



An Innovative and Promising Facile Route to Remove Heavy Metals and Dyes using Environmentally Friendly Slag-based Geopolymer Cement

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Abstract

Our goal for this study is to investigate the use of eco-friendly geopolymer cement in the treatment of wastewater that contains heavy elements and dyes using an immobilization technique to offer a new suggested method for dealing with these wastes. Our data indicates that using the prepared slag-based geopolymer pastes, the reactive yellow-145 dye's colour completely disappeared as well as the presence of copper ions in the leaching solution. Our data suggests that we were able to decrease pollutants and purifying the water in the industrial system. We investigated the removal efficiency of both organic dye pollutant reactive yellow-145 and copper ions with two different concentrations (700 ppm & 2700 ppm) using geopolymer mix [90% slag-10% fly ash] in the presence of 15% wt sodium silicate : 15% wt sodium hydroxide as an alkali activator, at varied hydration ages up to 14 days. The quantity of pollutant dye that was immobilised was measured using UV-Vis spectrophotometric analysis. On the other hand, the quantity of leachate of copper ions measured by atomic absorption spectroscopy. We also investigate how a mix of reactive dye and copper ions affects slag-based geopolymer paste hydration characteristics. The effects of the reactive dye, Cu²⁺ ions, and a combination of both on the microstructure of the geopolymer pastes were studied using FTIR and XRD measurements

Keywords : Reactive yellow 145, Slag, Copper ions, Geopolymer cement, Immobilization

1. Introduction

Alkali activation of waste materials has played an important role as a recent research topics since it is feasible to employ industrial and natural wastes such fly ash, metakaolin, cement kiln dust, ground granulated blast furnace slag (GGBFS), kaolinite clay and red mud to produce cheap, environmentally friendly cementitious materials with the added benefit of low carbon dioxide emissions [1, 2]. For better durability and environmental efficiency, new binders are recognized worldwide as being required to substitute for Portland cement (OPC). Between 5 and 7% of the present global anthropogenic CO₂ emissions are generated by the manufacture of OPC [3]. The importance of protecting the environment has increased significantly. There are a lot of studies on employing extra cementitious materials as a result [4, 5]. The resulting products, termed as geopolymer cement, outperforms Portland cement also in terms of engineering parameters like as compressive strength and resistance to hostile media [6]. Geopolymer is

characterized [7] as an amorphous aluminosilicate cementitious material based on natural or industrial by-products. It is generated in a high pH environment by polymerizing aluminosilicate raw materials with alkali. As part of the polymerization procedure, Si-Al minerals form three-dimensional polymeric chains to produce rings with Si-O-Si bonds [8]. Low carbon dioxide output accomplished by including extra cementitious materials such as fly ash or ground granulated blast-furnace slag, both of which have a considerable harmful impact on health [9]. Several research [10-14] have found that incorporating fly ash (FA) into the GBFS geopolymer improved the mechanical and microstructure features of the system.

Industrial development has resulted in the release heavy metals and many dyes into the aquatic environment, and wastewater treatment has become a complicated issue. Synthetic nondegradable dyes not only contaminate water resources, but their poisonous nature also has a negative impact on human health.

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Receive Date: 16 October 2022, Revise Date: 31 October 2022, Accept Date: 31 October 2022

DOI: 10.21608/EJCHEM.2022.169221.7099

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Even at low concentrations, their presence in aquatic environments inhibits light penetration resulting in an adverse influence on photosynthesis [15]. On the other hand, heavy metal contamination has evolved into a highly serious global environmental problem that is growing with time. Excessive concentrations of heavy metals in soil, water, and air may lead to heavy metal bioaccumulation in both animals and humans. Removing hazardous heavy metal pollutants from wastewater is currently one of the most studied and researched topics. There are numerous methods for removing heavy metals and dyes from wastewater, including; ultrafiltration, electrodialysis, ion exchange, coagulation–flocculation, solvent extraction, and chemical precipitation[16]. Although these technologies are effective, they have several limitations, including the use of enormous amounts of chemicals and energy, the exorbitant prices, and the formation of massive quantities of waste trash and sludge. Furthermore, many of these procedures have limitations in removing trace and ultra-trace quantities of metals from water and fail to achieve the intended results [16]. Adsorption has grown in popularity in recent years because to its easy protocol, powerful and efficient outcomes, and low cost [16]. Because of their high ion exchange efficiency and ability to harden toxic waste, geopolymers have the potential to be employed as adsorbent materials [17].

