

Effect of Parameters on the Biosorption of Methylene Blue from Aqueous Solution using Charcoal Alginate-Iron Hydrogel Beads

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Abstract: The present study investigated the removal of methylene blue (MB) from aqueous solution by using charcoal alginate-Fe beads. Batch experimental procedure was used for the biosorption study. Biosorption experiments were conducted to study the effect of parameters such as pH, initial concentration and contact time on the biosorption process. The residual concentration of MB after treating with bead was determined by spectrophotometer at 665 nm. The adsorption capacity has been observed to increase drastically with increasing in pH of the solution. At a pH value of 8, the percentage removal of MB from the aqueous solution was found to be 99.5%. The percentage removal of dye decreased with an increase in initial concentration. 99.5% removal was observed with an initial concentration of 20 mgL⁻¹ whereas only 78.8% removal was observed at an initial concentration of 50 mgL⁻¹. Biosorption of MB dye increases with increasing contact time. The results of the present investigation demonstrated that charcoal alginate-Fe beads can be used as an effective and alternative biosorbant for the removal of MB dye from wastewater.

Keywords: Charcoal-alginate hydrogel beads, methylene blue (MB), biosorption, Effect of parameters

I. INTRODUCTION

Environmental pollution is defined as the contamination of air, water and land by human activities. Environmental pollution can take many different forms, such as noise pollution, soil contamination, water pollution, and air pollution [1]. The rate of discharge of pollutants into the environment is far higher than the rates of their purification. Among various environmental pollution, pollution of water resources is very important. The main sources of water pollution include chemical discharges, untreated sewage, petroleum leaks and spills, dumping in old mines and pits and agricultural chemicals that are run off from cultivation fields.

Water pollution has been growingly becoming a pressing issue for the security of water resource in present century. Abuse of water resource and improper management had led to historically high level of pollution of acid, alkali and oxidation in rivers, underground water and nearby sea areas. Among various environmental pollution, pollution of water resources is very important. The main sources of water pollution include chemical discharges, untreated sewage, petroleum leaks and spills, dumping in old mines and pits and agricultural chemicals that are run off from cultivation fields. The World Health Organization (WHO) estimates that 485,000 people die each year from diseases that spread through water [2].

Among the different pollutants of aquatic ecosystem, dyes are a large and important group of chemicals. With 1,000,000 tons produced worldwide, dyes are used in tanneries, food, cosmetic, textile, and medical industries, among other small- and large-scale enterprises. The textile industry is mostly responsible for the emissions of dyes into the environment. Every year, only dyeing industries release roughly 7.5 metric tons [3]. Dyes are widely used in industries



such as textiles, paper, rubber, plastics, cosmetics, etc. These dyes are left in the industrial wastes and consequently discharged mostly in surface water resources. Dyes even in low concentrations are visually detected, and affect the aquatic life and food chain. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight into the stream and reducing the photosynthetic reaction. Due to the large degree of organic compound in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [4].

Methylene Blue is an aromatic heterocyclic basic dye having a molecular weight of $319.85 \text{ g mol}^{-1}$ [5]. It is commonly used for dyeing of silk, leather, plastic, paper, cotton mordanted with tannin and also in manufacturing of paints and printing inks [6]. It finds application in aquaculture as an alternative to malachite green for treatment of fungal infections. In the dairy industry it is used to determine the microbial load in the milk [7]. Although methylene blue is not hazardous compared to other commercial dyes, acute exposure to methylene blue can cause various health issues. MB causes numerous threats to human health such as respiratory distress, gastrointestinal diseases, eyesight, and digestive and mental disorders [8, 9]. It also causes nausea, diarrhea, vomiting, cyanosis, shock, gastritis, jaundice, methemoglobinemia, tissue necrosis, and elevated heart rate, triggering the death of premature cells in tissues and skin/eye irritations [10]. On inhalation, it can give rise to short periods of rapid or difficult breathing (dyspnea), while ingestion through mouth produces a burning sensation [11, 12] potential exposure to methylene blue can also cause hyper tension, pre-cordial pain, dizziness, profuse sweating and hemolytic anaemia [13]. Structure of MB is shown in Fig.1.

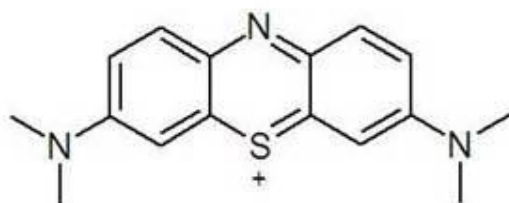


Figure 1: Structure of methylene Blue

Various physical, chemical, and biological methods have been used for the treatment of dye containing wastewater. These methods are extremely expensive or inefficient, especially for large quantity and relatively very low concentrations [14]. Another major disadvantage of conventional treatment technologies is the production of toxic chemical sludge, where its disposal and treatment become costly and often not eco-friendly [15]. These include adsorption/biosorption, phytoremediation, coagulation, electrocoagulation, vacuum membrane distillation, liquid-liquid extraction, ultrafiltration, nanofiltration, microwave treatment, biodegradation, hybrid systems [10]. Among various adsorption techniques, biosorption has been considered as an alternative method with higher efficiency and inexpensive treatment of the hazardous wastewaters. Biological processes such as biosorption, bioaccumulation, and biodegradation have been proposed as potential techniques for the removal of dyes from textile effluents.

