



Decolorization of Reactive Dyes, Part II: Eco-Friendly Approach of Reactive Dye Effluents Decolorization Using Geopolymer Cement Based on Slag

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Abstract

We carried out this study in order to reduce pollution rates by treating the water produced from dyeing operations using reactive dyes, by removing the color from the liquid wastes of yellow 145 using two different types of slag-based geopolymer. The factors affecting the decolorization were optimized according to various parameters such as the dose of adsorbents, treatment time, at different pH and dose of the dye used.

Keywords: Reactive dyes, Geopolymer, Slag.

1. Introduction

Cement and concrete are broadly used in building and construction material in the world. Manufacture of Portland cement consumes huge amounts of energy and raw materials and emits a lot of CO₂ which responsible for global warming. Global annual cement production is predicted to be 5.9 billion tons with more than 4.8 billion tons CO₂ production by 2020[1]. The alkali activation of waste materials has become an important area of research because of the possibility for using industrial wastes like ground granulated blast furnace slag (GGBFS), fly ash and metakaolin, to convert them to useful environmental friendly, inexpensive, technologically advantageous cementitious materials with the added advantages of low carbon-dioxide emissions[2,3]. Geopolymer was described by Davidovits [4] as a type of amorphous alumino-silicate cementitious material which prepared from natural aluminosilicate or industrial by-product such as metakaolin, fly ash and ground granulated blast furnace slag. It is produced by the alkali activation of aluminosilicate raw materials by polymerization in presence of high pH environment. The polymerization reaction includes the formation of three-dimensional polymeric chains by Si-Al minerals to form a ring structure which consist of Si-O-Si bonds [5]. These binders may resolve the

problems of construction industry. Geopolymer cements GPC reduces 80% CO₂ and is more economical and at the same time uses industrial/agricultural wastes [1,6]. Pozzolanic materials must contain of siliceous or a combination of siliceous and aluminous material in a very finely divided form, and they react with calcium hydroxide in the presence of moisture at ordinary temperatures, to form compounds have comparable performance to ordinary Portland cements OPC. Several studies suggested that various industrial waste materials have been used as a source of alumina and silica for the preparation of geopolymers[1,7,8]. Ground granulated blast furnace slag (GGBFS) is a pozzolanic material and can be identified as a by-product obtained in the manufacture of pig iron in the blast furnace and is formed by the combination of iron ore with limestone flux. GBFS used as a base material consists of aluminosilicate raw material that can be activated by alkali hydroxide and silicate. Alkali activation of slag leads to a reaction product similar to calcium silicate hydrates (C-S-H) gel (a major product of OPC hydration)[7]. Many researchers examined the incorporation of slag with industrial waste products such as fly ash (FA), cement kiln dust CKD and silica fume SF [9 – 12]. Geopolymers can be used in different applications

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Receive Date: 20 June 2022, Revise Date: 22 June 2022, Accept Date: 22 June 2022.

DOI: [10.21608/ejchem.2022.146015.6355](https://doi.org/10.21608/ejchem.2022.146015.6355).

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such as refractory and heat resistant coatings and adhesives, pharmaceutical applications, new adhesives for refractory fiber composites, removal of toxic and radioactive waste, and new cement materials for concrete. Recently, geopolymers have become one of the important adsorbents due to their low cost, simple preparation, and their unique three-dimensional network structure, with fixed-size pores that can be used to remove pollutants (such as dyestuffs and hazardous materials) from the environment [13]. Recent studies have suggested the use of geopolymer cements as adsorbents for the removal of different types of dyes [14-16]. The high demand for dyes for the textile industry over the last decade indicates that they are likely to be toxic substances. It is estimated that about 30-40% of the dye remains in the waste water during the dyeing process. The most common dyes are reactive dyes because they have many advantages such as stable structure, bright color and function under mild conditions. Various physical and chemical decolorization processes such as adsorption, precipitation, oxidation, coagulation, reduction, electrolysis, and membrane extraction are used to remove the dye [17-25]. The ideal process for treating small amounts of wastewater is the adsorption process [26-35]. The aim of this study is to remove the color of the reactive yellow dye 145 residual in the dyeing bath instead of dumping this hazardous waste without treatment by using slag-based geopolymer cement as a new approach that is environmentally safe and inexpensive.

Materials and Methods

2.1. Materials

Reactive yellow 145 was utilized for the decolorization studies. The structures of this dyes is shown.

