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Removal of Methyl Violet from Synthetic Wastewater Using Nano Aluminium Oxyhydroxide

Abiyu Kerebo, Adane Desta and Ramesh Duraisamy
Department Of Chemistry, College of Natural Sciences, Arba Minch University, Arbaminch, Ethiopia

Abstract: Dyes are one of the pollutants and due to their toxicity, carcinogenesis and irreversible the environment and humans. Clean, safe and adequate fresh water is crucial to all living organism and normal functioning of ecosystems, communities and economics. Absorption is an economical and commonly method to uptake of dye. In this study, the nano scale aluminum oxyhydroxide (nano.AlOOH) is used to remove methyl violet from wastewater. Batch experiments were done to investigate the contact time, effect of pH, initial dye concentration and Langmuir isotherm models were used to describe the interaction between the adsorbate and adsorbent.

Keywords: Dye, Pollutant, Wastewater, AlOOH nanoparticles, and Adsorption capacity.

I. INTRODUCTION

1.1 Background of Study

Dyes are organic compound that imparts color to substances such as textile fibre, leather, hair, plastic materials or wax either is solution or dispersion. Man has long known dyes and in the prehistoric time, they were derived from natural plants mainly for coloring the fabric. At present almost all the dyes are manufactured artificially even the natural dyes. The artificial dyes are thoughtfully delimited to have distinctive characteristics such as ability to impart specific color to the substance, resistance to fade when exposed to light, chemicals in washing and resistance towards acids and bases [1]. The groups that modify the ability of chromophores to absorb light are called auxochromes (NO_2, NO, N=N). The part of molecules which provides the color by adsorbing wavelength is called chromophores (OH, NH_2, NHR, NR_2, CI and COOH). Dyes are classified broadly in to two ways either based up on chemical composition or application.

Dyes have a wide range of application and are used as coloring agent for many different substances. There are also used in food industries, printing and leather industries [2]. Recently, dyes have gained popularity in another field that is in hair coloring [3]. The scale and growth of the dyes industry has been inextricably linked to that of textile industry. World textile production has grown steadily to an estimated 35×10^6 tons in 1990 [4].The two most important textile fibers are cotton and polyesters. Methyl violet is a basic dye with high brilliant and intense and is highly used in industries. Molecular structure of methyl violet is shown below. Reports have shown that methyl violet could hinder the growth of bacteria and photosynthesis of aquatic plants [5]. Methyl may be harmful by ingestion, inhalation and skin contact and long term exposure can cause eye and skins.

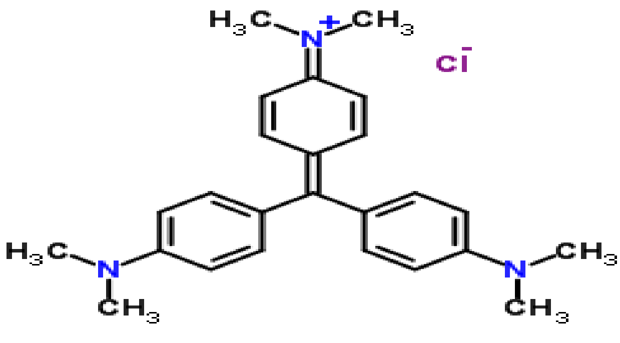

Figure.1 Molecular structure of Methyl violet (MV).

Dyes are mainly classified into cationic, anionic, and non ionic dyes. The removal of dyes is considered as the most challenging task as they are water soluble and produce very bright colours in water with acidic properties.

It has been estimated that the total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and about 10-15% of these dyes are release as effluent during the dyeing processes [6, 7]. These dyes are invariably left in the industrial wastes. Since they have a synthetic organic and complex aromatic molecular structures, which make them inert and difficult to biodegrade when discharged in to waste streams, people overlook their undesirable nature [8]. The presence of even very low concentration of dyes in effluent is highly visible and undesirable. Furthermore, some dyes and their degradation products may be carcinogenic and toxic and consequently they are important sources of water pollutions and their treatment become a major problem for environmental managers. Some dyes are harmful to aquatic life in rivers where they are discharged. Since dye can reduce the light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth [9]. According to Kadirvelu et al. [10] dyes also can cause severe damage to human beings, such as disfunction of kidney, reproductive systems, liver, brain and central nervous system [11].