Methylene Blue removal from aqueous solutions has been investigated using a number of biosorbents and adsorbents based on nanoparticles. Although biosorbents are readily available and appealing, their practical application is limited by the relatively low adsorption capacities or poor regeneration efficiency of many described materials [16]. Thus, the present study was undertaken to examine the biosorption potential of charcoal alginate-iron beads for the removal of methylene blue (MB) from aqueous solution. Alginates, the main constituent of the cell wall of the brown algae, are reported to have superior ability for heavy metal uptake from contaminated water. Alginate is a linear copolymer composed of (1–4) linked β -D-Mannuronic acid (M) and α -L-Guluronic acid (G) residues. The alginic acid or alginate with monovalent ions is soluble, which limits its application for removing heavy metals. Sodium alginate may be



converted into an insoluble hydrogel by an ion exchange reaction with multivalent metal ions [17]. Various forms of alginate such as beads, films, fibers etc are proven to be efficient biosorbents for detoxifying waste water.

II. MATERIALS AND METHODS

2.1 MATERIALS

All chemicals used were of analytical grade and were obtained from E. Merck India Ltd. Double distilled water and deionized water with a specific conductivity less than $1 \mu\text{Scm}^{-1}$ at 30°C was used throughout the study. The reagents NaOH and HCl (both from E. Merck India Ltd.) were used for making their dilute solutions for pH adjustments.

METHODS

2.2.1. Preparation of alginate gel beads entrapped with activated carbon

About 1g of Sodium alginate was dissolved in 100 ml hot water and stirred vigorously with magnetic stirrer for 10 minutes to obtain a thick uniform solution. It is then mixed with 250 mg of activated charcoal. This mixture was dropped into the beaker, which contains 0.1 M Ferric chloride solution. The beads formed are filtered and dried.

2.2.2. Preparation of methylene blue solution

A stock solution of 1000 mgL^{-1} methylene blue was prepared by dissolving 1g methylene blue powder in 1000 mL of double distilled water. Methylene blue solution for equilibrium studies was prepared using subsequent dilution of the stock solution. The concentration of methylene blue was estimated using spectrophotometer at 665 nm.

2.2.3. Biosorption Experiments

The batch experiments were carried out in 250 mL borosil conical flask and 50 mL of methylene blue solution was mixed with 0.5g of beads and equilibrated them with shaking (200 rpm) at a fixed temperature using a water bath shaker for different duration (20,30 and 50) for separate sample solutions. The filtrate was withdrawn at regular time intervals and the residual concentration of dye was determined by using UV-Visible spectrophotometer at 665nm. The effect of several parameters such as pH, concentration and the quantity of biosorbent on the biosorption of dye was studied. The pH was controlled by the addition of 0.1 M HCl and NaOH. The kinetic batch experiments were performed to examine the uptake of dye from solution.

Percentage removal of dye at equilibrium

$$= (C_o - C_e) / C_o \times 100 \dots\dots\dots (1)$$

The amount of biosorption, $q_e (\text{mgg}^{-1})$ was calculated as follows:

$$q_e = (C_o - C_e) / w \times V \dots\dots\dots (2)$$

Where, $C_o (\text{mgL}^{-1})$ and $C_e (\text{mgL}^{-1})$ are the initial and equilibrium dye concentrations (mgL^{-1}) respectively. V is the volume of the solution (L) and m is the amount of biosorbent used (g). All the experiments were carried out in triplicate and the mean values are presented.

III. RESULTS AND DISCUSSIONS

Methylene blue (MB), a cationic dye, is most commonly used as the colouring agent for cotton, wool and silk. It is also used as a staining agent to make certain body fluids and tissues easier to view during surgery and diagnostic examinations. The medical applications of MB also include the treatment of methaemoglobinemia and cyanide poisoning. In spite of several applications, this dye has a number of negative impacts on human beings and animals; such as irritation of mouth, throat, oesophagus and stomach with symptoms of nausea, abdominal discomfort, vomiting and diarrhoea. Skin contact may cause mechanical irritation resulting in redness and itching. Thus, removal of MB dye from wastewater is of great concern from human and environmental point of view.

3.1 EFFECT OF PARAMETERS ON THE BIOSORPTION OF MB

3.1.1. pH

The effect of pH on removal of MB dye by sodium alginate-Activated charcoal beads are depicted in **Fig.2**.



