Cumhuriyet Sci. J., 43(4) (2022) 638-644
DOI: https://doi.org/10.17776/csj.1116265

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Decolourization of Methylene Blue in Aqueous Solution by Photocatalytic Oxidation, Fenton Oxidation and Biosorption

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Research Article

History
Received: 16/05/2022
Accepted: 04/12/2022

ABSTRACT

The aim of the study was to investigate decolourization of Methylene Blue (MB) in aqueous solution using advanced oxidation processes (AOPs) and biosorption comparatively. Photocatalytic decolourization of MB was studied using TiO_2 as catalyst. The photocatalytic decolourization of MB by direct UV irradiation alone, only TiO_2 and TiO_2/UV processes was investigated. It was found that decolourization by photocatalytic process of MB increased with decreasing pH, and decolourization rate also increased in the presence of TiO_2/UV when compared to UV irradiation alone. Decolourization of MB was also studied with using the Fenton process (Fe(II)/H_2O_2). Concentrations of Fe(II) and H_2O_2 on decolourization ratio were investigated. The optimum catalyst to H_2O_2 ratio was found 1:3 at pH 4.0. In the second part of the study, the biosorption process was conducted with using plant gall immobilised alumina. The removal percentages were calculated with both plant gall immobilised alumina and alumina alone. The immobilisation of plant gall increased the removal percentages from 60-70% to 90-95%. The proposed methods (AOPs and biosorption) have both advantages and disadvantages compared to each other.

Keywords: Biosorption, Dye, Fenton Oxidation, Photocatalytic Oxidation, TiO_2.

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Introduction

Dyes or colorant materials are important feedstock of many industries such as cosmetic, textile, paper dyeing, dyeing, drug and food processing [1]. The industrial effluents are generally heavily charged with unconsumed organic molecules such as dyes and inorganic molecules. Depositions of these molecules cause high damage to the environment [2,3]. According to researchers, even small quantities of colorant materials can colour large wetland and can cause reduction of penetration of light and photosynthetic activity [2]. Because of toxic effect of accumulated organic and inorganic substances, removal or degradation of these molecules has been an important task for scientist.

Several physicochemical and biological methods are being used to decompose, degrade or removal of waste effluents, but most of these methods are suffering from ineffective decolourization yield [4]. According to Hsueh et al., the ozonation process can effectively decolorize water soluble dyes, such as reactive dyes [5]. However, ozonation precess is generally lead to inefficient decolourization yields for water insoluble dyes, such as disperse dyes. Water insoluble dyes can be decolorized by coagulation with high yield, but coagulation is ineffective for soluble dyes [5].

AOPs can be thought as a combination of different methods including ozonation, photocatalysis, electrochemical oxidation techniques, Fenton and Fenton-like processes [6]. AOPs are very important techniques for the decolourization of organic compounds of wastewater as a pre- or post-treatment step [7]. The method can also be employed for removal of taste and odor compounds [8]. The techniques are mainly based on the generation of the hydroxyl radical ($OH^{\cdot}$) and generated hydroxyl radical has a great oxidation power and is able to oxidize nearly all organic substances to carbon dioxide and water [7,9,10]. Heterogeneous photocatalysis through illumination of UV on semiconductor surface is an attractive AOPs [11]. In AOPs, Titanium dioxide (TiO_2) is generally used for water and air purification since many environmental pollutants can be degraded by oxidation and reduction processes on TiO_2 [12]. Besides, TiO_2 is relatively inexpensive photocatalyst and has unique characteristics such as a chemically stability, non-toxicity, highly efficiency, and, has been widely used surface [7]. Photocatalytic oxidation processes are usually referred to as AOPs. When a photon with an energy which matches or exceeds the band gap energy of the semi-conductor is incident on a semiconductor surface, a conductive band electron will jump to its valence band leaving a positively charged hole behind [13]. The initial step in this type of photo-oxidation process is believed to be the formation of free hydroxyl radicals [14,15]. Hydroxyl radicals are generated by the oxidation of water (OH⁻ ions) at the valence band positively charged holes.

