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Adsorption of Methylene Blue from Textile Effluent by Using Biosolid as Adsorbent

Dr. Sachin Madhavrao Kanawade

Abstract

The mechanism of Methylene Blue adsorption on biosolid (waste sludge) has been studied through batch experiments. The effects of various experimental parameters, such as pH (3-11), biosolid dosage (1-10 g/l), contact time (5-1440 min) and initial dye concentration were investigated. The results showed that the dye removal increased with increase in the initial concentration of the dye and also increased in amount of biosolid used and initial pH. Adsorption data was modeled using the Freundlich adsorption isotherm. The results show that biosolid could be employed effective and low cost material for removal of dyes and colour from aqueous solution.

Keywords: Methylene blue, dye, Freundlich adsorption isotherm

1. Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution^[1]. Many dyes and their break down products may be toxic for living organisms^[2]. Therefore, decolorizations of dyes are important aspects of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems^[3]. Generally biological aerobic wastewater systems are not successful for decolorization of majority of dyes^[2]. Therefore, color removal was extensively studied with physico-chemical methods as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation^[2, 4]. Among these methods, adsorption is a widely used for dye removal from wastewaters^[4, 5]. Granulated activated carbon (GAC) or powdered activated carbon (PAC) is commonly used for dye removal^[5, 6, 7]. However, they are expensive and the regeneration or disposal of it has several problems. Thus, the use of several low cost adsorbents has been studied by many researchers. They have studied the feasibility of using low cost materials, such as waste orange peel^[8]; banana bith^[9]; cotton waste, rice husk^[10]; betonite clay^[11]; Neem leaf powder^[5]; powdered activated sludge^[4]; perlite^[12]; bamboo dust, coconut shell, groundnut shell, rice husk, and straw^[2]; duck weed^[13] and sewage sludge^[14] as a adsorbents for removal of various dyes from wastewaters. Among these materials, adsorption of Methylene Blue (basic dye) was investigated by above mentioned references^[2, 5, 12, 13, 14]. Biological wastewater treatment produces a biological sludge (biosolid) including of inert materials and microorganisms. Return activated sludge (RAS) or waste activated sludge (WAS) can be used for biosorption of dye-contaminated industrial effluents. RAS consists of a variety of living organisms. However, waste activated sludge (WAS) consists of the non-living microorganisms. In this sense, in this study, dewatered nonliving WAS was used after belt filtration. Waste sludge was conditioned with lime before belt-filter. So, filter cake (biosolid) was used for dye (Methylene Blue) removal studies. This study was designed to investigate the effects of sorbent concentration, pH contact time and initial dye concentration on the sorption capacity by using Methylene Blue dye. Freundlich isotherm was performed for interpretation of results.

2. Material and Methods

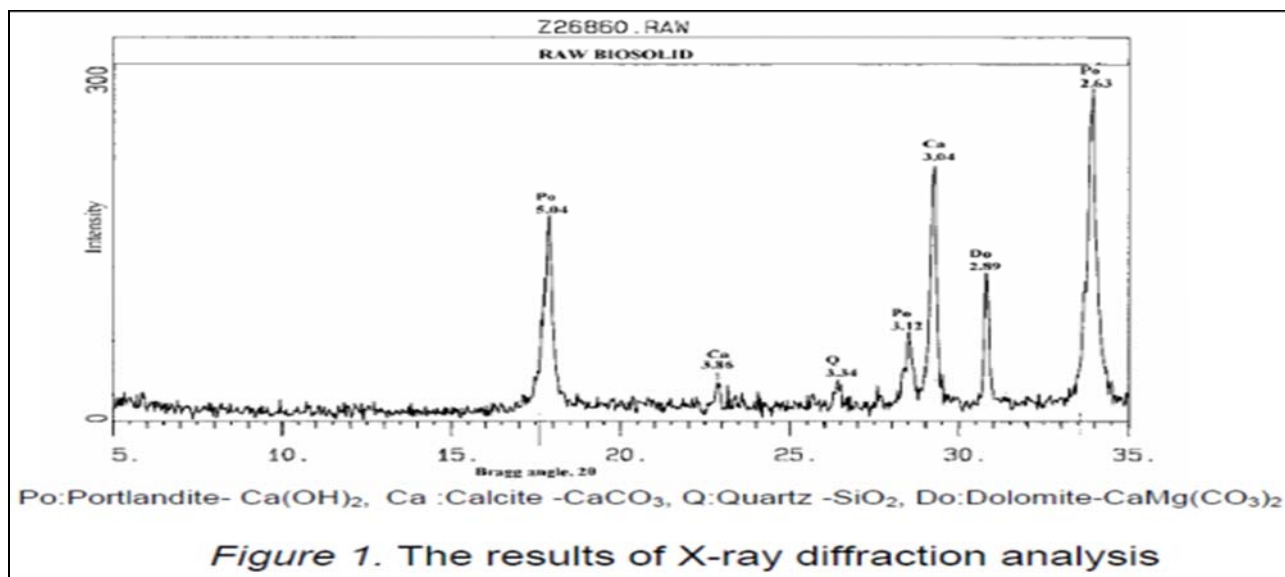
The adsorption experiments were carried out in a batch process by using aqueous solution of Methylene Blue. Variables parameters were initial Methylene Blue concentration, adsorbent amount, contact time, temperature and pH of the medium. Standard solutions containing 50-1000 mg/l Methylene Blue were prepared by dilution of dye stock solution containing 1000 mg/l of metal ion. All experiments were performed by using beakers of 100 ml capacity containing 1-10 g/l of biosolid suspended in 50 ml of dye solution. The initial pH adjustment