Several research [18-21] have discovered that geopolymer cement binders have superior heavy metal adsorption and solidification/ stabilisation properties. Geopolymers, on the other hand, have emerged as one of the most significant adsorbents that may be used to remove pollutants such as dyestuff waste from the environment, particularly in the wastewater treatment industry [22-27]. According to recent studies, another novel approach for eliminating dye-contaminated water in particular is the stabilization/solidification method [28, 29]. Many studies [30-34] have been carried out to examine the removal activities of various types of geopolymer cement against copper ions.

The aim of this study is to investigate a new suitable method to stabilize a mixture from heavy metals and organic dye wastes using supplementary cementitious materials or geopolymer binders. Also, study the effect of both reactive yellow-145 dye and copper ions in the hydration characteristics of slag based geopolymer pastes at different hydration time till 14 days. The solidification/stabilization test was carried out for three different geopolymer mixes from 90% slag + 10% fly ash (SF), first one (SF-Cu²⁺) in presence of 700 ppm of copper ions only, second mix

contain organic dye pollutant reactive yellow 145 only (SF-dye) and the third one (SF-dye-Cu²⁺) contain a mixture of organic dye pollutant and copper ions with two different concentration (A=700 & B= 2700 ppm). Our findings suggest the use of slag/fly ash geopolymer paste as an excellent copper ions and organic dye pollutant stabilizers.

2. Materials and Experimental Techniques

2.1 Dyeing Procedures

2.1.1 Dyeing of cotton or wool fabric

We have done the process of dyeing cotton or wool, following the same method described in our previous research [28]

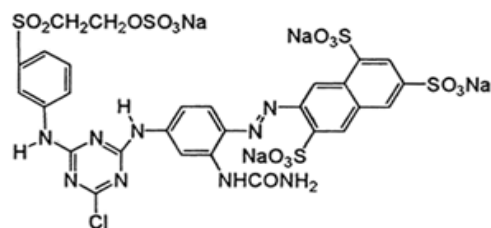


Figure 1. C.I. Reactive Yellow 145

2.2 Materials:

GGBFS, or ground granulated blast furnace slag, is purchased from the Helwan Company of Egyptian Iron & Steel. Slag has a Blaine surface area of 4700 x 50 cm² per gram and Tab lists its chemical oxide composition (1). Burg Al-Arab, Egypt-based Sika Chemical Company, provides Class F fly ash (FA). The Table (1) provides its chemical oxide. Copper chloride anhydrous with 99% purity, Sodium hydroxide (NaOH) and liquid sodium silicate (Na₂SiO₃) were used. NaOH flakes and copper chloride anhydrous are supplied by the EL-Goumhouria Chemical Company in Cairo, Egypt. The Silica Egypt Company in Alexandria, Egypt, supplies commercial liquid sodium silicate (LSS). The silica modulus of SiO₂/Na₂O equals 2.80 and the composition of liquid sodium silicate is 11.7 wt% Na₂O, 32.8 wt% SiO₂, and 55.5 wt% H₂O.