Industrial wastewater is considered as one of the major pollutants of the environment [12]. Moreover, textiles industries are basic industries among each country's and have colored wastewater due to making use of colored materials [13]. Overall, colored wastewater is produced by various industries such as textile, dying, pharmaceutical, food, cosmetics and health care, paper, and leather industries. Discharging of industrial wastewater containing dyes to aquatic environment can contaminate surface water bodies and ground water. Thus resulting in serious damage to aquatic flora and fauna as dyes may be toxic and mutagenic [14, 15]. One of the major environmental pollution is wastewater. Wastewater pollution gives bad effects on public water supplies which can cause health problem such as diarrhea. one of the major environmental pollution is wastewater. Wastewater is the spent water after home, commercial establishment, industries and public institutions which used water for various purposes. This polluted water comes from the domestic and also from the industries since the increasing of population and industrial expansion. These contaminants such as heavy metal, color and turbidity from the industries [16] are polluting the environment.

Decolourization of waste water has become one of the major issues in wastewater pollution. This is because many industries such as textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries are using dyes to colour their product. Especially, the textile finishing industry has specific water consumption. (approx.1L/kg of product), which is due to dying and rinsing processes [6 of current =10 million kg/year], every year 1-2 million kg of active dyes enter into the biosphere, either dissolved or suspended in water [17]. The removal of dyes from wastewater is considered as an environmental challenge and government legislation requires textile wastewater to be treated, therefore there is a constant need to have an effective process that can efficiently remove these dyes [18]. The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk.

Most of dyes are known to be non-biodegradable. Thus the conventional primary and secondary systems are not suitable to treat these effluents [19]. Some investigations have focused on the development of a treatment process for dye waste water, such as biological and advanced oxidation process. The former method has been found that it may be efficient in the removal of suspended solids and reduction of chemical oxygen demand but is largely ineffective in removing colour from waste water. Many chemical and physical processes for colour removal have been applied including coagulation and flocculation, biosorpition, photo-decomposition and ultrafilitration, oxidizing agents, membrane and electrochemical. The advantage and disadvantage of these techniques have been extensively reviewed [20]. Among these methods, adsorption is widely used because this method requires simple operation procedure, low cost compared to other separation process and no sludge formation. Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants [21, 22]. It is also has been found to be superior to other technique for wastewater treatment in terms of less initial costs, simplicity of design, its higher capacity of adsorption and insensitivity to toxic substance [23].

Nanoparticle research is currently the most studied branch of science with the number of uses of nanoparticles in various fields. The particles have been wide variety of potential applications in biomedical, optical, electronic fields etc. In the last decades, nanotechnologies have developed quickly in various fields and anemometric materials have attracted much attention for their special properties and there has been growing interest in the application of nanoparticles as adsorbents for removal of dyes. Researchers found nano aluminum oxy hydroxide has shown superior adsorption capacity. Aluminum trihydroxide, $Al(OH)_3$, and aluminium monohydroxide (AlOOH) exhibit polymorphism and exist in many structure forms [24]. The structure of aluminium cations located in octahedrally coordinated interstices. The packing of oxygen ions inside the layer can be either hexagonal or cubic; whereas the symmetry of the overall structure for each hydroxide is determined by the distribution of hydrogen. The relative distance between hydroxyl groups, both within and between the layers has been suggested to control the mechanism of dehydration for the particular hydroxide [25].

1.2 Statements of problem

Many studies have been conducted on the removal of either anionic or cationic dyes. However, as a mixture of dyes dose commonly exist together in wastewater, therefore it is of greater interest to have a material that can remove both types of dyes.

Approach: Preparation of an inexpensive and efficient sorbent of nano alumunium oxyhydroxide for the removal of methyl violet from wastewater. Different chemical modifications were preformed on nanoAlOOH and a comparison study about the uptake of dyes was carried out. The experiment selected on the removal of methyl violet from wastewater using nano AlOOH. Therefore, the aim of this study is to assess the removal of methyl violet from synthetic wastewater by using nano aluminum oxyhydroxide (AlOOH). Effect of contact time, adsorbent dose, initial concentration and pH will be investigated. Now-a-days the efficient utilization of nanomaterials to adsorb organic and inorganic pollutants has attracted much attention. So, the manufacturing of metal oxide nanoparticle as AlOOH is the most widely used for the removal of methyl violet from wastewater, owing to superior adsorption capacity, low cost and easy of availability.