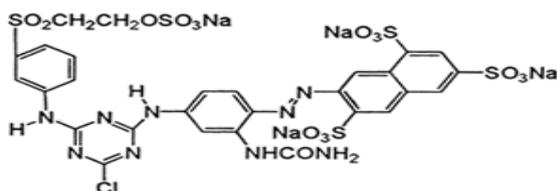


Figure 1. C.I. Reactive Yellow 145

2.2 Preparation of Hydrolyzed Reactive Dye

Hydrolysis of the reactive dyestuff was accomplished by the addition of 3 mL/L sodium hydroxide solution (33%) and 5 g/L sodium carbonate and heating under stirring for 2 h at 80°C. Finally, the hydrolyzed dye was cooled and neutralized with dilute sulfuric acid [28].

2.3 Adsorbent preparation

2.3.1 Starting materials

- Ground granulated blast-furnace slag (GGBFS) and fly ash (FA).

- The alkaline activator in this study was sodium hydroxide (NaOH) and liquid sodium silicate (Na₂SiO₃).

- Ground granulated blast furnace slag is obtained from the Egyptian iron & steel of Helwan Company. The chemical oxide composition is given in Table (1).

- Fly ash (FA) is supplied from Sika Chemical Company, Burg Al-Arab, Egypt. Its chemical oxide composition is given in Table (1).

- The NaOH flakes are obtained from EL-Goumhouria chemical company, Cairo, Egypt with purity 99%. Commercial liquid sodium silicate (LSS) is obtained from Silica Egypt Company, Burg Al-Arab, Alexandria, Egypt.

- The chemical composition of liquid sodium silicate is 11.7 wt% Na₂O, 32.8 wt% SiO₂, and 55.5 wt% H₂O and silica modulus SiO₂/ Na₂O equal 2.80. The chemical compositions of the starting materials are given in Table (1).

2.3.2. Geopolymer Synthesis

Preparation of specimens:

Each of the considered additives (GGBFS and FA) are firstly mixed thoroughly in the dry state to attain complete homogeneity. The composition of the various mixes in addition to, the water/solid ratio which gave standard consistency and setting times are given in Table (2).

S & SF1 samples are prepared by using 100% GGBFS and mixing it with 10% of Fly Ash respectively as shown in Table (2).

In the first the alkali activator (AA) is prepared by mixing sodium silicate liquid (SSL) and sodium hydroxide pellets (SH) then stirred them, initially the temperature of the mixture was quite high then left few minutes to reach to room temperature before the proceeding. Then by the addition of different mixing ratio of alkali activator solution to each dry mix and mixing them on a smooth and non absorbent surface for about 5 minutes. After complete mixing we confirm the water consistency of the geopolymer pastes by standard Vicat apparatus. Then the pastes are put in stainless steel moulds of one-inch dimension (cubic-shaped molds); the moulds are kept under relative humidity 100% for the first 24 hours to attain the final setting and getting hard. After molding the cubes demolded and kept under relative humidity 100% for 7 days of hydration.

2.4. Methods of Investigation

2.4.1. Water of consistency:

The standard water of consistency are determined according to ASTM specification using VicateApparatus [38]. The quantity of liquid required to produce a paste of standard consistency

will be that required to give a paste permitted the settlement of the vicat plunger (10 mm in diameter) to a point 5 to 7 mm from the bottom of the vicat mould.

2.4.2. Stopping of hydration

The cubes which subjected to be tested is took and crushed then put in the stopping solution consists of ethanol / acetone (1:1 by volume), the mixture is left on electrical magnetic stirrer for 30 minutes. The residue is filtered and washed with ethanol and then is dried at 50 °C for 24 hrs. Then dried samples were ground to obtain a mean particle diameter of 100 μ m and stored in a desiccator.

2.5 Adsorption experiments

Specific amount of the adsorbent were shaking at 30 oC and 140 rpm with 100 mL of dye solution. The supernatant of the samples solutions were separated by filtration. Absorbance at maximum wavelength ($\lambda_{max} = 475$ n m for yellow 145 dye) using SHIMADZU spectrophotometrically was estimated and computing concentration from the calibration curve. The amount of dye adsorbed onto the adsorbent, q_e (mg/g) was calculated by mass balance relationship.

$$q_e = (C_o - C) V/W \quad (1)$$

Where C_o , is initial dye concentrations (mg/L); C , is the equilibrium liquid-phase concentrations of dye (mg/L); V the volume of solution (L) and W the weight of the adsorbent (g).

$$\text{Removal efficiency\%} = 100(q_e / C_o) \quad (2)$$

3. Results and discussion

3.1. Characterization of the adsorbent

The chemical compositions of the starting materials and various mixes in addition to, the water/solid ratio of prepared geopolymer pastes were listed in tables 1 and 2.

Table (1): Chemical oxide composition of starting materials by XRF, mass%.