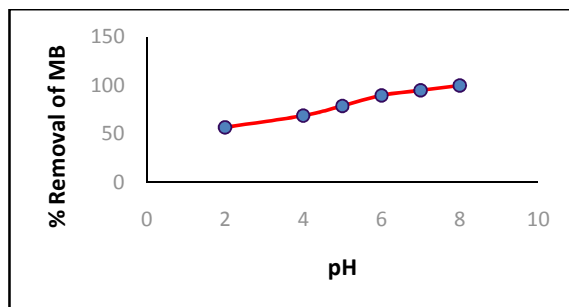


Fig.2: The effect of pH on removal of MB dye by charcoal alginate- iron beads

The adsorption capacity has been observed to increase drastically with increasing in pH of the solution. In acidic conditions (i.e. the lower range of pH), the adsorbent surface has positive charge resulting an electrostatic repulsion with cationic MB dye. With the increase of pH, the adsorption capacity increases due to decrease of repulsive force between adsorbent– adsorbate systems. The finding is in agreement with the existing hypothesis of increasing negatively charged sites/decreasing positively charged sites of adsorbent with increase of pH. pH 8 is selected as optimum pH for this study. At a pH value of 8, the percentage removal of MB from the aqueous solution was found to be 99.5%.

3.1.2. Initial concentration

Effect of initial MB dye concentration on biosorption at 25°C and initial pH 8 is shown in **Fig.3**. The percentage removal of dye decreased with an increase in initial concentration (20, 30 and 50 mgL⁻¹). 99.5% removal was observed with an initial concentration of 20 mgL⁻¹ whereas only 78.8% removal was observed at an initial concentration of 50 mgL⁻¹. This observation indicates that while elevated initial dye concentrations increased the quantity of methylene blue adsorbed per unit mass of biosorbent, the percentage removal remained constrained by the limited availability of biosorption sites. Elevated initial concentrations facilitated more efficient utilization of the accessible biosorption sites, thereby enhancing the overall biosorption capacity [18, 19].

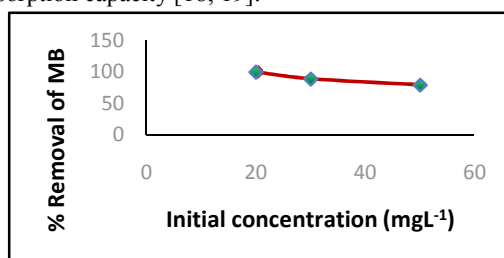


Fig.3: Effect of initial MB dye concentration on biosorption

3.1.3. Contact time

Effect of contact time on the biosorption of methylene blue is shown in **Fig.4**. Biosorption increases with increasing contact time. Usually, the biosorption process occur in two steps: an initial fast step which lasts for a shorter time followed by the slower second phase which continues until the equilibrium reached. Lower adsorption rate at the latter stage may be due to the difficulty faced by the dye to occupy the remaining vacant surface sites because of the force exist between the solute molecules of the solid and bulk phase.



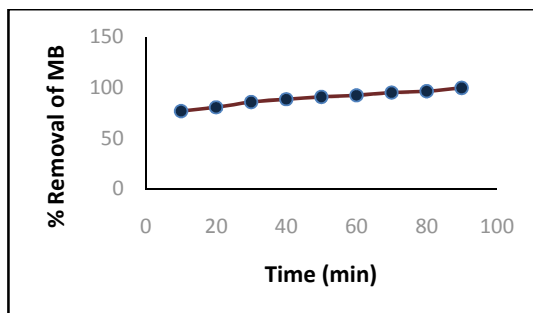


Fig.4: Effect of contact time on biosorption of MB

IV. CONCLUSION

Population explosion and industrial advancements have resulted in a sharp deterioration of several ecosystems, posing serious threats to human health and environment. Several civic bodies have promulgated regulations monitoring the emission of contaminants from industrial waste streams. Among the different pollutants of aquatic ecosystem, dyes are a large and important group of chemicals. It is reported that there are over 100,000 commercially available dyes with a production of over 7×10^5 metric tonnes per year. Dyes are generally believed to be toxic and carcinogenic, or derived from other known carcinogens. Among the several chemical and physical methods used for the removal of dyes, biosorption process is one of the effective techniques that have been successfully employed for the removal dyes from wastewater. The present study focused on the removal of methylene blue (MB) from aqueous solution by using charcoal alginate- iron beads. Batch experimental procedure was used for the biosorption study. Biosorption experiments were carried out to study the effect of parameters such as pH, initial concentration and contact time. The residual concentration of MB after treating with bead was determined by spectrophotometer at 665nm. The results of the present investigation demonstrate that charcoal alginate- iron beads can be used as an effective and alternative biosorbant for the removal of MB dye from wastewater.

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