$$\mathrm{TiO2}(s) + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

$$h^+_{VB} + OH^-_{(TiO_2 surface)} \rightarrow OH^\bullet \quad (2)$$

$$h^+_{VB} + H_2O_{(adsorbed \quad on \quad surface)} \rightarrow OH^\bullet + H^+ \quad (3)$$

$$OH^\bullet + Organic \quad Molecule \longrightarrow Degradation \quad products \quad (4)$$

On the other hand, the dissolved O2 molecules are transformed to anionic superoxide ($O_2^{-\bullet}$) radicals via electrons from conductive band.

$$e^-_{CB} + O_2 \quad (adsorbed \quad on \quad surface) \longrightarrow O_2^{-\bullet} \quad (5)$$

The most commonly studied photocatalysts are TiO_2, ZnO, ZnS and CdS [16]. Additionally, In_2O_3, $SrTiO_3$, SnO_2 and WO_3 have been used as photocatalysts but all showed lower levels of photo-activity [16,17], and SiO_2 and MgO are found to be inactive. The usability of most metal oxides and sulphides as photocatalyst is not feasible due to their irreversible photo-corrosion on the surface for long term treatment processes [18]. Transition metal doping with silver which enhances the interfacial charge-transfer reactions of TiO_2 bulk phase and colloidal particles, can increase the photocatalytic activity of TiO_2 [19].

Another process named 'Fenton method' that is widely used for degradation of both water soluble and insoluble dyes [5]. According to Kim et. al., compared to other oxidation processes, such as UV-peroxide process, operation costs of Fenton method are quite low [20] . Fenton method has been lately and widely used for different chemical compounds because of its ease of operation, requires simple operation systems and the possibility to work in a wide temperatures ranges [20] . Fenton's reagent has been used extensively for oxidation of organic matter in water. The main advantage is the complete destruction of contaminant to harmless compounds, e.g. CO_2, water and inorganic salts [21].

Adsorption has been reported as an effective way for the removal of dye molecules from waste waters [22]. An effective and expensive way of adsorption can be carried out with activated carbon. On the other hand, the operation cost is too expensive with activated carbon when treating high amount of waste effluents. The polymeric materials and resins are also widely employed for treatment of heavily contaminated dye effluents [23–26]. An important drawback of polymeric resins is the consumption of chemicals for the synthesis of adsorbent. Recently, a number of studies were about the removal or decolourization of dyes with using biomaterials [27]. The waste biomaterials such as agricultural wastes, plant materials, fungus and alga were used as sorbent with or without pre-treatment [4,28–31], . The main advantages of using biomaterials as sorbent are the low cost of the process and generally, the easy availability of these materials. Some of the biomaterials have reported that they have excellent exchange capacity [32]. Another important feature of biopolymers is that they generally possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility [33].

The present study consists of two main parts: the first is the decolourization of MB with AOPs (with TiO_2/UV system and Fenton method) and the second is removal of the dye with biosorption process. In second part of the study, the removal of MB was achieved with using alumina and plant gall modified alumina. The modification was easy and the removal percentage was increased significantly with modification of alumina. According to Bağda, plant galls contains huge amount of tannic acid and adjacent hydroxyl group of the molecule assumed as the active binding sides for adsorption process [2,34,35].

Material and Methods

The stock 10 ppm MB solution was prepared in deionized water. The pH of the dye solutions was adjusted with 0.1 mol L^{-1} of HCl and 0.1 mol L^{-1} of NaOH. TiO_2 (Anatase, 99.9%) was supplied by Aldrich chemical company (Surface area of TiO_2 9.35 m^2 g^{-1}). Hydrogen peroxide (33 %) and Alumina (α-Al_2O_3) was supplied from Merck Chemicals (Darmstadt, Germany).