This study was aimed the removal of methyl violet dye from synthetic wastewater using adsorption techniques. Also, this study focused to assess the adsorption potential of nano aluminum oxyhydroxide (AlOOH) as adsorbent for methyl violet dyes removal from synthetically created wastewater; to investigate the effect of contact time, adsorbent dose, initial concentration of dye and pH and to establish the adsorption isotherms of methyl violet.

II. MATERIALS AND EXPERIMENTAL METHODS

2.1 Chemicals and Instruments

Reagents used in this studies are analytical grade (AR) supplied by Merck. Other chemicals are used for this study is 40% hydrochloric acid (HCl), sodium hydroxide (NaOH), distilled water, aluminum sulphate ($Al_2(SO_4).14H_2O$. Methods are used for this study UV-vis spectrophotometer, p^H meter.

2.2 Preparation of Nano Aluminium oxyhydroxide (NAH)

Aluminium sulphate (Alum) was used as a starting material for the production of aluminium oxyhydroxide. About 300g of $Al_2(SO_4)_3.14H_2O$ was added into 1500 ml of distilled water and stirred well continuously throughout the day (app.24 hrs.) by using magnetic stirrer taken in 2 litre conical flask until complete dissolution. The resulting lower p^H ($\approx$ 2.7) was adjusted to p^H of 7.00 by adding 2.0 M NaOH. The precipitated aluminium oxyhydroxide was filtered using Whatman filter paper no.41 and dried well in sun light. It is used as adsorbent for this study.

2.3 Preparation of methyl violet solution

Stock solution of methyl violet (500 mg L^{-1}) was prepared by dissolving 0.50 g of dye taken into 1000 mL volumetric flask with double distilled deionized water. It is used as synthetic effluent called adsorbate for the present work. Every trial of experiment was carried out by using a fresh solution of dye effluent.

2.4 Batch adsorption studies [26]

2.4.1 Contact time Variation

Optimization of contact time of dye removal was carried out by adding 5 mg/L NAH used as adsorbent taken in to 250 mL Erlenmeyer flasks containing 50mL of stock dye (methyl violet) solution. This was kept at room temperature and the flasks were agitated (200 rpm speed, about $\approx$ 30 minutes) in an orbital shaker and agitation was continued until equilibrium was reached. The residual dye concentrations were measured upon different contact times (by every ten minutes up to 80 minutes) using UV-visible spectrophotometer at λ_{max} 500 nm. The adsorption at equilibrium, q_e (mg g^{-1}), was calculated using the equation:

$$q_e = (c_o - c_e)V / W$$

Where,

C_o - Initial concentration of dye (mg L^{-1}); C_e - Equilibrium concentration of dye after time; V - Volume of the solution ; W - Weight (g) of dry sorbent

The effect of adsorbent (AlOOH) dose (2 - 9mg/L), and feed solution pH (2-10) of methyl violet were investigated upon similar to the above (session 2.4.1) procedure by varying any one of the parameters and keeping the other parameters as constant with uniform speed of agitation (200 rpm about on $\approx$ 30 minutes). On varying the pH for this study, the pH was adjusted by adding appropriate amount of both 0.1M NaOH or 0.1M HCl solution on before each run and it was measured using pH meter.

2.5 Absorbance measurements

Concentrations of the dye were measured at the wavelength of maximum absorbance (λ_{max}) that was determined by using UV-vis spectrophotometer. The final dye concentration was determined spectrometrically corresponding to λ_{max} of the dye using Beer-Lambert equation:

$$\text{Absorbance} = \mathcal{E}\mathbf{C}_s L$$

Where, Ɛ is the molar absorptive, Cs the concentration of sample and L the thickness of sample tube (1 cm).

III. RESULT AND DISCUSSION

3.1 Effect of Contact time

Effect of contact time on the removal of methyl violet described in figure.1, that shows the concentration of methyl violet adsorbed on AlOOH as a function of time at controlled initial pH. The rate of adsorption slowly increases in the initial stage of the adsorption process and gradually increases later after 10 minutes until end of the run. Thus the results reveal that the adsorption takes place slower rate at initial on the surface of adsorbent. Further the experimental results indicate that the particle has a principal influence on the rate of methyl violet uptake.