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

Oxides, %	FA	GGBFS
SiO ₂	63.10	32.86
Fe ₂ O ₃	5.40	1.14
CaO	2.33	42.56
Al ₂ O ₃	26.54	7.02
Cl	0.85	----
TiO ₂	----	----
P ₂ O ₅	----	----
MgO	0.52	11.58
SO ₃	----	2.50
Na ₂ O	----	0.29
K ₂ O	0.09	0.15
L.O.I	----	0.93
Total	98.83	99.03

2.3. Preparation of geopolymer mixes samples

2.3.1. Preparation of alkaline activator/ dye / heavy metals solutions

Mechanical stirring is applied to combine the liquid sodium silicate solution and sodium hydroxide pellets in a set ratio of 15: 15 wt % from slag-FA solid content until a homogeneous gel is formed [34]. The temperature of the combination is initially high; therefore, it is allowed to cool for a few minutes before continuing. Then add 100 ml of each of the following solutions separately: 1) the pre-treated reactive yellow 145 dye; 2) copper ions solutions at a concentration of 700 ppm; and 3) the pre-treated reactive yellow-145 dye mixed with two different concentrations of copper ions (A = 700 ppm & B = 2700 ppm) to the activator solution and mixed for half an hour before being used.

2.3.2. Geopolymer sample preparation

To produce different geopolymer pastes, dry components of 90% slag (GGBFS) and 10% fly ash (FA) must be thoroughly mixed to achieve total homogeneity. The varied alkaline activator solutions (in the absence and presence of pre-treated dye and copper ions) are mixed with the raw materials to create a homogenous geopolymer pastes SF, SF-Cu²⁺, SF-dye and SF-D-Cu²⁺ with two different Cu²⁺ concentrations = A) 700 ppm and B) 2700 ppm. Following each mixing, we evaluate the geopolymer pastes' water-consistency. The pastes are then placed in stainless steel moulds with a one-inch diameter (cubic-shaped molds). To improve the compaction of the pastes, the mould is then vibrated for a short period of time to remove all air bubbles. Using a thin-edged trowel, the paste's surface is smoothed. The pastes are immediately cured in relative humidity (100% R.H.) at 60°C for 24 hours after molding. After this period, the cubes are then taken out of the mould and cured for different hydration times. Table (2) lists the ingredients of the various mixtures as well as the water/solid ratio that provided standard consistency.

2.4. Methods of Investigation

1. Leaching test by using slag based - geopolymer paste:

Five cubes from each geopolymer mix (SF-Cu²⁺, SF-dye, and SF-D-Cu²⁺) are immersed in 100 mL of water to test their leachability at different hydration times 1,3, 7, and 14 days. The cubes were taken out of their curing condition after each hydration interval, and the compressive strength and total porosity data were checked. On the other hand, the percentage of dye present in the leachates was evaluated using a UV-Visible spectrophotometer (SpectrophotometerV-670). Additionally, an Atomic Absorption

Spectrophotometer (Savant AA-GBC Scientific Equipment, Australia) was employed to examine the concentration of copper ions in the leachate solution. So, Equation 1 was used to measure the leaching percentage (percent L) of organic dye [29].

$$\text{Leaching \%} = (\text{CL}/\text{CT}) \times 100 \quad (1)$$

Where CL is the concentration of the dye or copper ions leached out (mg/L) of the geopolymer mix cube and CT is the total concentration (mg/L) of the organic dye or incorporated in the geopolymer mix [29].

To determine the amount of copper ions that are immobilized in the hardened geopolymer pastes that were used equation 2 [35,36] :

$$x \text{ (grams in L)} = \text{Concentration (ppm)} \times 10^{-3}$$

Original Wt. of metal ion = wt. of cube X original concentration of the ions X total leachate volume

$$\begin{aligned} \text{Leaching \%} &= (x/\text{original wt. of metal ion}) \times 100 \\ \text{Immobilization} &= 100 - \text{Leaching \%} \end{aligned} \quad (2)$$

2. Compressive strength measurement:

The compressive strength of each hardened paste is measured using a set of three cubes. The results are reported in kg/cm² as the average of the three results. In this work, a manually operated compression testing machine was used to determine compressive strength (D550-control type, Milano-Italy).

