Avrupa Bilim ve Teknoloji Dergisi
Özel Sayı 28, S. 1437-1441, Kasım 2021

Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
Special Issue 28, pp. 1437-1441, November 2021

Research Article

Removal of Methylene Blue from Aqueous Solutions with Fly Ash Based Geopolymer Foam

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(1st International Conference on Applied Engineering and Natural Sciences ICAENS 2021, November 1-3, 2021)

(**DOI:** 10.31590/ejosat.1016237)

ATIF/REFERENCE: Büke, G.B. & Arioz, E. (2021). Removal of Methylene Blue from Aqueous Solutions with Fly Ash Based Geopolymer Foam. *European Journal of Science and Technology*, (28), 1437-1441.

Abstract

Geopolymers are ceramic like materials synthesized by alkali activation of aluminosilicate powder at relatively low temperatures. Geopolymers have excellent properties such as high mechanical strength, high acid resistance, and high fire resistance. Depending on the properties of geopolymers, they have many application fields like adsorption, waste encapsulation, and construction industry. Adsorption is one of the remarkable application areas of geopolymers. Due to the increasing demand for clean water resources, the need for developments in water treatment is also increasing. Geopolymers offer cost effective and environmentally friendly alternatives to adsorbent materials. Many waste materials including fly ash and blast furnace slag can be used to synthesize geopolymeric materials. In this experimental study fly ash was used as raw material and geopolymer foam was produced by using 4 M sodium hydroxide and sodium silicate. Hydrogen peroxide was utilized to obtain foamed material. Fresh geopolymer paste cured at 80°C for 4 hours and then aged at laboratory conditions. Samples aged for 28 days were used in methylene blue removal from an aqueous solution. Adsorption experiments were carried out at laboratory conditions under normal light and under UV lamp in the presence of TiO_2. The concentration of the solution obtained at the end of the adsorption contact time was determined by UV/VIS spectrophotometer at 665 nm. The effect of adsorbent ratio and temperature on removal efficiency and adsorption capacity were investigated. The highest removal efficiency values were obtained as 92% and 83% under UV lamp and normal light, respectively. The results indicated that geopolymers are very promising materials that can be used in methylene blue removal.

Keywords: Geopolymer, Adsorption, Methylene blue.

Uçucu Kül Esaslı Geopolimer Köpük ile Sulu Çözeltilerden Metilen Mavisi Giderimi

Öz

Geopolimerler, alüminosilikat içeren toz halindeki malzemenin alkali aktivasyonu ile nispeten düşük sıcaklıklarda sentezlenen seramik benzeri malzemelerdir. Geopolimerler, yüksek mekanik mukavemet, yüksek asit direnci, yüksek yangın direnci gibi mükemmel özelliklere sahiptirler. Geopolimerler, özelliklerine bağlı olarak adsorpsiyon, atık kapsülleme ve inşaat sektörü gibi birçok uygulama alanına sahiptirler. Adsorpsiyon, geopolimerlerin dikkat çekici uygulamalarından birisidir. Temiz su kaynaklarına olan talebin artması nedeniyle su arıtımındaki gelişmelere duyulan ihtiyaç da artmaktadır. Geopolimerler, uygun maliyetli ve çevre dostu olmalarıyla adsorban olarak kullanılan malzemelere alternatifler sunmaktadırlar. Uçucu kül ve yüksek fırın cürufu dahil olmak üzere birçok atık malzeme, geopolimerik malzemelerin sentezinde kullanılabilirler. Bu deneysel çalışmada, hammadde kaynağı olarak uçucu kül kullanılmıştır. 4 M sodyum hidroksit, sodyum silikat ile karıştırılmış ve uçucu küle eklenmiştir. Geopolimer köpük eldesi amacı ile karışıma hidrojen peroksit ilave edilmiştir. Geopolimer karışımı 80°C'de 4 saat kür edilmiştir ve laboratuvar koşullarında yaşlandırılmıştır. Sulu çözeltiden metilen mavisi gideriminde 28 günlük numuneler kullanılmıştır. Adsorpsiyon deneyleri, laboratuvar koşullarında normal ışık altında ve UV lambası altında TiO_2 varlığında gerçekleştirilmiştir. Adsorpsiyon süresinin sonunda elde edilen çözeltinin konsantrasyonu, 665 nm dalga boyunda UV/VIS spektrofotometre ile belirlenmiştir. Adsorban oranı ve sıcaklığın, giderim verimi ve adsorpsiyon kapasitesi üzerindeki etkisi araştırılmıştır. En yüksek giderim verimi UV lambası altında %92, normal ışık altında ise %83 olarak elde edilmiştir. Sonuçlar, geopolimerlerin metilen mavisi gideriminde kullanılabilecek çok umut verici malzemeler olduğunu göstermiştir.

