



A Facile Route for Removal of Reactive Dye Red 195 by Using Geopolymer Based on Bentonite.

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Abstract

The fundamental circulation of life on earth depends on water. Clean water resources have suffered as a result of increased industry and urbanisation. The water resources have been contaminated by a variety of pollutants, including pesticides, heavy metals, and dyes. The most widely used method for removing heavy metals, dyes, and other contaminants from wastewater is adsorption because it is efficient, easy to use, and affordable. In the current work, the possible utility of bentonite based geopolymer as a low-cost adsorbent to remove reactive red 195 dye from wastewater was thoroughly examined. The pH value, duration, geopolymer dose, and dye concentration are the different parameters used to defines the reactive red 195 dye's adsorption mechanism.

Keywords: Reactive dye, Bentonite geopolymer, Slag, Fly ash, Adsorption.

1. Introduction

Water is inadequate for human consumption as a result of limited drinking water supplies and water contamination. Synthetic dyes are among the most significant water contaminants. One of the major consumers of water is the textile industry, followed by the tannery industry [1]. Large quantities of dyes are lost in the effluents during the textile dyeing process which causes a hazardous effect and various diseases on human health [2]. The harmful impacts of synthetic dyes because of containing more organic compounds, extremely poisonous toxicity, and inability to degrade in the environment [3]. Moreover, dye residues lower the amount of light that reaches bodies of water, which decreases the effectiveness of photosynthesis in aquatic plants and prevents them from growing healthily [4,5]. The main categories of synthetic dyes utilized in the dyeing process of fabrics include the azo type, that consist of reactive, dispersion, and acid dye [6]. The first artificial color

to be patented for use in textile dyeing was Reactive Red195 in 1856 [7].

So, it is crucial to eliminate dyes from aqueous systems in order to protect the environment, people's health, and other aquatic life. The removal of dyes from water can be done using a variety of methods, including adsorption, electrochemical treatment, filtration via membranes, progressive oxidation, ion exchange, and chemically precipitating [8]. Along with the effectiveness of treatment that is attained, which differs depending on the method, these methods differ in terms of the unique benefits and drawbacks that they have. These restrictions may be related to the excessive use of chemicals or energy, the production of process wastes, or the development of potentially hazardous byproducts. Due to the capacity to adapt an adsorbent to a specific pollutant and to its high efficacy even for extremely diluted solutions, adsorption represents a general harmless treatment approach with high efficiency [9,10]. Some research has focused on using geopolymers as adsorbent to remove contaminants like metals and

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dyes from aqueous systems because of its porous structure and cation exchange characteristics [11-13]. Geopolymers are amorphous inorganic polymers generated through the polymerization of aluminosilicates, which can be found in geological materials like (kaolin, bentonite, and diatomite) as well as in industrial wastes including (slag, fly ash, red mud, and recycled glass) with alkaline activator agent [14]. Moreover, geopolymer have a comparatively low-cost, green, and straightforward creation [15].

Bentonite (BT) is a naturally occurring substance that mainly made up of the mineral montmorillonite from the smectite group [16]. The montmorillonite has three-dimensional structure with 2:1 clay mineral represented two layers of tetrahedral silica sheets sandwiched a single layer of octahedral alumina [17,18]. The rheological and absorbent characteristics of bentonites are remarkable [19]. Industrial waste by-products such fly ash (FA), granulated blast furnace slag (GBFS), cement kiln dust (CKD), and silica fume (SF) can be used to produce various geopolymers, according to a number of research [20-23]

Granulated blast furnace slag is a particular type of granular substance created by molten blast furnace slag following rapid cooling by water quenching during the blast furnace iron making process. Slag always exists in an amorphous form since minerals have no chance to crystallize in a setting of rapid cooling caused by water quenching [24]. Slag production accounts for 25–50% of iron output and totals over 60 million tons per year. Large quantities of blast furnace slag not only fill many fields, impede traffic, and obstruct waterways, but also significantly pollute the environment [25].

Whereas fly ash is finely fragmented residue resulting from the burning of ground or powdered coal that gets carried by flue gases from the zone of combustion to the particle removal system. FA is considered as an excellent artificial pozzolana due to its high SiO₂ content [26].

The adsorption of wastewater-borne dyes like methylene blue (MB), congo red (CR), methyl violet (MV), and methyl orange (MO) has been effectively accomplished using geopolymers [27-30].