Were carried out either by hydrochloric acid or sodium hydroxide solutions before adding the biosolid and was recorded as pH in. WTW (Inolab) pH meter was used for the pH measurements and was calibrated with buffer solutions at pH 4 and pH 7 prior to use. The suspensions were mixed at predetermined periods (5-1440 min) at constant temperature (25 °C) in a shaker at 150 rpm until equilibrium was reached. The solution reaction mixture was centrifuged at 5000 rpm for 20 min and the absorbance of dye solution was determined by The Pharmacia Nova Model spectrophotometer at a 663 nm wavelength, at which the maximum absorbency occurred. The amounts of dye adsorbed were calculated from the concentrations in solutions before and after adsorption.

2.1. Biosolid Preparation

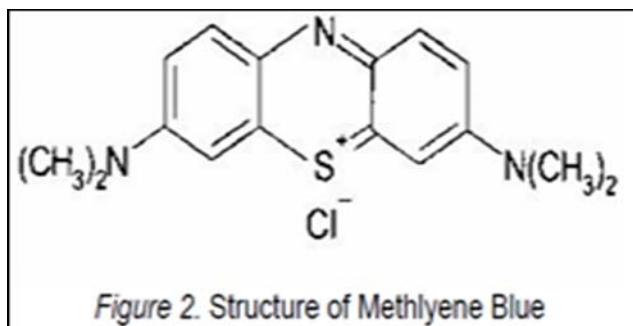
Waste sludge (biosolid) was taken from Cumhuriyet University Wastewater Treatment Plant consisting of

mechanical treatment, activated sludge unit and belt filter press. Domestic wastewater is given to treatment system. Biosolids were collected from belt filter press. The sludge was conditioned with lime before belt filtration. In the experiments, dry ground biosolids were used. The biosolid sample was ground and sieved to 0.0063-0.125 mm particle size and then washed with distilled water to remove any non-adhesive impurities and small particles, and then dried at 103 °C for 24 h to remove moisture. The mineralogical features at samples were determined using Rigaku D Max III C X-ray diffractometer (XRD) in Cumhuriyet University. The results of XRD analysis demonstrated the main minerals to be portlandite and calcite (Fig.1).



2.2. Preparation of basic Dye Solution

Methylene Blue, $C_{16}H_{18}N_3SCl \cdot 3H_2O$, is a cationic dye. It was chosen in this study because of its known strong adsorption onto solids. The structure of this dye is shown in Figure 2. The dye is not regarded as acutely toxic, but it can have various harmful effects.



Basic dye, Methylene Blue, was used without further purification. Methylene Blue was dried at 110 °C for 2h before use. All of the Methylene Blue solution was prepared with distilled water.

The stock solution of 1000 mg/l was prepared by dissolving Methylene Blue in 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.3. Batch Adsorption Experiments

2.3.1. Effects of Initial Dye Concentration

1 g of biosolid as adsorbent with 100 ml of dye solution was kept constant for batch experiments. Initial Methylene Blue solution concentrations of 50, 100, 250, 500, 750, 1000 mg/l were performed at 25 °C on a rotary shaker operated at 150 rpm for 24 h. Then optimum initial dye concentration was identified. The effects of adsorbent, contact time, adsorbent dosage, pH and temperature were conducted.

