concrete, modified concrete and concrete covered by rubber powder: To investigate the effect

Table 3: Optimal amount of parameters

pH	Contact Time (min)	Initial concentration (ppm)	Adsorbent dose (Weight %)
9	90	30	35

Table 4: Compressive strength results

Weight Percentage of rubber	Density (Kg/m³)	Compressive Strength (Kg/cm²)	Percentage of strength decrease
0%	2355	271.6	0
5%	2305	241.4	11.12
15%	2183	150.88	44.45
25%	2050	73.28	73.02
35%	1925	43.11	84.13

Table 5: Comparison of the efficiency of concrete in different forms

Concrete Type	Modified concrete	Covered Concrete	Plain concrete
Removal percentage	99.70	98.33	88.90

of rubber powder on improving the concrete properties as an adsorbent for MG dye, two samples with a volume of 250 ml and the optimum concentration of 30 ppm at pH=9 were contacted with plain concrete and modified concrete with rubber powder for 90 minutes. The results showed the removal efficiency of MG dye onto modified concrete increased significantly. In order to compare the applicability of the modified concrete with covered concrete with a layer of rubber powder, a set of experiments was carried out with the similar conditions including concentration of 30 ppm, volume of 250 ml, pH=9 and contact time of 90 minutes on both types of concrete. The results are shown in Table 5.

It should be noted that 64 gram of rubber powder was used for construction of modified concrete; however, 10 gram of rubber powder was required to make a layer on the concrete.

Kinetic study of adsorption: To determine the kinetic models and controlling mechanisms of adsorption, we used some data such as chemical reactions, diffusion control and mass transfer coefficients. The kinetics of dye adsorption is required for selecting the optimum operating conditions. Kinetics study specifies dye adsorption rate and contact time required at the interface of two phases. In order to investigate the adsorption mechanism of cationic and anionic dyes, various kinetics models have been suggested. In this study, two of the well-known models were investigated to find the best fitted model for the experimental data. The linear equation of pseudo first-order rate model can be generally represented in the following form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g) and k_1 is the pseudo first-order rate constant for the adsorption process (min^{-1}).

The pseudo second-order model can be described as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where k_2 is the pseudo second order rate constant for adsorption process (g/mg min).

In the pseudo first-order model, the rate of adsorption is directly proportional to the changes of saturated concentration and adsorbent dosage. In this study, both models were investigated to find the best fitted model for the experimental data. The results show that pseudo first-order is better fitted than pseudo second-order due to the higher R^2 factor (Table 6).

Table 6: Kinetic models

Kinetic models	R^2
First order model	0.93
Second order model	0.74

Evaluation of adsorption isotherms: Adsorption isotherm is an equilibrium relationship between the amount of adsorbate and its concentration in bulk fluid phase at a constant temperature. Adsorption isotherms were applied to explain the interaction between adsorbent and adsorbate and calculate the absorption capacity. Adsorption isotherms are important to understand the mechanism of adsorption. Adsorption may be either single-layer or multi-layer. Among the different isotherms suggested in several articles, Freundlich and Langmuir isotherms are widely used to describe the adsorption processes. Langmuir adsorption model is presented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \quad (5)$$

The Freundlich adsorption isotherm is

mathematically expressed as below:[3]

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (6)$$

The data of MG adsorption on concrete modified with rubber powder was analyzed for various concentrations from 10 ppm to 100 ppm at pH=9 with both Langmuir and Freundlich isotherms. Regression coefficients are shown in Table 7. According to the regression coefficients, the results were consistent with both Freundlich and Langmuir's isotherms.