Photocatalytic Decolorization of Methylene Blue

0.1 g of TiO_2 and 100 mL of dye solution were placed in a Pyrex flask with a condenser. pH of dye solution were adjusted to desired level and the stirred solution was irradiated with an OSRAM-Ultra Vitalux 300 W low pressure mercury lamp with a flux output of approximately 5.8 W at about 254 nm. At regular time intervals, an aliquot of 5.0 mL of irradiated samples were withdrawn and centrifuged at 5000 rpm for 10 min to separate TiO_2. The dye concentration was determined spectrophotometrically at 665 nm with Unicam UV 2 spectrophotometer.

Decolourization of Methylene Blue with Fenton Method

Experimental studies of Fenton's method were designed in a sealed flask. In the first stage 100 mL of dye solution and predetermined amount of catalysis were mixed. The pH of the solution was adjusted and H_2O_2 was added in to solution. The solution was stirred with a magnetic stirrer. 5 mL of sample solutions were withdrawn every 30 seconds and the dye concentrations were determined spectrophotometrically at 665 nm.

Plant Material and Modification of Alumina

The plant gall samples were collected from Karaçayır region of Sivas, Turkey. The crude dust of the sample was removed with soaking into water. The wet samples were dried in open air. The samples were granulated and stored in polyethylene bags.

The modification of Alumina was conducted as described below:

5.0 g of Al_2O_3, 0.1 g sodium dodecylsulphate (SDS) and 0.5 g of dried gall sample were triturated well and heated at 50 °C in an incubator. These processes were repeated until the sample was completely homogeneous.

The same processes were done without plant material to obtain non-modified alumina sorbent.

Optimization of Removal Conditions

To obtain high removal efficiency, each experimental parameter was optimised individually. The effects of solution pH, concentration of inert salt, initial concentration of dye, and mass of sorbent were optimized. For removal of MB with gall modified alumina and non-modified alumina, 50 mL of dye solutions were treated with predetermined amount of sorbents after pH adjustment with a multi magnetic stirrer. The final dye concentration was determined spectrophotometrically mentioned above. All absorbance values were recorded after separation of sorbent particles via centrifugation. To eliminate the effect of loss of dye and the effect of any contribution to absorbance because of soluble materials released from sorbent absorbance values were taken against blank solution (without dye) prepared with the same way.

Results and Discussions

The Experimental Parameters that Affect the Photocatalytic Decolourization of Methylene Blue

The pH is an important parameter that affects the photocatalytic decomposition process. The differentiation of surface charge of catalysis as well as the oxidation state of pollutant are generally depend on the pH of the solution. The pH optimization is an unavoidable step for photocatalytic decomposition studies.

The effect of pH on photocatalytic decolourization was studied in the range of 2-11. As can be seen from figure 1a, changing the pH from acidic region to neutral region, the decolourization yield increased. Similar trends were also observed in other studies [36].

At acidic pH, the surface charge of TiO_2 is positive [16], so at highly acidic regions, electrostatic repulsion between cationic methylene blue and partially positively charged TiO_2 molecules might be the reason of low removal yield. According to Bubacz et al., pH has an important role and at more basic pH region, electrostatic interactions between negative TiO^- and methylene blue cation leads to a strong adsorption with a corresponding high rate of degradation. But, at extremely high pH (e.g. pH 11, fig. 1.a), the repulsion between negatively charged moieties of both TiO_2 and methylene blue was the main reason for depression in removal yield. From the figure 1.a. It could be concluded that neutral pHs were the optimum for the photocatalytic decolourization of methylene blue.

The effect of UV irradiation of solution was studied and it can be seen that the in the absence of irradiation the insufficient decolourization yields were achieved. Besides, the insufficient decolourization yields also achieved with using only UV irradiation.As can be seen from the figure 1b, decolourization of dye was significantly higher when conducting the process with both TiO_2 and UV irradiation.