2.3.2. Effect of Contact Time

In these experiments, initial dye concentration was 250 mg/l. The effect of contact time was investigated for 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 90, 120, 240 and 1440 min at the pH 7 and 1g/100 ml sample dosage.

2.3.3. Effect of Adsorbent Dosage

Initial Methylene Blue solution concentration of 250 mg/l was used in conjunction with biosolid sample of 1, 3, 5, 7, 10 g/l. Contact times and pH were 120 min and 7, respectively.

2.4.4. Effect of pH and Temperature

Initial pH of solution was adjusted to 3, 5, 7, 9 and 11 at optimum condition of dye concentration, biosolid dosage, and contact time. Effects of temperature on the adsorption process were studied at between 25-45 °C.

3. Results and Discussion

3.1. Adsorption Rate

Adsorption rate was investigated using the values of dye adsorbed at different initial dye concentrations, adsorbent dosage, pH and temperatures as a function of time.

3.1.1. Effect of Initial Adsorbate Concentration on Adsorption Process

Initial concentrations of Methylene Blue solutions were changed in order to determine proper Methylene Blue

adsorption keeping the contact time 24 h, pH of 7. Figure 3 showed that the amount adsorbed q_e (mg/g) and percentage removal rate increased with an increase in the dye concentration. However, percentage dye removal rate (99%) was constant after 250 mg/l of Methylene Blue concentration. Therefore, the following experiments were done by considering 250 mg/l of Methylene Blue concentration.

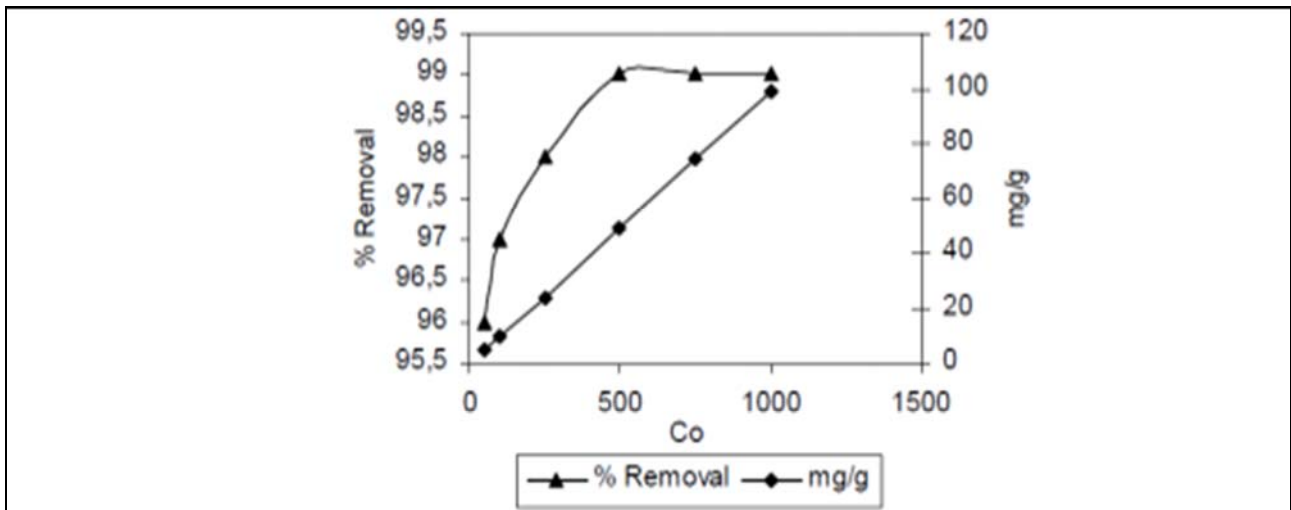


Figure 3. The effect of concentration on the result of Methylene Blue (pH 7, T 25°C, adsorbent dosage 1 g l⁻¹, contact time 24 h)