Table 7: Adsorption Isotherm

Isotherm	R^2
Langmuir	0.85
Freundlich	0.84

Real Samples: In order to examine the efficiency and determine the yield of the modified concrete samples used in this study in real-life conditions, we prepared and tested some samples of industrial wastewater containing MG dye. The samples were from the sewage of Isfahan textile factory before and after the treatment operation. Finally, the reduction in the percentage of sample absorption in the sewage sample was determined in 619 nm. After adjusting pH=9, the samples were exposed to adsorbent-coated concrete for 90 minutes; after this time, the absorbance rate of the samples was measured. Information is shown in Table 8.

Sample 1: Raw wastewater on modified cement with 35% weight of rubber powder

Sample 2: Raw wastewater on cement covered by rubber powder

Sample 3: Treatment of wastewater on modified cement with 35% weight of rubber powder

Discussion

Efficiency of MG removal increased at alkaline environment compared to acidic environment. At lower pH, the number of positively charged adsorbent surface sites increased;consequently, the electrostatic repulsion between the positively charged surface and the positively charged dye molecule increased. The surface of the rubber powder was negatively charged at higher pH, which increased the adsorption of cationic MG due to electrostatic force of attraction.[3] In order to achieve the maximum efficiency of dye removal, operational conditions were optimized. The maximum removal efficiency was reported at pH=9. This finding was in good agreement with those of similar research.[8] The results illustrated a direct relationship between the retention time and percentage of removal. With increase in the retention time, the contact time between MG dye and modified concrete rose; therefore, the adsorption rate increased. There was a faster rate of adsorption at the initial stage which went on decreasing later due to saturation of the adsorbent surface and occupation of active sites. Increasing the initial concentration from 10 to 30 ppm caused an increase in dye removal efficiency due to more effective interaction between the dye molecules and adsorbent surface and also the higher driving force for mass transfer. On the other hand, with the increase from 30 to 100 ppm, the total removal efficiency was decreased due to the excessive increase in the dye molecules, poor interaction between them and adsorbent surface, and saturation of adsorption sites on the adsorbent surface.[9] The optimum amount of rubber powder was 35% of the fine aggregate weight. The initial concentration of 30 ppm MG led to the maximum removal efficiency which was in a good agreement with results of the study done by Sharna et al.[14] The increase in the dosage of adsorbent led to an increase in the available active sites on the surface. Consequently, the effective contacts of the dye molecules with adsorbent's active sites increased and more dye molecules were removed from the solution. This indicates that variation in the adsorption dosage has a significant effect on the efficiency of MG dye removal.

In comparison between modified and plain concrete, a maximum efficiency of 99.7% was reached which was 11% more than removal efficiency obtained by using plain concrete. Besides that, the effectiveness of concrete modified with rubber powder and concrete covered by a layer of rubber powder was compared. Findings illustrated that the removal efficiency onto modified concrete was more. Results of standard tests demonstrated that compressive strength of concrete containing 35% of rubber powder decreased 84.13% compared to plain concrete.[18, 19] In order to study the kinetics of the process, pseudo first-order and second-order models were applied and experimental data followed first-order kinetics equation.[8] The adsorption equilibrium data showed a good fit to both Langmuir and Freundlich's isotherms. Mohd et al. and Baek et al. suggested similar kinetics model and adsorption isotherms.[4]

It was observed that the adsorption rate rose when using the adsorbent as the coating of the concrete surface. This is important in terms of

Table 8: Removal of MG from actual wastewater

Samples No	1	2	3
Reduce percentage of absorption (%)	14	27	9

both efficiency and economics, regarding the fact that when coating the concrete surface, much less amount of adsorbent was used. The reason for the increased removal rate at this stage may be the increased contact surface and the degree of collision between the adsorbent and MG. Some research conducted by Asrari showed similar results.[18, 19]

Conclusion

In this study, removal of malachite green dye from colored waste water was successfully investigated by using modified concrete with rubber powder as a low-cost and effective adsorbent. It seems that for equilibriums tank used in sewage and industrial wastewater treatment, using modified concrete by rubber powder can be suggested as a good solution for removing thedyes such MG.

Conflict of Interest: None declared.

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