Our goal in this work is to use geopolymer cement based on bentonite to remove the colour of any leftover reactive red 195 dye in the dyeing bath, which correlates with previous work [31-36] that focused on eliminating any residual reactive dyes from dyeing baths. In this study, geopolymer is prepared with bentonite containing either GBFS or FA (30 %). The adsorption characteristics of the two geopolymer on reactive red 195 dye effluent are also examined.

2. Materials and Methods

2.1. Materials

In this work, reactive red 195 dye was used for our investigation. Its chemical structure is displayed in Figure (1).

The aluminosilicate source used in creation of geopolymer are bentonite, slag, and fly ash. Bentonite (Sphinx Milling Station in Alexandria, Egypt) was chosen as the primary component of the geopolymer matrix. In laboratory furnace, bentonite clay is ignited to 800 °C at a rate of 5 °C per minute and soaked for two hours at that temperature. Then it was cooled in the furnace. The appropriate size (less than 200 mesh) is then achieved through grinding followed sieving.

The supplier of fly ash (FA) is Sika Chemical Company in Burg Al-Arab, Egypt. GBFS (Egyptian iron & steel of Helwan Company, Egypt) has surface area of 4700±50 cm²/g.

The alkaline activator used are sodium hydroxide (NaOH) pellets (El goumhouria chemical company, Cairo, Egypt) with 99% purity and sodium silicate liquid (SSL) (Silica Egypt company, Alexandria, Egypt) with SiO₂/Na₂O = 2.80.

The chemical composition of BT, GBFS, FA, and SSL examined by X-ray fluorescence is represented in Table (1).

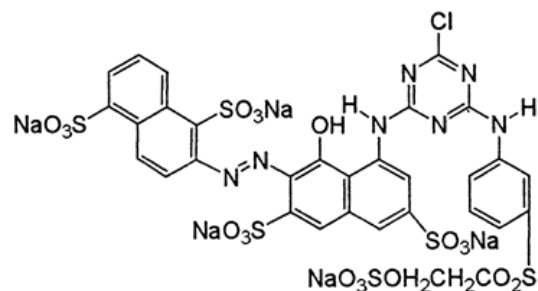


Figure (1): Chemical structure of reactive red 195 dye

Table (1): Chemical composition of raw materials (wt.%)

Oxides	BT	FA	GBFS	SSL
SiO ₂	48.52	63.10	32.86	32.8
Fe ₂ O ₃	18.81	5.40	1.14	--
Al ₂ O ₃	9.68	26.54	7.02	--
Na ₂ O	0.14	--	0.29	11.7
CaO	17.04	2.33	42.56	--
MgO	3.97	0.52	11.58	--
SO ₃	0.07	--	2.5	--
K ₂ O	1.77	0.09	0.15	--
Cl	--	0.85	--	--
H ₂ O	--	--	--	55.5
Total	100	98.83	98.1	100

2.2. Mix design

Two bentonite geopolymer was synthesized by two different additives (slag, fly ash). Each of them was added by 30 % to bentonite. The liquid to solid ratio (L/S) of geopolymer pastes BS1 and BF1 were 0.5, 0.39, respectively. The mix proportion are shown in Table (2).

2.2.3. Preparation of geopolymer

Firstly, in order to prepare the alkali activator, NaOH (12 M) was added to a sodium silicate liquid (water glass) and stirred till dissolved with sodium hydroxide/ water glass ratio (1:2.5). The activator must be cooled before use because the process of dissolution was exothermic. Then the alkaline activator was added to raw materials according to mix proportion in Table (2). The geopolymer mixes was transferred to cubic stainless-steel mold of 5 mm x 5 mm x 5 mm and cured at 70 °C for 24 hours. The cubes were demolded and placed in a 100% relative humidity for seven days.

2.4. Adsorbent preparation

After 7 days, the samples were crushed and added to solution of ethanol/acetone (1:1) on an electric magnetic stirrer for 30 minutes to stop hydration. To remove the surplus alkali liquor, the residue is filtered, repeatedly washed with HCl, and distilled water and then dried for 24 hours at 50°C. Materials were sieved, and ground to a mean particle diameter of 100 µm before being kept in a desiccator.

Table (2): Mix proportion of designed mixes

Mix name	BT	GBFS	FA	SSL/NaOH ratio	L/S ratio
BS 1	70	30	--	2.5	0.50
BF1	70	--	30	2.5	0.39

2.5. Dye preparation

The reactive dyestuff was hydrolysed by adding a 3 mL/L sodium hydroxide solution (33%) and a 5 g/L sodium carbonate solution and heating them at 80°C for two hours while stirring. After cooling, the hydrolysed dye was neutralised with weak sulfuric acid [37].