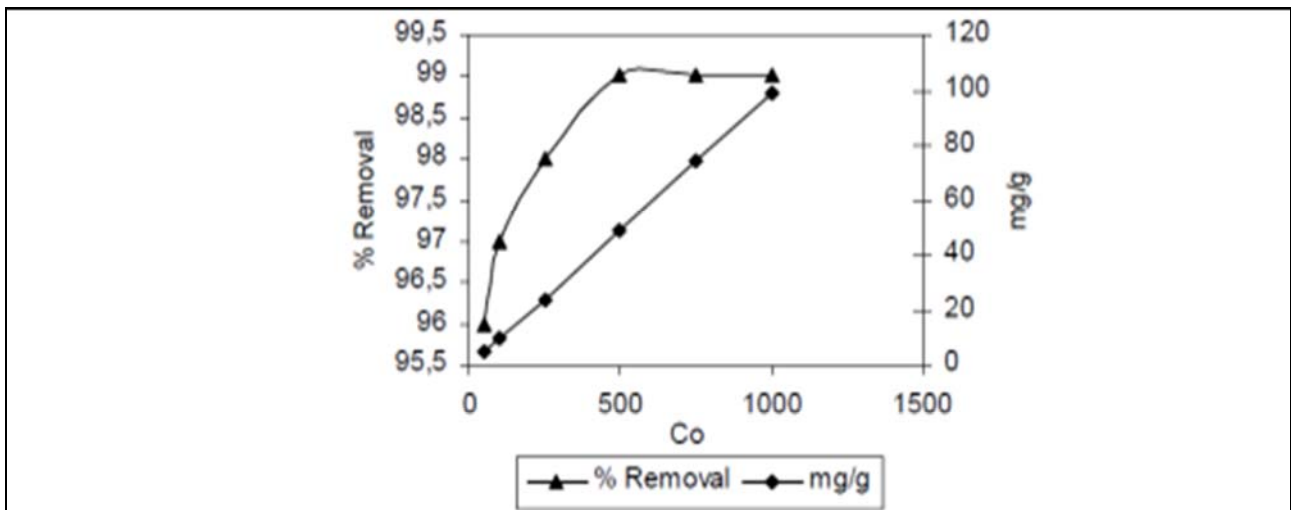
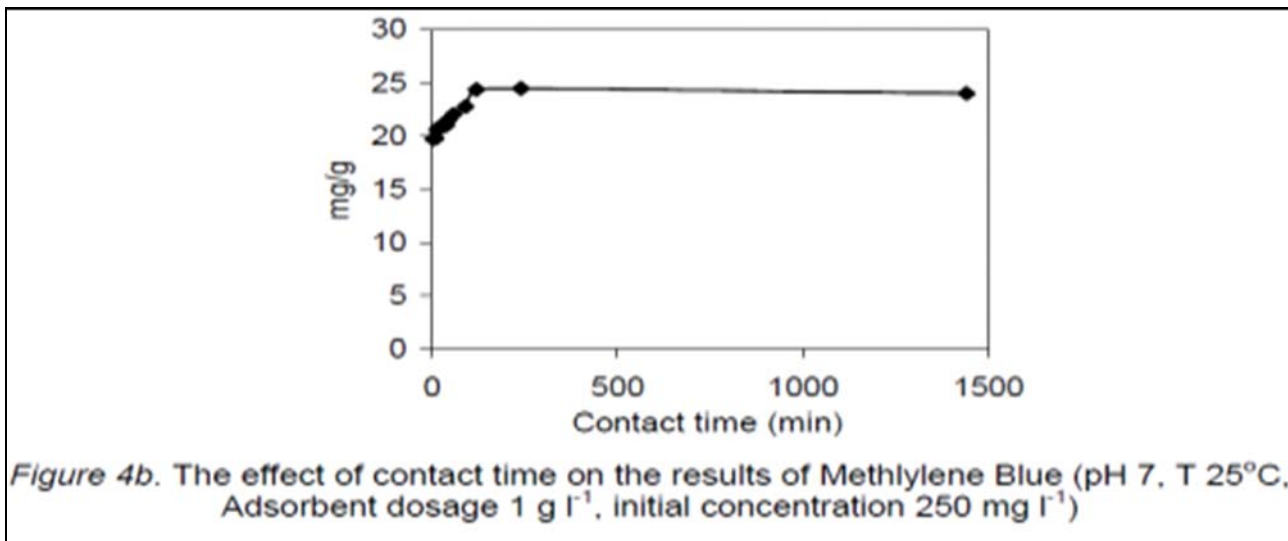
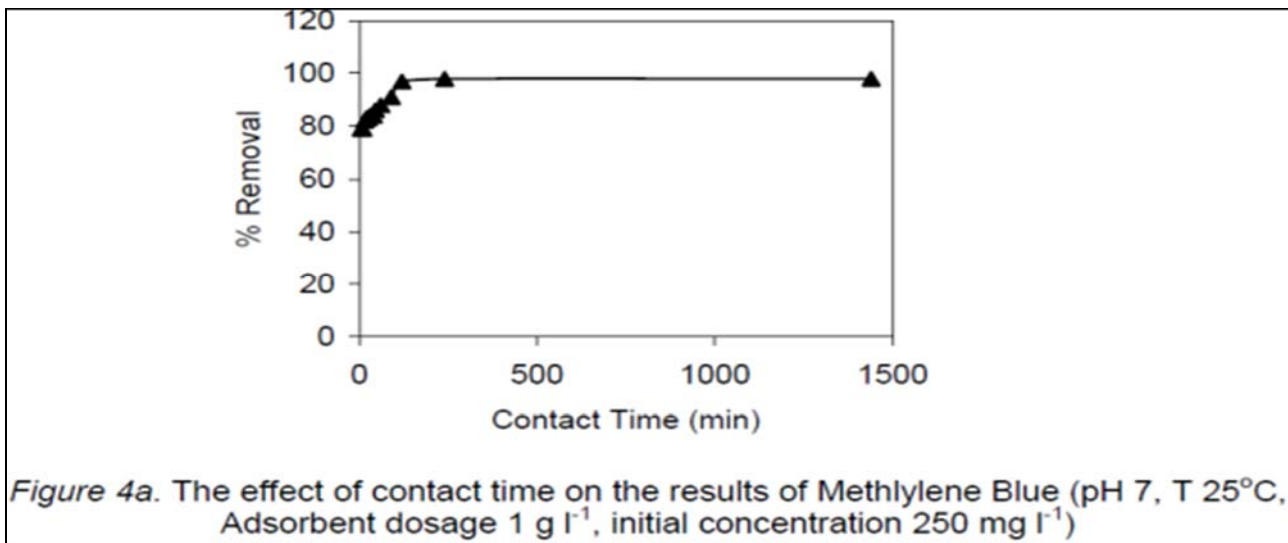