3. The stopping of hydration

Following the compressive strength test, the stopping of hydration is carried out on the crushed cubic specimens. The crushed specimens were collected, mixed with a stopping solution of alcohol/acetone (1:1) to prevent further hydration, and dried at 50 °C for 24 hours before being retained for further examination (XRD, FTIR).

4. Total porosity measurement:

Total porosity tests are performed by weighing samples of dry pastes in air and suspended in water, W1 and W2, respectively. These samples are subsequently dried at 100°C for roughly 24 hours to determine their weight in the air, W3. The following equation is used to determine the total porosity percentage (P%):

$$P \% = [(W1-W3)/(W1-W2)] \times 100$$

5. pH measurements :

The pH of leaching solutions was determined in terms of time (0, 1, 3, 7 and 14 days) for each geopolymer paste using an Adwa AD1000) pH meter,

6. X-ray diffraction analysis (XRD).

X-ray diffraction analysis is used to evaluate the phase composition of the hydration products of different geopolymer mix samples. The XRD was done using a Ni-filtered diffractometer (Empyrean diffractometer, Holland) with Cu-K radiation with a

wavelength of $\lambda = 1.5418 \text{ \AA}$ and a pixel detector set to 40 kV and 40 mA.

7. The Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements are used to determine the functional groups of the hydration products formed. It was performed using potassium bromide (KBr) pellets on an infrared spectrophotometer (Perkin Elmer-1430 infrared spectrophotometer, USA). Infrared spectra exhibited wave numbers ranging from 400 to 4000 cm^{-1} .

3. Results and discussion

3.1. Effect of dye and copper ions on physicochemical properties of different geopolymer mixes

3.1.1. Compressive strength

The compressive strength values of hardened alkali activated mixes SF in the presence and absence of dye and copper ions cured in water, for different hydration times of 1, 3, 7 and 14 days, are given in Table (3). As we notice from the table, the values of the compressive strength of all geopolymer mixes (SF, SF-Cu²⁺, SF-dye, SF-D-Cu²⁺) increase with curing age. This is attributed to the higher rate of hydration as well as the formation of more hydration products such as sodium and calcium aluminum silicate hydrate. The values for compressive strength for SF1-dye-Cu²⁺ mixes show the maximum values compared to other mixes, which may be attributed to both the dye's and heavy metals' incorporation into the slag-based geopolymer matrix and lead to decrease its pore size. Additionally, we noted from Table (3) that the compressive strength values for SF-Cu²⁺ mix show the lowest values of compressive strength, which may be attributed to the retardation effect of hydration reaction by heavy metal ions according to the last study [35, 36].

3.1.2. Total porosity (P%)

Table (4) shows the total porosity of hardened SF, SF-Cu²⁺, SF-dye, and SF-D-Cu²⁺ specimens that were cured for 1, 3, 7, and 14 days. It has been shown that total porosity decreases with curing time for all geopolymer mixes. This is described by the pozzolanic activity of slag and fly ash, which react with water and produce excess hydration products. These hydration products precipitated in the remaining open pores, reducing the total porosity values. The presence of copper ions and dyes in geopolymer mixes lowers total porosity values when compared to other geopolymer mixes. This could be attributable to the dye and heavy metal ions being incorporated and precipitated inside the geopolymer matrix, which reduced the size of the pores.

3.1.3. X-ray diffraction analysis (XRD)

Figure (2) illustrates the XRD patterns of the alkali activated mixes (SF, SF-dye, SF-Cu²⁺, and SF-D-Cu²⁺) after three days of hydration curing in water (3). A strong quartz peak can be seen in the figure at $d = 3.34 \text{ \AA}$; this peak may be produced by unreacted silica from the raw materials. A broad and diffuse peak around the range of 2.78 to 3.34 \AA is also observed in XRD diagrams, revealing the presence of amorphous phases that are characteristic of alkali-activated GBFS-FA. The calcium silicate hydrate phase is responsible for the considerable peak at $d = 3.05 \text{ \AA}$ [37]. Figure (2) shows that in geopolymer pastes, the presence of the dye and copper ions has no effect on the nature of the hydration product formed. From the XRD patterns, there is a decrease in the intensity of the characteristic peaks of CSH in the amount of copper ions.