Anahtar Kelimeler: Geopolimer, Adsorpsiyon, Metilen mavisi.

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1. Introduction

The increase in population and industrialization have caused the pollution of clean water resources. Many pollutants such as dyes, heavy metals, surfactants cause pollution of water resources. The contamination of surface and ground water is harmful to both ecosystem and humans [1,2]. Dyes are widely used contaminants in many industries.

Dyes are widely used in the textile, leather, printing, paper, food, cosmetics, gasoline, pharmaceutical, automotive, and other coloring industries [3, 4]. More than 100,000 different types of dye are produced annually, about 700,000 tons. Many techniques such as adsorption, photodegradation, and membrane separation are used in wastewater treatment [3, 5]. Adsorption is the most widely used technique due to its simple design, ease of use and cost-effectiveness [4]. Photodegradation is the degradation of organic pollutants under UV light [6]. TiO_2 is often used as a photocatalyst because of its chemical stability and non-toxicity [7].

Various adsorbent materials including activated carbon, clay, zeolites, fly ash and geopolymers are used to remove pollutants from wastewater [1, 3]. In recent years, researchers have focused on the production of cost-effective and environmentally friendly adsorbent materials [8].

Geopolymers are low-cost, environmentally friendly materials with superior properties and thermal stability [9, 10]. Geopolymers can be used in many fields such as adhesives, coatings and hydroceramics [11].

Geopolymerization begins with the dissolution of the species exist in the raw material. The dissolved species form a gel phase and condense to form a three dimensional network [12, 13] with the empirical formula: $M_n[-(SiO_2)_z-AlO_2]_n.wH_2O$, where z is 1, 2 or 3; M is an alkali cation such as potassium or sodium and n is the degree of polymerization [14, 15].

Geopolymers, also called inorganic polymers, can be synthesized by both natural raw materials and waste materials [16, 13]. Geopolymers exhibit superior properties and characteristics such as high compressive strength, low shrinkage, resistance to acids, and low thermal conductivity [11]. Waste materials rich in silicon and alumina can be used for geopolymerization. Different raw materials result in geopolymers with different properties, structures and fields of application [17].

Fly ash is a by-product of coal combustion thermal power plant. Fly ash consists of fine particles and is rich in silicon and aluminum. The content of fly ash makes it a suitable raw material for geopolymerization [18]. Worlwide, 780 million tonnes of fly ash is produced annually, but about 17–20% of it is utilized [19].

In this study, fly ash based geopolymer foam was used for methylene blue removal from aqueous solutions. Methylene blue is a cationic dye used primarily used in the textile industry, leather dyeing and furniture coloring [4, 20, 21]. Methylene blue should be removed from wastewater because it is biohazardous and carcinogenic for some marine species [22].

2. Material and Method

2.1. Synthesis of Geopolymer

Class F fly ash was used in the production of geopolymer foam. 4 M sodium hydroxide was added to sodium silicate to obtain the activator solution. The activator solution was poured onto the fly ash and stirred for 5 minutes. Hydrogen peroxide was added to the geopolymer slurry. After mixing, geopolymer foam paste was cast into 4x4x16 mm moulds. The pastes were cured in a laboratory oven at 80°C for 4 hours.

The cured samples removed from the oven were aged for 7 and 28 days under atmospheric conditions. Compressive strength tests were carried out on samples aged for 7 and 28 days. Samples cured for 28 days were crushed and used as an adsorbent for methylene blue removal.