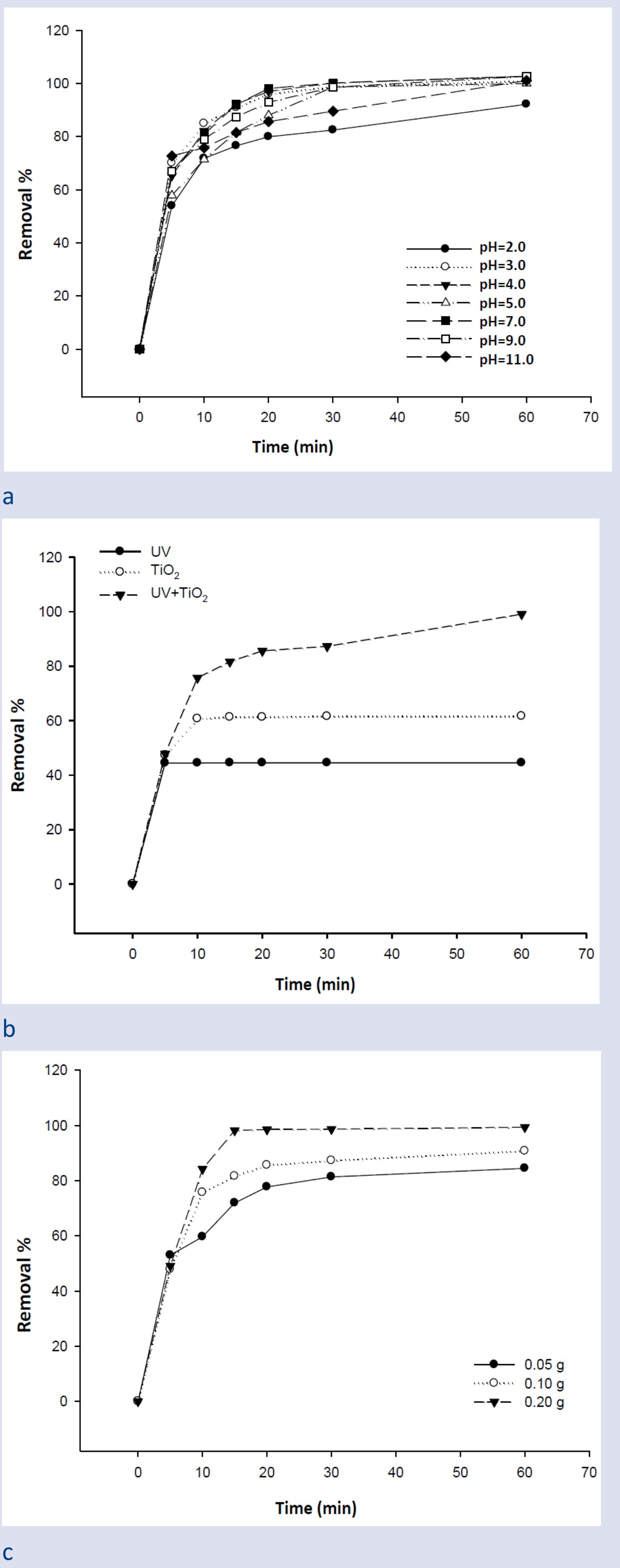


Figure 1. Effect of a. pH, b. UV irradiation, c. amount of TiO_2 on photocatalytic decolourization of MB

The decolourization yield was quantitative and almost 100 % of decolourization was achieved within only 60 min