3.1.4. Fourier Transform infrared spectroscopy (FTIR)

The FTIR of slag-based geopolymer mixes SF, SF-dye and SF-Cu²⁺ after three days of hydration, is shown in Figures (3). On the other hand, figure (4) illustrated IR bands associated with SF-D-Cu²⁺A and SF-D-Cu²⁺B geopolymer mixes. All geopolymer systems showed absorption bands at 3400–3200 cm^{-1} , which is associated with the stretching vibration mode of the O-H group, and the bending vibration mode of the H-O-H group, which is at 1644–1649 cm^{-1} . The stretching vibration of the C-O bond in CO₃ groups, which is formed during the carbonation process of CH, is what causes the band around 1420–1450 and 875 cm^{-1} . Figures (3, 4) shows that the carbonation process is decreased by the presence of reactive yellow-145 dye. For geopolymer mixes, the peak in the 1016–1000 cm^{-1} range was associated with the asymmetric stretching vibration of Si–O–T (T = Si or Al). Furthermore, the geopolymerization process and the formation of amorphous aluminosilicate gels (C-S-H and N-(C)-A-S-H) in geopolymer binders could be regarded as the causes of this band shift to lower wave numbers. According to Figure 4, this band is shifted to 965 cm^{-1} in the case of geopolymer containing both dye and heavy metals in its matrix. These results prove the positive impact of dye and heavy metals on the geopolymerization process. The geopolymerization process was also indicated by a reduction in the strong peak of alumina's intensity at 798 cm^{-1} . Furthermore, the occurrence of the Si-O-Si bending vibration mode at around (449–451) cm^{-1} was related to unreacted quartz.

Table (2): Mix composition of the examined mixture and liquid/solid (L/S) ratio

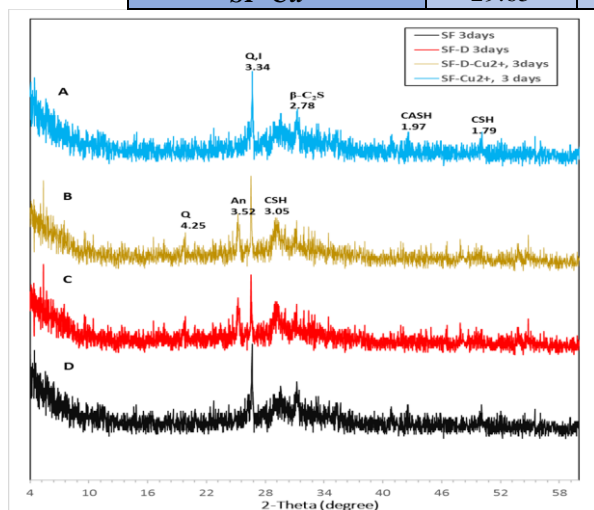
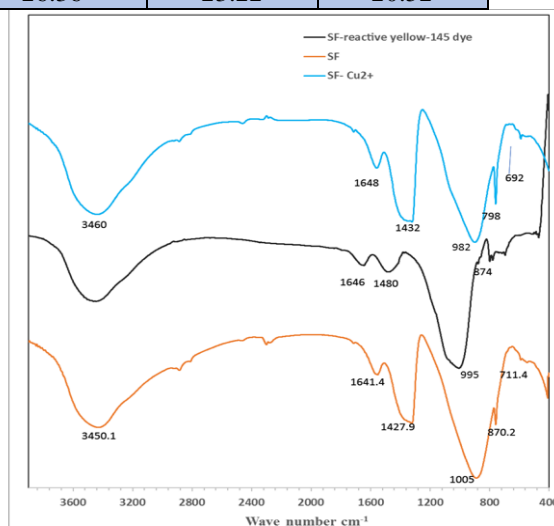
Mix Name	slag	FA	NaOH ml	Na ₂ SiO ₃ ml	Dye ml	Cu ²⁺ solution ml	L/S ratio
SF	90	10	40	40	-----	-----	0.40
SF-Cu ²⁺	90	10	40	40	-----	100	0.35
SF-dye	90	10	40	40	100	-----	0.38
SF-D-Cu ²⁺	90	10	40	40	100 ml		0.36