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2.2. Adsorption Experiments

Adsorption experiments were carried out in two groups, under normal conditions and under UV lamp in the presence of TiO_2. A methylene blue solution was prepared at a concentration of 200 mg/L concentration. The amount of geopolymer foam sample ground as adsorbent varied between 0.1 g and 1 g. The effects of temperature (30°C and 40°C) and contact time (1h, 2h and 3h) on the removal efficiency and adsorption capacity were investigated. Photocatalytic degradation experiments of methylene blue were carried out under a UV TiO_2 –catalyzed UV lamp. TiO_2 amount remained constant as 0.5 g in all experiments. At the end of the adsorption experiments, the mixtures were centrifuged and the concentrations of the solutions at the given contact times were determined by UV/VIS spectroscopy at a wavelength of 665 nm. The removal efficiency and adsorption capacity were calculated using the equations given below:

$$\text{Removal Efficiency (\%)} = \frac{C_o - C_t}{C_o} \, x \, 100$$

$$\text{Adsorption Capacity} = q_t = \frac{(C_o - C_t)\, V}{m}$$

where C_o is the initial concentration, C_t is the concentration at given time t, V is the volume of the solution and m is the adsorbent amount.

3. Results and Discussion

3.1. Characteristics of Geopolymer Sample

The compressive strength of the 7-day and 28-day aged samples were measured as 3.1 MPa and 4 MPa, respectively. The FTIR spectrum of the 28-day aged geopolymer sample is given in Figure 1.

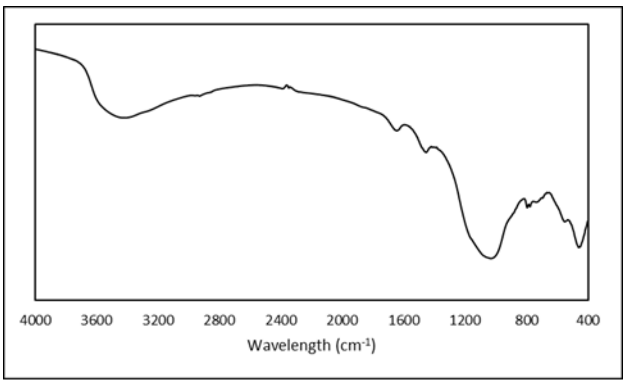

Fig. 1 FTIR spectrum of sample cured for 28 days

The main peak which is the fingerprint of geopolymers observed at about 1000 cm^{-1}, is assigned to the Si–O–Si stretching vibration [23]. Si–O–Si and Si–O–Al (bending mode) vibrations were observed at 470 cm^{-1} [24]. The band seen at 1450 cm^{-1} is attributed to stretching vibrations of C=O confirming the presence of carbonate groups [25]. The broad band seen at 3400 cm^{-1} is associated with –OH stretching, and the band at 1655 cm^{-1} corresponds to H – O – H bending [15].

3.2. Adsorption Experiments

The adsorption experiments were carried out at normal conditions and UV light at 30°C and 40°C with varying adsorbent amount. The removal efficiency percentages obtained at 30°C under normal conditions are given in Figure 2.

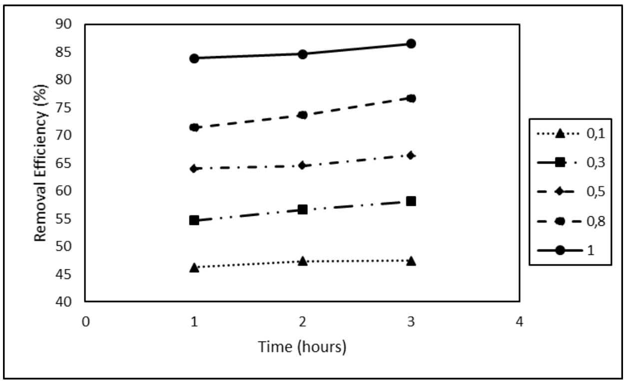

Fig. 2 Removal efficiency values obtained at 30°C

With the increasing amount of geopolymer foam, the removal efficiency percentages increased significantly. The highest removal percentage was obtained as 86.5% in 3 hours contact time when 1 gr adsorbent was used. Contact time did not significantly affect methylene blue removal. The adsorption capacity (q_t) under the same conditions is given in Figure 3.