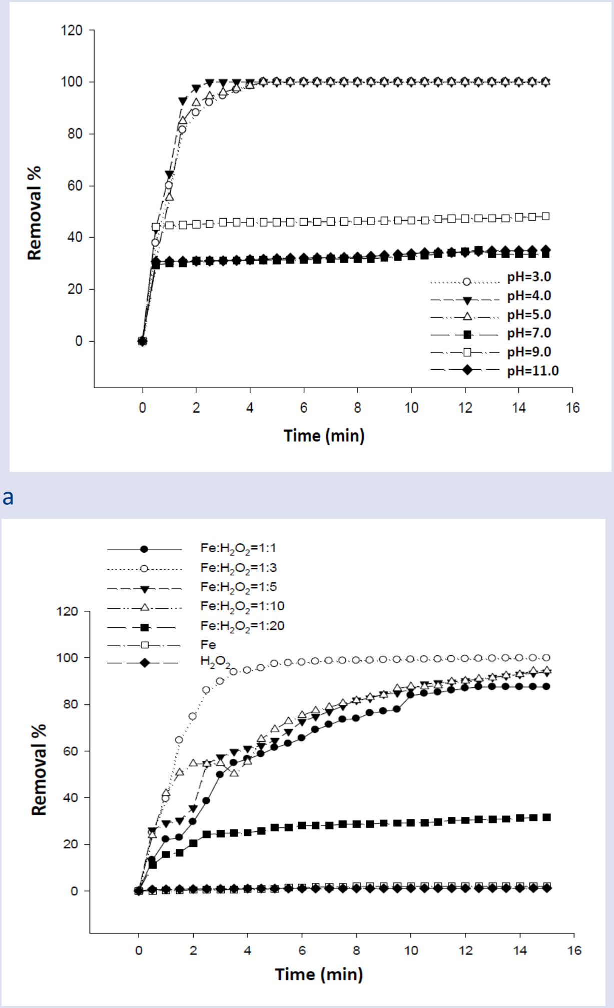
The amount of TiO_2 affects decolourization of MB. It can be seen that, the decolourization degree increased as increasing the TiO_2 amount (figure 1c). As expected, an increase in available surface area was caused by an increase in the amount of TiO_2. So, increasing TiO_2 amount led an increase in the adsorption of dye molecules on to catalysis surface which resulted in an increase in decolourization rate.

The Experimental Parameters that Affect the Fenton's Decolourization of Methylene Blue

The effect of pH on decolourization of MB was studied in the range of 2-11. As shown from figure 2a, the decolourization of dye is higher at especially acidic region. This might be due to the reduction tendency of Fe^{3+} ions to Fe^{2+} ions in the acidic region according to reaction below:

$$Fe^{3+} + e \xrightarrow{\quad\quad} Fe^{2+} \quad E^o = 0.771\ V$$

On the other hand, at alkaline pH ranges, the precipitation of iron species as hydroxides causes low Fenton's decolourization yields. According to Kim et. al, the Fenton oxidation is not applicable in alkaline medium and iron (II) ion begins to form floc and precipitates and hydrogen peroxide is also unstable and may decompose to give oxygen and water, and finally loses its oxidation ability [20].



a

b

Figure 2. Effect of a. pH, b. Fe:H2O2 ratio on Fenton's degradation of MB.

The effect of catalysis to peroxide ratio was investigated in the range of 1:1, 1:3, 1:5, 1:10, and 1:20. As can be seen from the figure 2b, the maximum removal yield was achieved for the ratio 1:3.

Parameters that Effect on Biosorption of Methylene Blue Yields

Adsorption is a cheap and easy alternative way for treatment of organic and inorganic pollutants. With using appropriate adsorbents, high removal of pollutants can be achieved. Due to their widely availability, low cost and high number of functional moieties, biological materials get attentions as alternative adsorbent.

In the present study, alumina and plant gall modified alumina were employed as adsorbent. The parameters which affects the adsorption yield were investigated for high removal yield. The pH is may be the most important parameters that affect the adsorption of a molecule, for example of a dye. The surface charge of both sorbent and dye depends on the pH of solution. In the present study, the effect of solution pH was studied in the range of 2-12.

The pH dependence of dye removal is shown in figure 3a and 3b. As seen from figures, the removal of dye molecules at low pH range is significantly low; the low removal yield may be due to competition between cationic dye molecules with H_3O^+ ions to bind active sides of surface. H_3O^+ ions are smaller, might be more labile and can easily cover the active sides of the sorbent molecules. On the other hand, surface of the sorbent is mainly positive and the main interaction between sorbent and the cationic dye molecule was electrostatic repulsion at acidic region. As increasing the pH of the solution, the removal yield increased significantly as a result of high numbers of negatively charged active sides of the sorbent. At basic region predominant interaction between sorbent and dye molecules might be the electrostatic attraction.