Table (3): Compressive strength (kg/cm²) of SF, SF-dye, SF-dye1-Cu²⁺ and SF-Cu²⁺ curing in H₂O at different hydration ages.

Geopolymer mix	Compressive strength (kg/cm ²)			
	1 day	3 days	7 days	14 days
SF	320	360	385	420
SF-dye	300	350	380	450
SF-D-Cu ²⁺ A	500	550	600	650
SF-D-Cu ²⁺ B	350	400	450	500
SF-Cu ²⁺	150	200	250	300

Table (4): Total porosity (P %) of different geopolymer mixes curing in H₂O at different hydration ages.

Geopolymer mix	Total porosity (P %)			
	1 day	3 days	7 days	14 days
SF	35.12	34.38	33.45	32.65
SF-dye	34.22	33.85	32.65	31.22
SF-D-Cu ²⁺ A	28.05	27.41	21.77	10.52
SF-D-Cu ²⁺ B	25.01	24.20	23.38	17.15
SF-Cu ²⁺	29.65	26.36	23.22	20.52

**Fig (2):** XRD diffractograms of different geopolymer mixes cured in water at 3 days, a) SF-Cu²⁺, b) SF-dye-Cu²⁺, c) SF-dye, d) SF**Fig (3):** FTIR spectra of different geopolymer mixes cured in water after 3 days with and without reactive yellow-145 dye and copper ions.

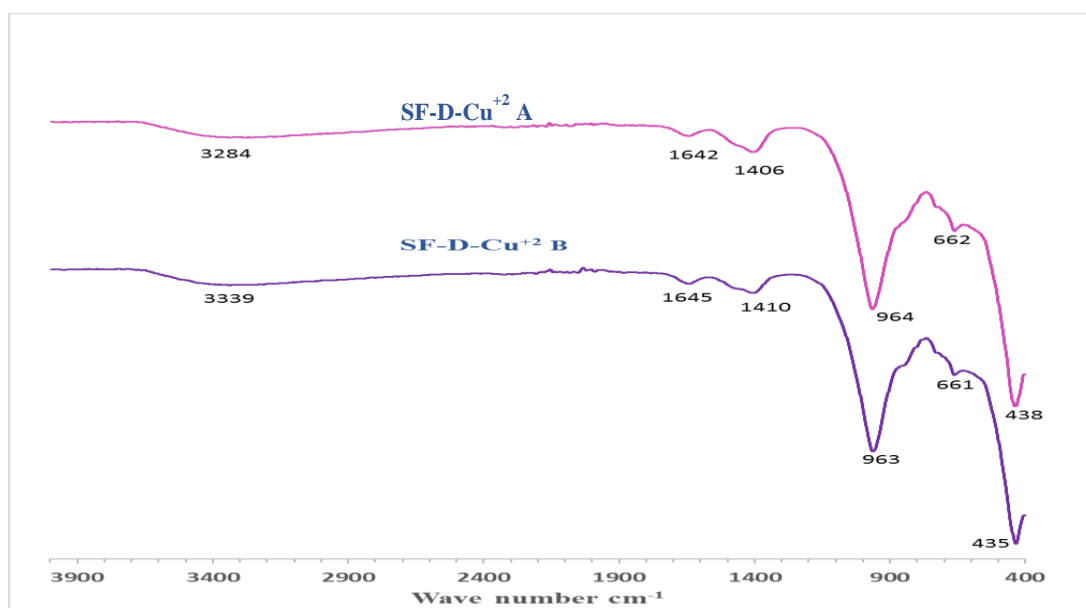


Fig (4): FTIR spectra of different geopolymer mixes cured in water after 3 days contain reactive yellow-145 dye and copper ions with two different concentration, A) 670 ppm, B) 2700 ppm