2.2. Methods

2.2.1. Adsorption experiments

The investigation of the reactive red dye 195 adsorption behavior was performed on the bentonite geopolymer under various adsorption circumstances.

In the pH range of 2.0 to 8.0, the influence of pH on the adsorption efficiency was examined. Furthermore, the geopolymer dosage was diverse from 0.05 to 0.5 g/30mL. Regarding the study on contact time, the samples were examined at various period (30, 60, 180, and 360 min.). Ultimately, the

impact of initial concentration of reactive red 195 dye effluent was studied at (56, 75, 113 and 136 mg/l).

A UV spectrophotometer (Spectrophotometer V-670) is used to measure the concentration reactive red 195 dye effluent. The dye removal rate (removal efficiency) (R, %) and adsorption capacity (q_e, mg/g) were calculated according to equations (1) and (2), respectively [38, 39].

$$\text{Removal efficiency } R = (C_0 - C) / C_0 \times 100 \quad (1)$$

$$\text{Adsorption capacity } q_e = (C_0 - C) V / W \quad (2)$$

C₀ (mg/L) indicate the initial concentration of dye, C (mg/L) refer to remaining concentrations of the dye at equilibrium. V (L) donates the volume of solution and W (g) is the geopolymer weight.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the reactive red 195 dye effluent adsorption efficiency of the bentonite geopolymer pastes is shown in Fig. (2). The adsorption capacity is illustrated in Table (3).

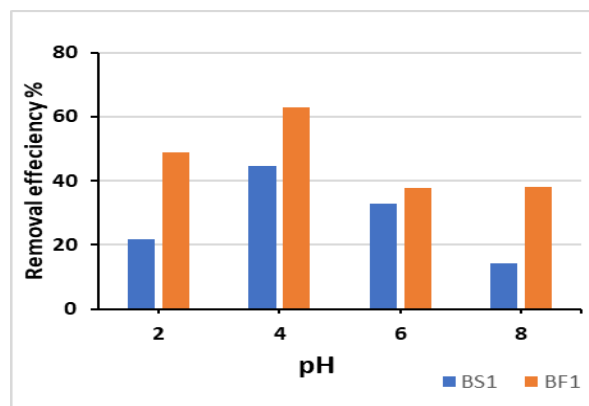


Figure (2): The removal effectiveness as a function of pH

Table (3): The adsorption capacity of BS1 and BF1 geopolymer mixes

Mix name	pH=2	pH=4	pH=6	pH=8
BS1	7.32	12.00	11.10	14.20
BF1	16.50	21.30	12.78	12.90

The results showed that the removal efficiency of BS1 is increases with increase pH level up to 4 and then decrease. Similar behaviour is observed for BF1. The maximum removal efficiency of BS1 and BF1 is 35.4, 62.8 % respectively at pH=4. Moreover, the removal characteristic of BF1 mix is more powerful than BS1 mix. The adsorption capacities of two mixes are increase and reach to maximum at pH=4 and then decrease.

Therefore, pH 4 is chosen for the next investigation.

3.2. Effect of dosage

The variation in reactive red 195 dye effluent removal efficiency% while using different adsorbent dosage (at pH=4) is displayed in Fig. (3).

For BS1, as the amount of adsorbent increase from 0.05 to 0.5 (g/30ml), the removal efficiency increases. However, the removal efficiency of BF1 mix increase with increasing dosage up to 0.3 (g/30ml) and then decrease with further increase in dose.

The adsorption capacity of mixes is decrease gradually as the adsorbent dosage increases as shown in Table (4).

Table (4): The adsorption capacity of BS1 and BF1 geopolymer mixes

Mix name	0.05 (g/30ml)	0.1 (g/30ml)	0.3 (g/30ml)	0.5 (g/30ml)
BS1	30.3	12.0	6.6	5.7
BF1	52.3	21.3	10.8	6.1