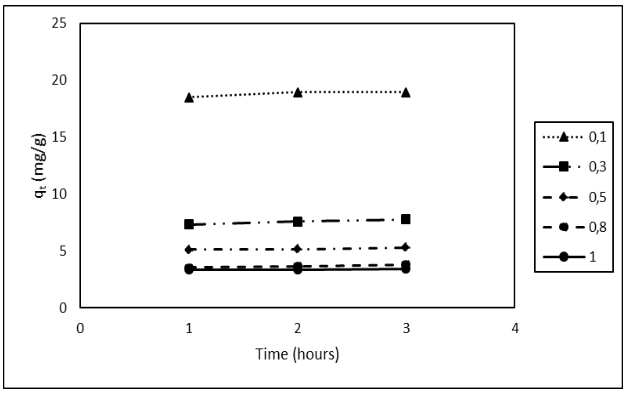

Fig. 3 Adsorption capacity values obtained at 30°C

Adsorption capacity values decreased with increasing amount of adsorbent due to the formula, but the decrease was very sharp when the amount of adsorbent increased from 0.1 g to 0.3 g. The capacities were approximately the same when the amounts of geopolymer foam were 0.8 g and 1 g. The removal efficiencies achieved at 40°C are given in Figure 4.

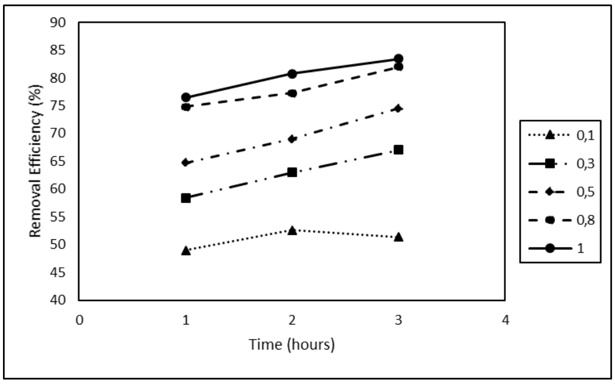

Fig. 4 Removal efficiency values obtained at 40°C

As expected, efficiencies increased with increasing adsorbent amount. The highest removal efficiency was found as 83.5% It was observed that the removal efficiency increased slightly with increasing temperature. The adsorption capacity (q_t) values at 40°C are given in Figure 5.

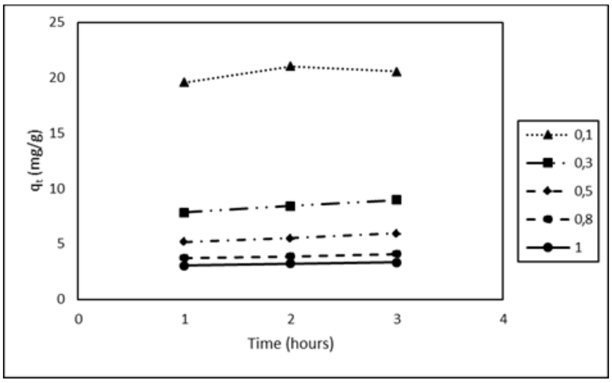

Fig. 5 Adsorption capacity values obtained at 40°C

The change in the amount of adsorbent with the adsorption capacity is the same as at 30°C. The capacities decreased with the increasing amount of adsorbent. Values were almost identical to capacities at 30°C.

Photocatalytic degradation experiments were carried out under UV lamp with a fixed amount of TiO_2 as catalyst. The removal efficiency obtained with 0.5 g TiO_2 at 40°C under UV light are given in Figure 6.

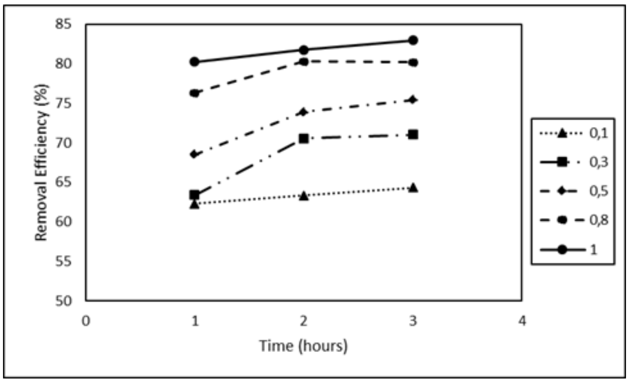

Fig. 6 Removal efficiency values obtained at 30°C under UV light

As the amount of geopolymer foam increased, the removal efficiency values also increased. Compared to the values found in the adsorption experiments performed under normal conditions, the removal values increased under UV light. The increase was low for the removal values obtained for 1 g under normal conditions. Adsorption capacities at 30°C under UV light are given in Figure 7.