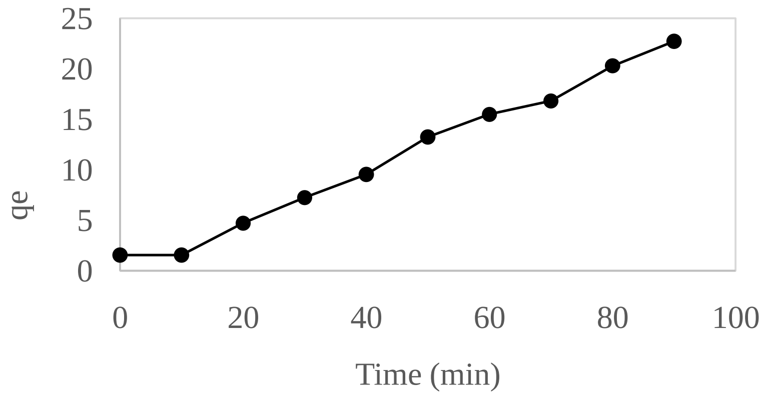

Fig.1 Effect of contact time on the adsorption of methyl violet on AlOOH
(C_o-12.5 mg/L; Weight of adsorbent -0.25g/L)

3.2 Effect of amount of adsorbent

The figure.2 shows that the results on removal of methyl violet from an aqueous medium yield by an increment of NAH. The experiments were conducted by varying the adsorbent doses from 2-9 mg/L at constant initial dye concentration of methyl violet. As it can be seen the results (in figure.2) adsorption of dye get increases with increasing adsorbent dose. This is because for a fixed concentration of dye, while increasing the adsorbent dose provides a greater adsorption sites [27].

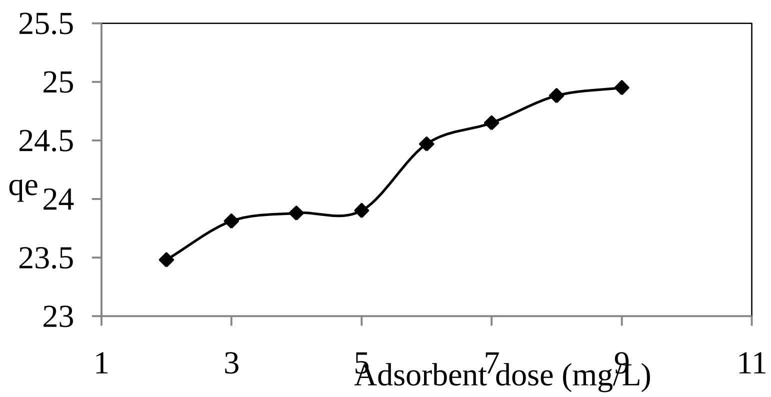

Fig.2 Effect of adsorbent dose on the adsorption of methyl violet (C_o 12.5 mgL^{-1})

The graph indicates that the adsorbent dosage increases proportionality to the availability of the adsorbent sites. The decrease of adsorbent sites and surface area of contact with the dyes decrease the amount of dye uptakes.

3.3 Effect of p^H

The efficiency of sorption is dependent on the pH of the solution [28] because variation in pH leads to the variation in degree of ionization and the surface properties of the sorbent [29]. In view of this, experiments were performed over a pH range 2.0-10, it is revealed that the solution pH does affect the amount of methyl violet adsorption. The dye removal was found to be increase with increasing pH (see figure.3), and also shows the removal efficiency does increasing slowly from 2-3. The maximum removal of dye appeared at alkaline pH.

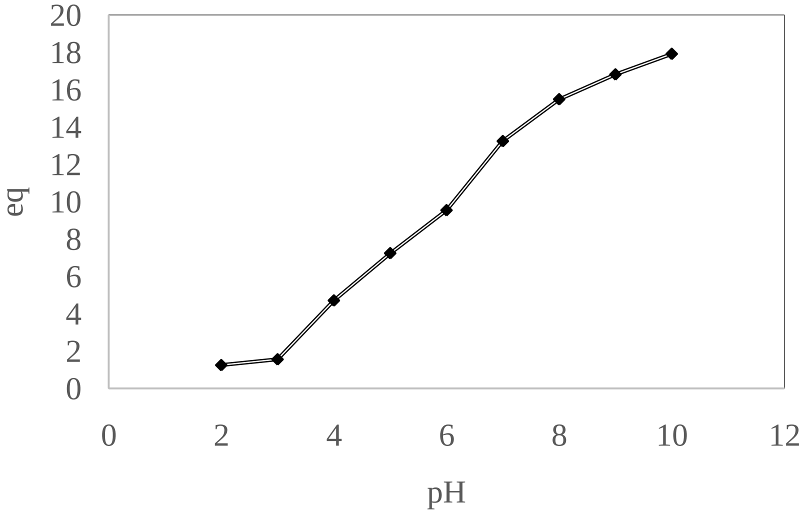

Fig.3 Effect of pH on the methyl violet on AlOOH (C_0 - 12.5mg/g^{-1} and weigh of adsorbent is 0.25 g)