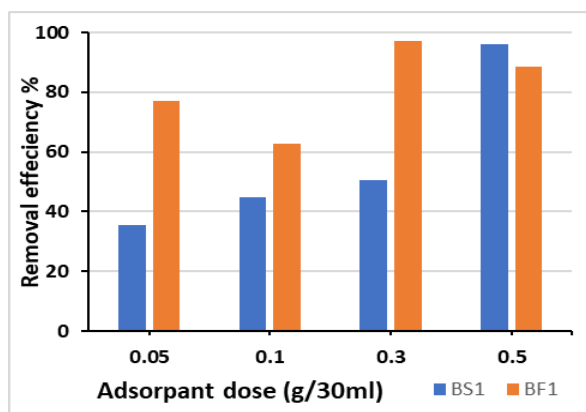


Figure (3): The removal effectiveness as a function of adsorbent dose

3.3. Effect of time

The ideal time for reactive dyes to interact with the bentonite-based-geopolymer mixesis also evaluated. The removal efficiencies and adsorption capacity of mixes at different time intervals are illustrated in Fig. (4) and Table (5), respectively. The rate of removal efficiency increased sharply at first 60 min. and then decreased at 360 min. The same behaviour is represented for two mixes. The maximum adsorption obtained at 60 min. for both BS1 and BF1 is 95.9 and 97.2, respectively. As the contact time increase, the adsorption capacity increased up to 60 minutes. However, increasing time to 360 minutes leads to decrease in adsorption capacity.

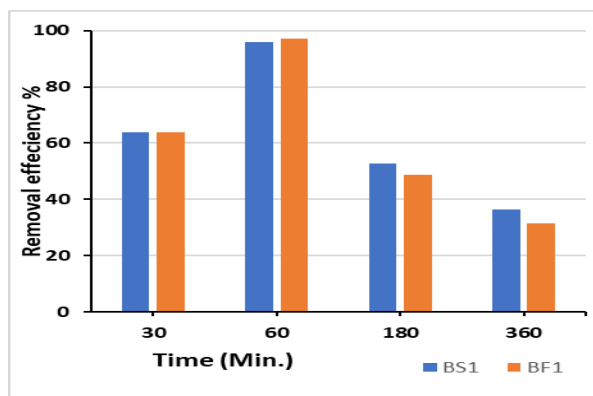


Figure (4): The removal effectiveness as a function of contact time.

Table (5): The adsorption capacity of BS1 and BF1 geopolymer mixes

Mix name	30 Min.	60 Min.	180 Min.	360 Min.
BS1	4.3	5.7	3.5	2.5
BF1	7.2	10.8	5.5	3.6

3.4. Effect of initial concentration of reactive red 195 dye

Figure (5) demonstrates the relationship between dye concentration and removal effectiveness (%) at fixed weight of the two mixes using both the ideal pH (4) and the ideal duration (60 min.). Maximum removal effectiveness is achieved for both BS1 and BF1 at a dye concentration of 113 mg/l.

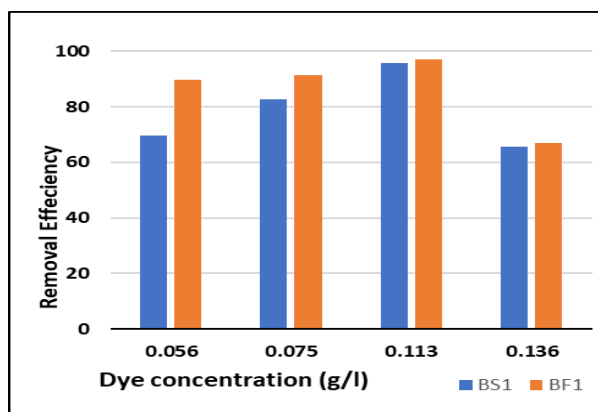


Figure (5): The removal effectiveness as a function of dye concentration

The adsorption capabilities of several geopolymer mixtures are shown in Table (6). The adsorption capacity of BS1 and BF1 raised with slow growth rate with the increasing initial concentration of dye to 113 mg/l and then slightly decreased.

Table (6): The adsorption capacity of BS1 and BF1 geopolymer mixes

Mix name	56 mg/l	75 mg/l	113 mg/l	136 mg/l
BS1	2.8	3.1	5.7	5.3
BF1	5.1	6.7	10.8	9.1

4. Conclusion

The purpose of the current study is to examine the reactive red 195 dye adsorption behaviour of bentonite-based geopolymer incorporated with 30% of each slag and fly ash and to suggest a method to enhance dye removal efficiency. The maximum removal efficiency of geopolymer mixes BS1 and BF1 is 95.9 % and 97.2 % respectively, which is achieved at pH 4, at an initial dye concentration of 113 mg/L after 60 min for both geopolymer mixes. On the other hand, the adsorbent dose giving maximum removal efficiency was 0.5 g/30 ml for BS1 and 0.3 g/30 ml for BF1. In general, the adsorption effectiveness of BF1 is greater than that of BS1.

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