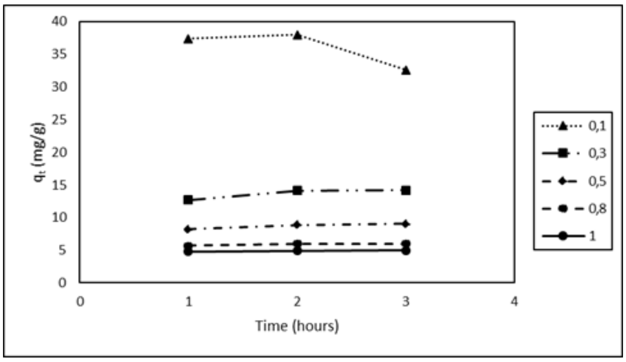

Fig. 7 Adsorption capacity values obtained at 30°C under UV light

As can be seen from the figure, the change in adsorption capacities was the same as found at 30°C, except for the increase in time when increased to 3 h for 0.1 g adsorbent. The values have increased approximately two times over the values found under normal conditions. Removal efficiencies at 40°C under UV light are given in Figure 8.

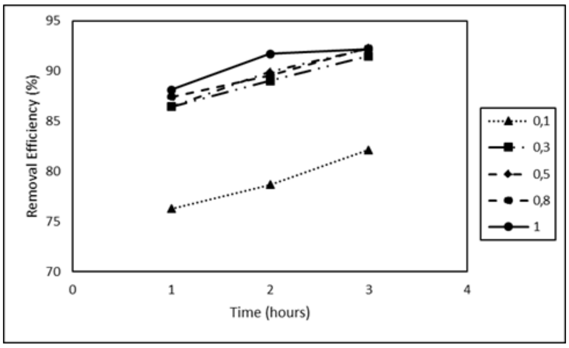

Fig. 8 Removal efficiency values obtained at 40°C under UV light

It is seen from the figüre that the efficiency values are close to each other for adsorbent amounts between 0.3 g and 1 g. The removal efficiency values varied between the lowest 76% and the highest 92% in 0.1 gr adsorbent for 1 hour and at 1 gr adsorbent for 3 hours, respectively. Adsorption capacities at 40°C under UV light are given in Figure 9.

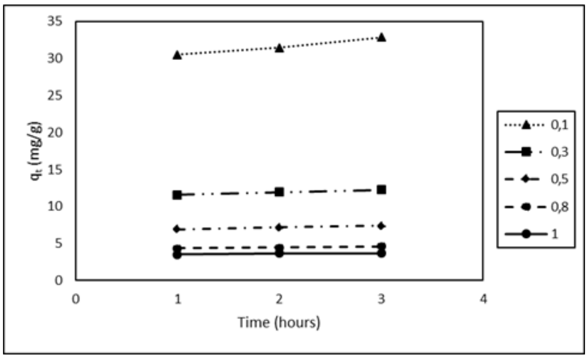

Fig. 9 Adsorption capacity values obtained at 40°C under UV light

Adsorption capacity values obtained under UV light were found to be approximately 2 times higher than those obtained under normal conditions. The highest adsorption capacity was found to be 32.9 mg/g for 0.1 g adsorbent for 3 hours.

Photodegradation under UV light with TiO_2 catalyst and increase in temperature positively affected the removal efficiency and adsorbent capacity. Removal efficiencies increased significantly with temperature under UV light.

4. Conclusions and Recommendations

The results obtained from the experimental study showed that the geopolymer foam was successfully synthesized by fly ash under the specified conditions. Fingerprinting of geopolymers observed in the FT-IR spectrum. The dye removal efficiency and the adsorption capacity values obtained in this experimental study were found to be quite high when compared with the literature [26, 21]. The results were promising, as the removal efficiency and adsorption capacity values were obtained at high values with high initial dye concentration.

The results revealed that the geopolymer foam synthesized in this study can be used for methylene blue removal. Geopolymer foams offer sustainable and environmentally friendly solutions for both the utilization of fly ash and wastewater treatment. Geopolymers can be synthesized under different conditions such as curing temperature and duration, sodium hydroxide ratio and can be studied for the removal of different types of dyes in further studies.

5. Acknowledge

This experimental study was supported by the Eskisehir Technical University research project No: 20ADP197.

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