The effect of sorbent amount is generally thought to be elevating factor in an adsorption process. It is generally expected that, the higher the amount of the sorbent, the greater the adsorption is. It is seen from the figure 3c, it is valid for the adsorption of MB to non-modified alumina sorbent. On the other hand, removal yield significantly decreased for the biosorption of MB on to modified alumina as increasing the amount of sorbent (figure 3d). According to Yahaya et al., this unexpected results was due to a process named as 'screening effect'. The higher loading of sorbent protects the binding sides and results in lower removal yield [37].

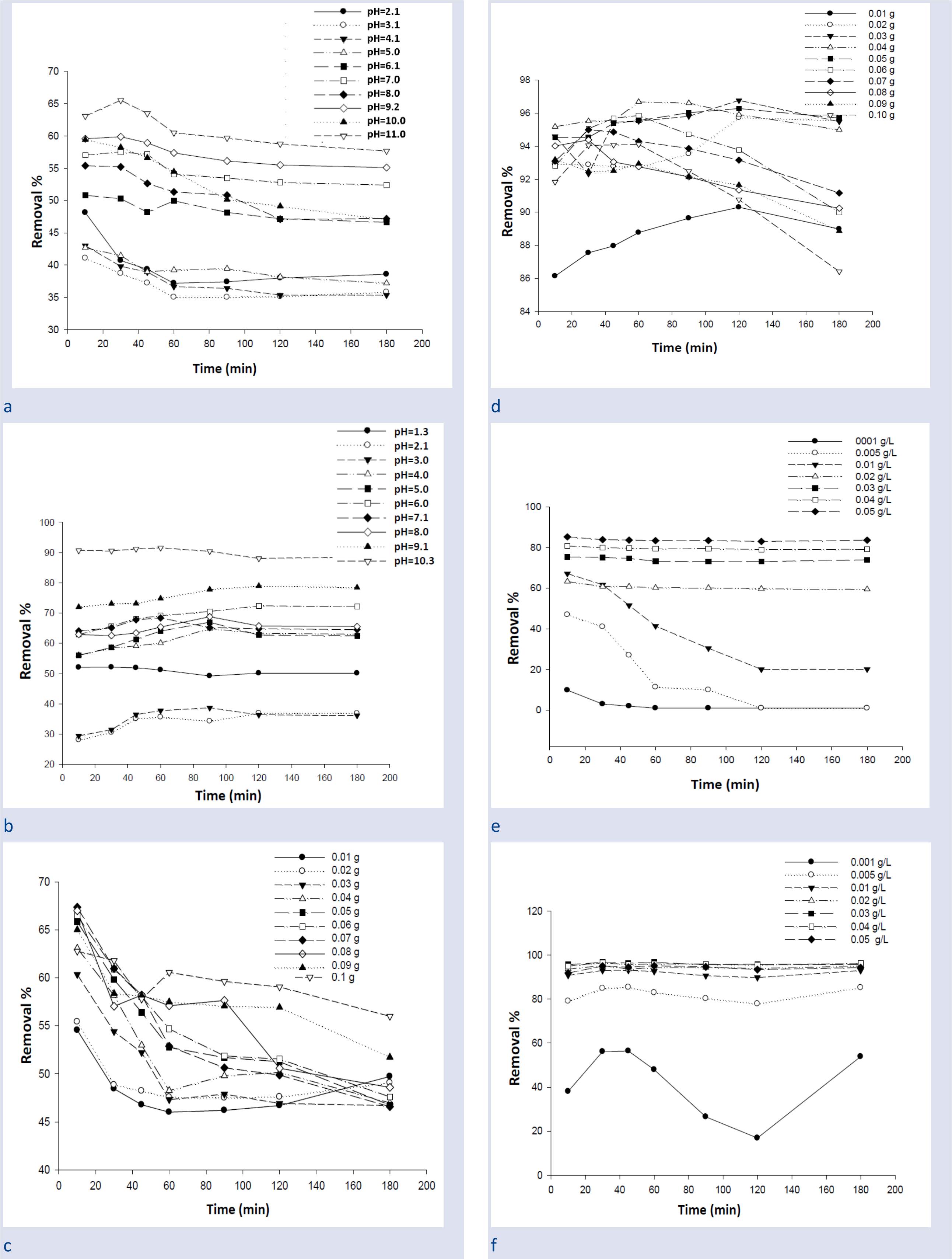


Figure 3 a. Effect of pH on removal of MB with non-modified alumina, b. Effect of pH on removal of MB with modified alumina, c. Effect of amount of sorbent on removal of MB with non-modified alumina, d. Effect of amount of sorbent on removal of MB with modified alumina, e. Effect of initial dye concentration on removal of MB with non-modified alumina, f. Effect of initial dye concentration on removal of MB with modified alumina.

The effect of initial dye concentration was also investigated in the range of 0.001-0.05 g L^{-1}. The modified and non-modified alumina sorbents were equilibrated in various concentration of MB and as shown from figure 3e and 3f, as expected, the removal yield increased, then reached equilibria almost at 0.01 g L^{-1} for modified alumina. On the other hand, the removal yields increased all through the experiments for non-modified alumina. Maximum yield was about 85% for non-modified alumina.

The effect of presence of a salt was studied in the range of 0.01-0.08 mol L^{-1} with using KNO_3. An increase in concentration of the salt is resulted in a decrease (about 15-20 percent for both modified and non-modified alumina sorbents) in the biosorption of the dye (Figure not shown). This might be due to coverage of the active sides of the sorbent with, small, more labile potassium ion rather than dye molecules.

Comparison of studied methods for decolourization of MB