3.4 Adsorption isotherm

Sorption studies describe the interaction of adsorbates with adsorbent and established adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phases and solid phases when the adsorption process reaches an equilibrium state. The interaction between adsorbate and adsorbent is characterized using adsorption isotherm models [30]. Equilibrium data in the present study describes how methyl violet interacts with adsorbent, aluminium oxyhydroxide. The data were modeled by Langmuir isotherm.

3.4.1 Langmuir isotherm model

Langmuir isotherm model assumes the uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. Also there is no transmigration of the adsorbent in the plane of the surface of the adsorbent [31]. On the other hand in the Langmuir model, it is assumed that inter molecular forces decrease rapidly with distance and this leads to the prediction that the coverage of AlOOH was a particular site of the adsorbent is occupied by an adsorbate molecule, no further adsorption takes place at the site. The linear form of Langmuir isotherm equation is:

$$Ce = 1 + 1 - Ce$$
$$qe = Q_0b + Q_0$$

Where, Ce is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b is the Langmuir constants related to adsorption capacity and rate of adsorption respectively.

When, C_e/q_e was plotted against C_e, a straight line with slop of $1/Q_0$ was obtained and shown in figure.4. The value of $Q_0$was determined from the Langmuir plot at the concentration range of 1.25-12.5 mg L^{-1} and then the value of b was calculated to be 0.799.The correlation coefficient of Langmuir isotherm, R^2 is 0.902.

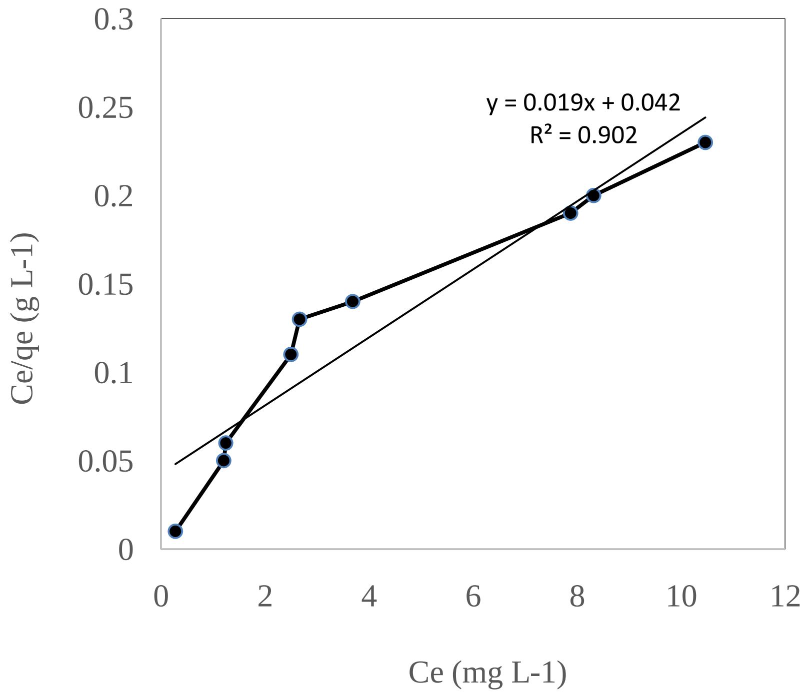

Fig.4 Langmuir isotherm for methyl violet sorption on AlOOH

CONCLUSIONS

The use of aluminium oxyhydroxide for the removal of methyl violet from aqueous solution was investigated. The effect of different parameters such as pH, sorbent dose, contact time and dye concentration was studied. Results showed that AlOOH sorbent can be effectively used as an adsorbent for the removal of dye. Langmuir model is the best model fitted to equilibrium data in this study to describe methyl violet and aluminium oxyhydroxide adsorption system. In addition, the AlOOH nanoparticles showed that much higher adsorption capacity. For dye pollution, reference of this method can be used to remove the dyes from harmful and wastewater and make a safe environment for human life and natural ecosystem.

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