Oxides, %	GGBFS	FA
SiO ₂	32.86	63.10
Al ₂ O ₃	7.02	26.54
Fe ₂ O ₃	1.14	5.40
CaO	42.56	2.33
MgO	11.58	0.52
SO ₃	2.50	----
Na ₂ O	0.29	----
K ₂ O	0.15	0.09
Cl ⁻	----	0.85

L.O.I	0.93	----
Total	99.03	98.83

Table (2): Mix composition of the investigated mixes and liquid/solid (L/S) ratio.

Mix No	Mix Name	GGBFS	FA	Na ₂ SiO ₃ %	NaOH %	L/S ratio
1	S	100	----	15	10	0.43
2	SF ₁	90	10	15	15	0.53

3.2 Factors affecting on the adsorption

3.2.1 Effect of pH

The change in the removal efficiency % when using the dye effluent of reactive yellow 145 dye under the pH of the adsorption bath is illustrated in Figure 2. In order to determine the optimum pH value of the geopolymer mixes treated dye was carried out at different pH (2-10). The results from Figure 2 show the following firstly that with all of the dyebaths effluents, the removal efficiency % increases with increasing pH up to extreme values and then decreases. Secondly, for the dye effluent of reactive yellow 145 dye, the maximum removal efficiency % was at pH 5 when using geopolymer mix S and pH 3 when using geopolymer mix SF₁, which reached its maximum value at 27.9% and 29.1%, respectively.

3.2.2 Effect of adsorbent dose

It is of value to mention here that figure 3 shows the effect of adsorbent concentration on the removal efficiency %. The adsorption of the dye under study was examined with different concentrations (0.01 – 0.2 g/100 mL) of the different geopolymer mixes, for 120 min for using the dye effluent of reactive yellow 145 dye. The dye concentration was (10 ppm) at pH 5 for geopolymer mix S and pH 3 for geopolymer mix SF₁, respectively. The results of figure 3 show an increase in the removal efficiency % of the dye by increasing the weight of the adsorbent until it reached the maximum degree at (0.03 g / 100 mL) for both treatment materials S and SF₁ where the decolorization peaks of the maximum value reached 41.3% and 52.5%, respectively. The reason may be in this high decolorization rate due to the increase in the number of ions competing for accessible binding sites on the surface of the adsorbent.

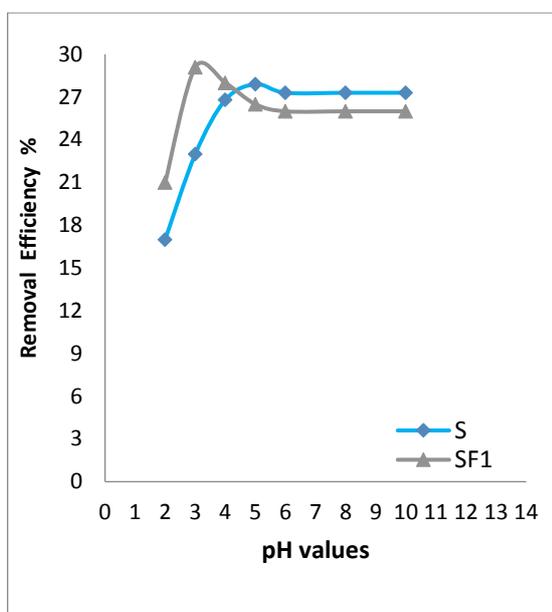


Figure 2. Effect of pH on dye removal efficiency % (Time 120 min, Temperature 30°C, weight of adsorbent 0.01g, concentration of dye 10 ppm)

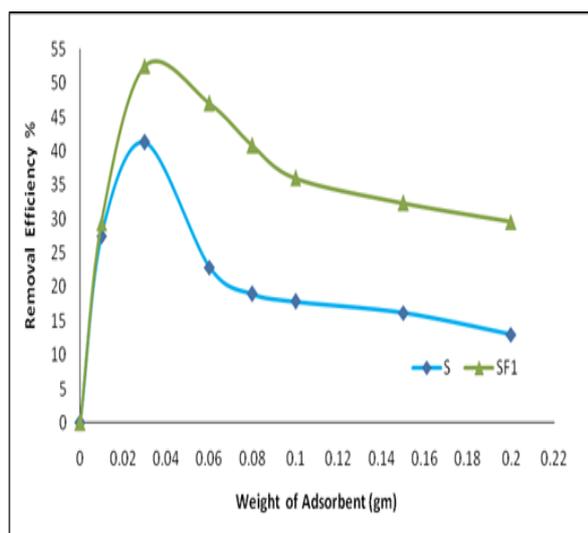


Figure 3. Effect of adsorbent weight on the removal efficiency % (Time 120 min, Temperature 30°C, concentration of dye 10 ppm, pH 5 for geopolymer mix S and pH 3 for geopolymer mix SF1)

3.2.3 Effect of time

It is also worth noting here that in order to determine the optimal duration of interaction of reactive dyes with the geopolymer mixes, the treatment was carried out according to fixed process parameters for different time periods (60-300 minutes). The results of figure 4 show that increasing the removal efficiency % of the dye by extending the adsorption time.