3.2. Leaching of reactive yellow-145 dye and copper ions from geopolymers mixes.

3.2. Leaching of reactive yellow-145 dye from geopolymers.

3.2.1 Absorbance measurements for reactive yellow dye in leachate solutions.

Applying the UV-Vis absorbance measurement of leachate solutions after various curing times (1, 3, 7 and 14 days), the performance of immobilizing reactive yellow-145 dye effluents (0.56 gm/L) inside the geopolymer matrix was examined. Figures (5-7) illustrate that the immobilization behaviour of different geopolymer mix cubes (SF-dye, SF-D-Cu²⁺ A and SF-Cu²⁺ B) toward reactive yellow dye is unaffected by the addition of different concentrations of copper ions. The UV-Vis absorption band spectra of the reactive yellow 145-dye have a maximum at 419 nm, as shown in Figures (5-7). On the other hand, for a series of geopolymer-dye mixes, SF-dye, SF-D-Cu²⁺A, and SF-D-Cu²⁺ B, the UV-Vis absorbance spectra of various leachate solutions at the λ -max of reactive yellow-145 dye (419 nm) are equivalent to zero from 1 day to 14 days of curing (Figures 5-7). This may be attributed to the superior adsorption properties of the geopolymer matrix and its hydration products (CH and CASH), which facilitate the elimination of pollutants such as heavy metals and organic dyes [38]. These findings

demonstrate that the dye is completely removed by solidifying inside the geopolymer matrix.

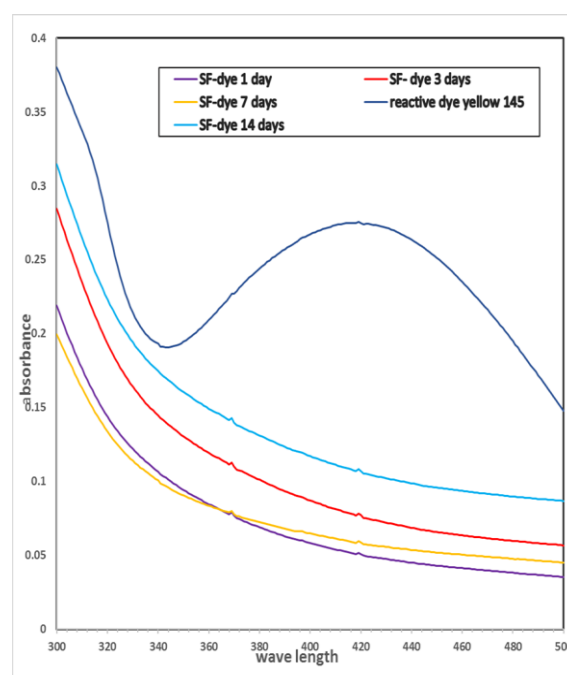


Fig (5): UV-Vis absorbance band spectra of reactive yellow-145 dye and different leachate solutions for SF-dye mix at different hydration age