Figure 3. The effect of concentration on the result of Methylene Blue (pH 7, T 25°C, adsorbent dosage 1 g l⁻¹, contact time 24 h)

3.1.2. Effect of Contact Time on Adsorption Process

The effect of contact time on the amount of dye adsorbed was investigated at the optimum initial concentration of dye. The extent of removal (in terms of q_e) of Methylene Blue by biosolid was found to increase, reach a maximum value with increase in contact time (Figure 4a and 4b). In same cases it almost become constant with increase in contact time, after 120 min. based on these results, 120 min was taken as the equilibrium time in adsorption experiments. The removal of

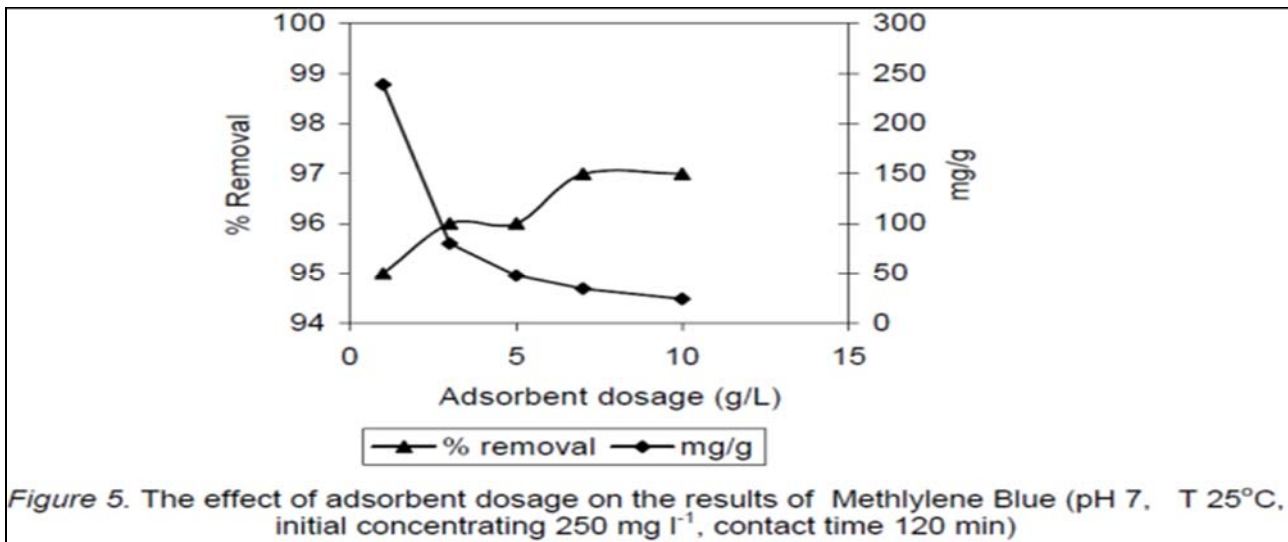
Methylene Blue from aqueous solutions by adsorption on biosolid increases with time, till the equilibrium is attained. Similar results have been reported in literature for removal of dyes [2, 15]. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent [16] and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the adsorbate species from the outer sites to interior sites of the adsorbent particulars [2].