The methods used in the present study have both advantageous and disadvantageous compared to each other. In terms of costs of the processes, required time to achieve high yields, ecological aspects are compared individually and given in Table 1.

Conclusion

In the present study, AOps and biosorption was employed for the efficient decolourization and the significant observations are briefly discussed below.

The effective and significantly higher removal yields were achieved with Fenton process for decolourization of MB. At especially acidic pH ranges, almost 100 % decolourization was obtained. The duration of the process for 100 % decolourization was about 2 minutes. The required time for complete decolourization was significantly shorter than the other studied process. However, in this process a strong oxidative agent, hydrogen peroxide and iron ions were used. This process can lead seconder environmental iron residues. Similarly, biosorption of MB with modified and non-modified alumina can lead seconder sludge. On the hand, biosorption process is thought to be economically quite feasible. The obtained maximum removal yield was above 90 % by modified alumina and was much lower for non-modified alumina. The modification of alumina by a simple modification procedure with an agricultural residue (with a type of plant gall) made the adsorption process more feasible. In photocatalytic decolorization method achieved maximum removal yield is > 98 % with using TiO_2/UV. In terms of ecological seconder residues and economically, TiO_2/UV decolorization method was rather feasible.

As a consequence, it can be said that all the used methods sufficiently capable of decolourization of MB dye solutions.

Table 1: Comparison of studied methods for decolourization of MB.

Method		**pH**		**Amounts of Reagents (g)**							
				$Fe:H_2O_2$		**TiO_2**		**Non-modifiedAlumina**		**Modified Alumina**	
Fenton		4 (~ 100%)	2 min.	1:3(>97%)	5 min.	-		-	-	-	
Photocatalytic		Neutral to basic (>90%)	15 min.	-	-	0.2 (>98)	15 min	-	-	-	
Biosorption	**Modified**	11 (>92%)	10 min.	-	-	-	-	-	-	0.03(> 96%)	240 min.
	Non-Modified	11 (>65 %)	30 min.	-	-	-	-	0.07 (> 67)	10 min.	-	

Conflicts of Interest

The authors declare no conflict of interest

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