The longer the time the increasing amount of the removed color until it reached a maximum value and then, removal efficiency % was stable. The decolorization rate of S geopolymer is 46% at 240 min and 58% at 180 min for SF1 mix.

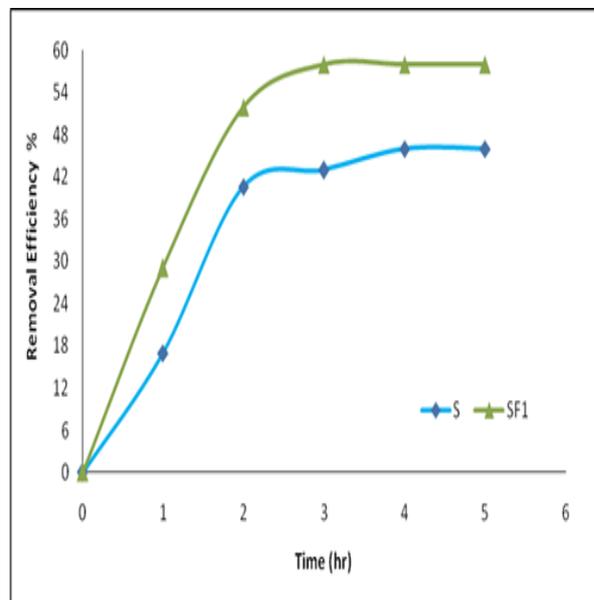


Figure 4. Effect of time on the removal efficiency % (Weight of adsorbent 0.03g, Temperature 30 °C, concentration of dye 10 ppm, pH 5 for geopolymer mix S and pH 3 for geopolymer mix SF1)

3.2.4 Effect of Dye concentration

We find that figure 5 shows the effect of dye concentration on the removal efficiency % when using a fixed weight of the two treated geopolymeric mixes S and SF1 and using both optimum pH and optimum time. The adsorption of the decolorization of dye under study was examined with different concentrations of dye (1 – 100 ppm).

The dye concentration (10 ppm) was at pH 5 and 240 min for S geopolymer mix giving the maximum removal efficiency % 45.8%. Also the same concentration of the dye achieved the goal at pH 3 and 180 min for SF1 geopolymer mix, with removal efficiency % 57.5%.

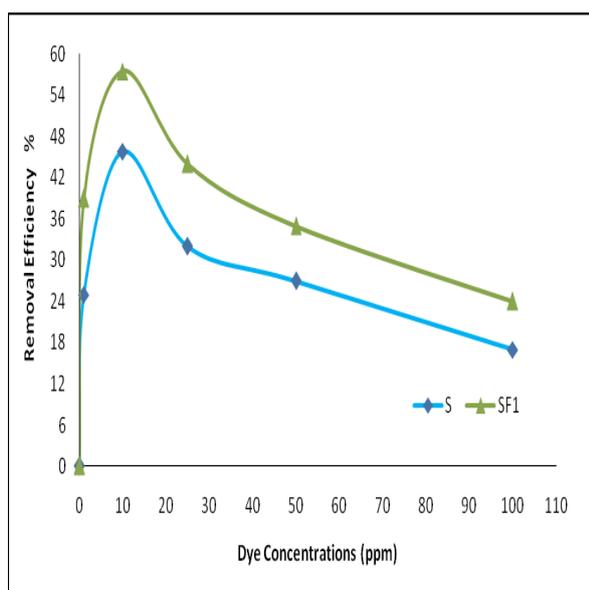


Figure 5. Effect of dye concentration on the removal efficiency % (Weight of adsorbent 0.03g, Temperature 30 °C, pH 5 for geopolymer mix S and pH 3 for geopolymer mix SF1, time 240 min for geopolymer mix S and 180 min for geopolymer mix SF1)

4. Conclusion

The present study can be considered as an indication of the suitability of using a geopolymeric cement material based on slag for reactive yellow 145 effluents. Factors affecting the dye removal efficiency % were studied, including the adsorbent dose, pH, treatment time and finally the dye dose. The maximum absorption capacity of the reactive yellow 145 dye under investigation geopolymer mix SF1 was better than geopolymer mix S, due to the geopolymer SF1 contains 10% of fly ash, while the other contain 100% slag.

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