3.1.3. Effect of Adsorbent Dosage on Adsorption Process

The adsorption of dyes increased with the sorbent dosage and reached an equilibrium value after 0.7 g of sorbent dosage (Figure 5). As one was expected, the percentage of dye removal increased with increasing amount of biosolid, however the ratio of dye sorbed to biosolid (mg/g) decreased

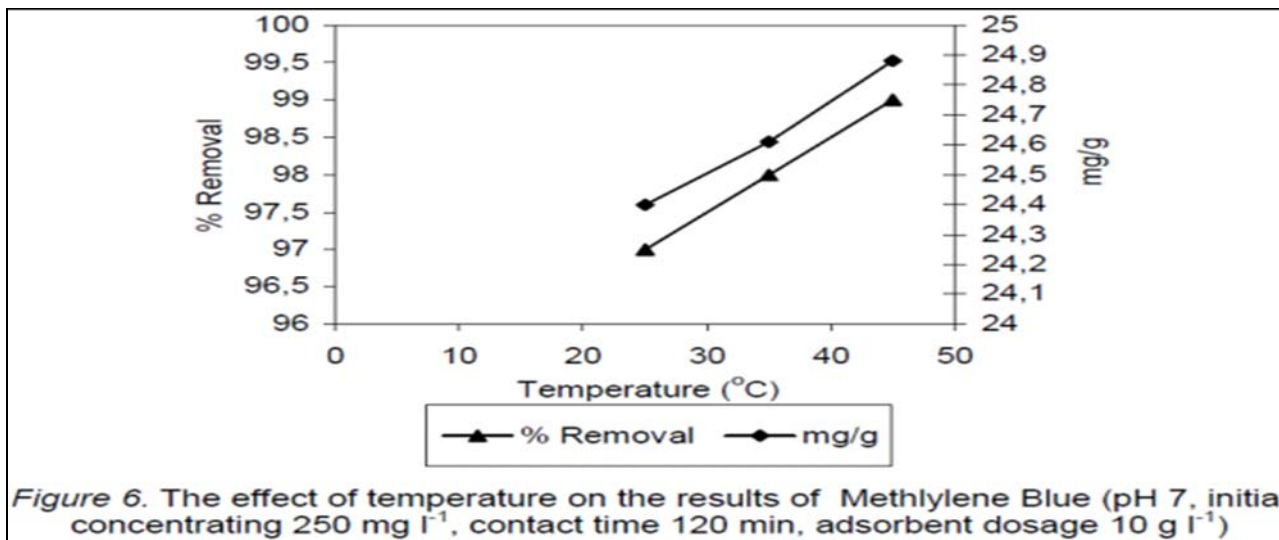
with the increasing amount of biosolid. The ratio of dye sorbent to biosolid was started to reach equilibrium at 0.7 g biosolid. When the biosolid was increased from 0.7 to 1 g, the ratio of dye sorbed to biomass (mg/g) showed no significant change. Thus 1 g of biosolid was chosen for next study on the effect of pH and temperature.



3.1.4. Effect of Temperature on Adsorption Process

Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increase [12]. Changing to temperature will change the equilibrium capacity of the

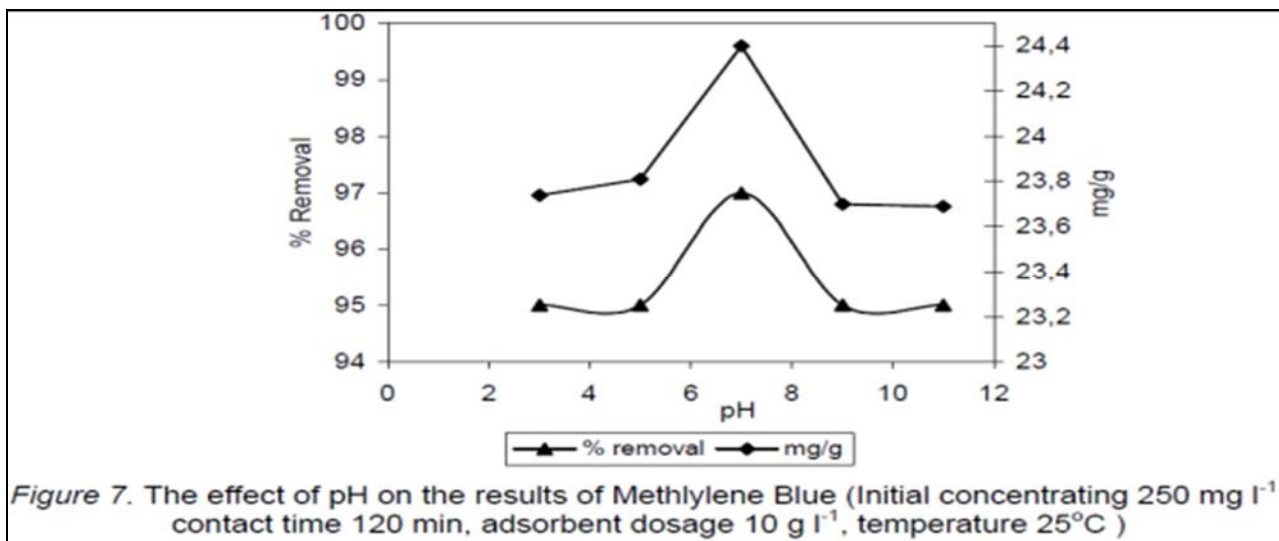
adsorbent for particular adsorbate [12, 17]. Figure 6 shows effects of different temperatures for Methylene Blue adsorption on biosolid. The removal of Methylene Blue by adsorption on biosolid increases slightly from 24.4 to 24.88 mg/g by increasing temperature of the solution from 25 to 45 °C, indicating the process to be endothermic



3.1.5. The Effects of pH

The pH is one of the most important factors controlling the adsorption of dye on to adsorbent. As the pH increases, it is usually expected that adsorption also increases. Fig 7 shows the adsorptions of dye at different pHs (3-11) as a function of reaction time. In this study pH did not importantly effect the

dye removal. However, the maximum adsorption capacity was found as 24.40 at pH 7. Above and under this point, adsorption of Methylene Blue on biosolid tends slightly to decrease. So pH 7 was chosen for the study on adsorption isotherm.



3.2. Adsorption Isotherm

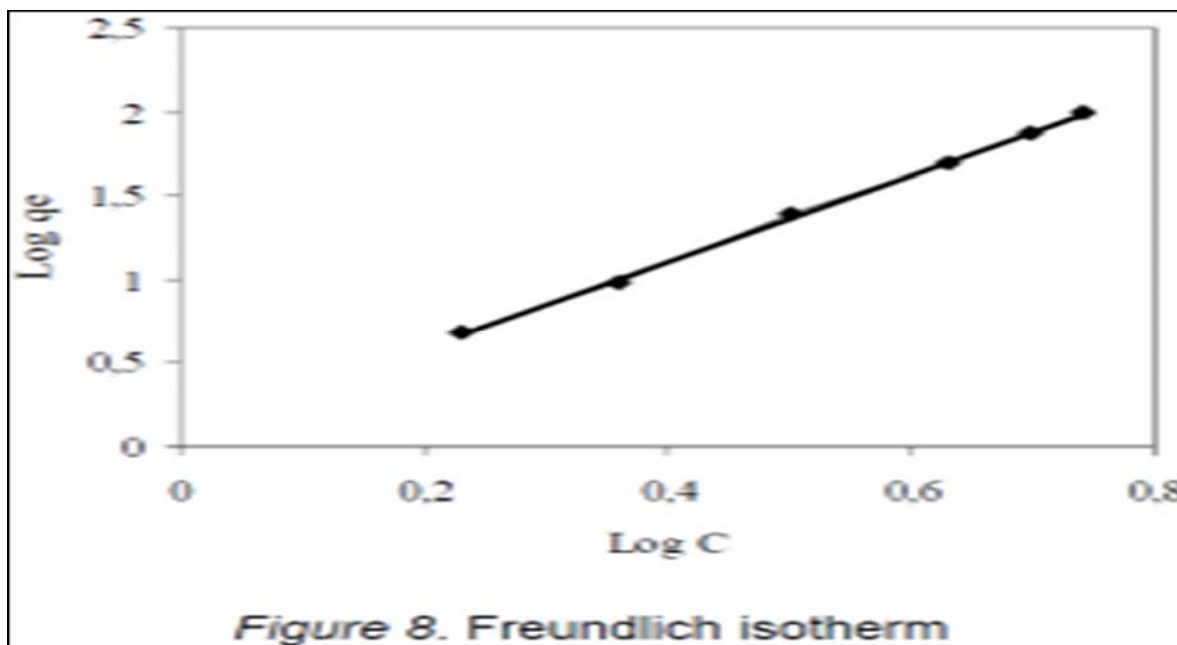
The adsorption data were analysed with the help of linear form of Freundlich isotherm. Freundlich model attempts to account for surface heterogeneity [18].

Freundlich isotherm:

$$\log q_e = \log k_f + (1/n) \log C_e$$

Where log k_f is roughly a measure of the adsorption capacity and 1/n is an indicator of adsorption effectiveness; q_e is the

amount of dye adsorbed per unit mass of adsorbent (in mg/g) and C_e is the equilibrium concentration of dye (in mg/l). The values of Freundlich parameters were obtained from the linear correlations between values of log q_e versus log C_e. The Freundlich isotherm parameters along with the k_f and n were found as 1.21 and 0.39, respectively (R² = 0.999). The Freundlich coefficient, n, which should have values in the range of 0 < n < 1 for favorable adsorption [5, 18].



4. Conclusion

Biosolid is a promising adsorbent for removal of the cationic dye, Methylene Blue from water.

1 g/l of adsorbent could almost completely decolorize solution of Methylene Blue (250 mg/l). The equilibrium adsorption is achieved in 120 min. The solution of pH and temperature did not have important effect on the extent of adsorption of the dye on biosolid, it could be considered that the pH of the medium controlled the adsorption process. The experimental data fit with Freundlich isotherm. The surface of the biosolid particles was heterogeneous, non-specific and non-uniform in nature. The adsorption of Methylene Blue on biosolid was slightly endothermic. This indicates that a temperature above the 25 °C would be favorable for removal of the dye. However, adsorption is quite high even at ambient temperature.

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Dr. Sachin Madhavrao Kanawade was born in 11 March 1978 at Nashik, Maharashtra, India. His native place is Nimgaonpaga, Tal-Sangamneer, Dist-A'Nagar, Maharashtra, India. He received his Bachelor's Degree in Chemical Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Pravaranagar (Loni) which is affiliated to Pune University in India in Nov. 2001. Then he worked as a Production Officer in different Multinational Chemical Industries in India (2001 to 2008) like M/S Watson Pharma Ltd, Ambernath, MIDC, Mumbai, MS, M/S Glenmark Pharmaceuticals Ltd, Mohol, Dist.Solapur, MS, M/S Sun Pharmaceutical Industries Ltd, A. Nagar, MIDC, MS for 7 years.

Then he changes his field. He joined K. K. Wagh College, Nasik, MS, India in 2008 & worked as Lecturer for 2 years. At the same time he received his Master of Engineering in Environmental Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Loni in Dec.2010. Then he joined Pravara Rural Education Society's Sir Visvesvaraya Institute of Technology, Chincholi, Tal-Sinnar, Dist-Nasik, M.S. India in 2010 & worked as Assistant Professor in Chemical Engineering Department for 5 years. In the same period he completed his PhD Degree in Chemical Engineering in session 2011-2014 from Kumar Bhaskar Varma Sanskrit and Ancient Studies University Nalbari, Assam, India.

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Presently he is Reviewer/Editorial Board Member/Advisory Board Member of 64 different International Journals of different fields. He having 21 International Professional Membership of different Organizations

He published 47 Technical Research Papers in different International Journals like International Journal of Wastewater Treatment & Green Chemistry, International Journal of Chemical Engineering, International Journal of Environmental Pollution Control & Management, International Journal of Multidisciplinary Approach & Studies, International Journal of Chemical Engineering & Applications, International Journal of Chemistry & Material Science & International Journal of Engineering Studies and Technical Approach etc.

His research topic includes & interested in Chemical Engineering, Environmental Engineering, Wastewater Treatment by Adsorption, Advanced Separation Process, Chemical Engineering Design, Mass Transfer, Chemical Process Synthesis, Chemical Engineering Thermodynamics etc.