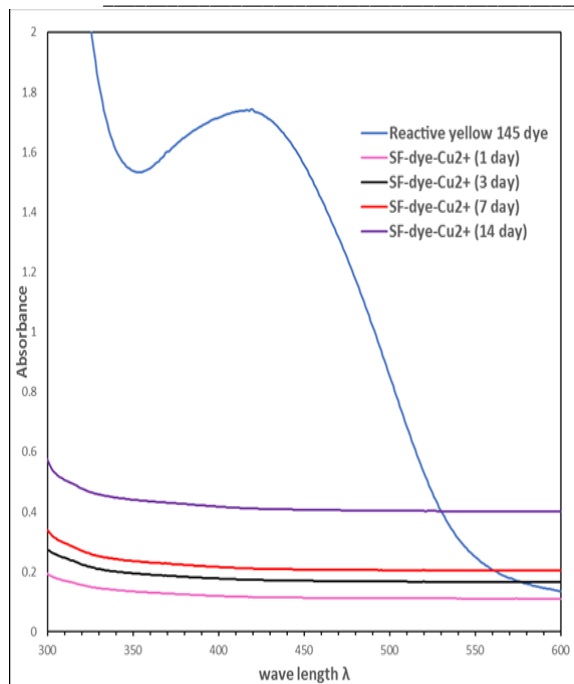


Fig (6): Absorbance band spectra of reactive yellow-145 dye and different leachate solutions for SF-D-Cu²⁺A mix at different hydration age

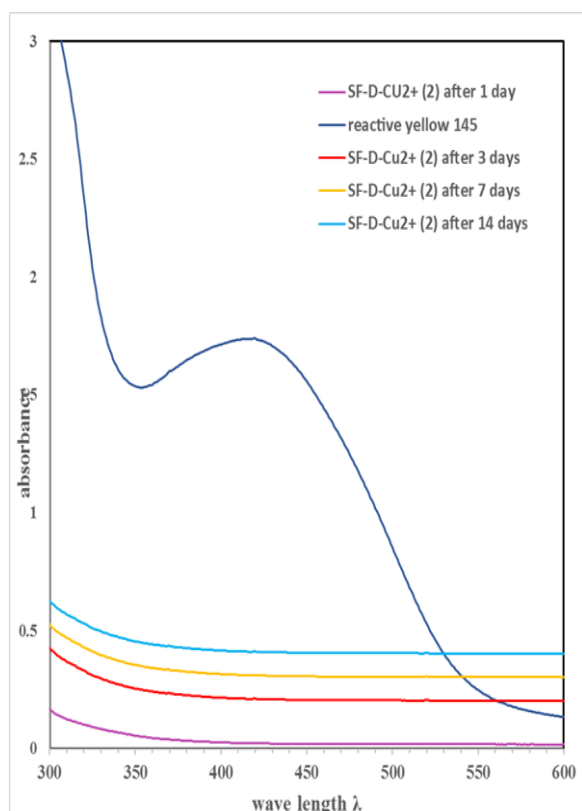


Fig (7): Absorbance band spectra of reactive yellow-145 dye and different leachate solutions for SF-D-Cu²⁺B mix at different hydration age.

3.2.2 Atomic Absorbance measurements for copper ions in leachate solution.

The performance of immobilising copper ions with different concentrations (670 ppm, 2700 ppm) in the absence and presence of effluents of reactive yellow-145 dye inside the geopolymer matrix was investigated using the atomic absorbance spectroscopy measurement of leachate solutions after various curing times (1, 3, 7 and 14 days). Table (5) summarizes the findings of the leaching percentage of the various geopolymer mixes: SF-Cu²⁺, SF-D-Cu²⁺A, and SF-D-Cu²⁺B. In the case of the geopolymer mixture SF-D-Cu²⁺A, it is observed that after 14 days of hydration, the leaching percentage equals zero. This is attributed to the high immobilization efficiency of the geopolymer paste for copper ions, which completely solidify inside the geopolymer matrix during 14 days of curing. All geopolymer mixes are thought to have exceptionally high levels of copper ion immobilisation. This demonstrates the prepared slag-based geopolymer's excellent efficiency in immobilising copper ions as well as reactive yellow-145 dye and transforming hazardous slag into user- and environment-friendly construction materials.

3.2.3. pH measurements for leaching solutions as a function of contact time with geopolymer mixes

The pH of leachate solutions was examined as a function of contact time (0, 3 hours, 1, 3, 7 and 14 days) for different geopolymer mix cubes containing reactive yellow-145 dye and copper chloride with various concentrations (SF-Cu²⁺, SF-dye, SF-D-Cu²⁺A & SF-D-Cu²⁺B) as seen in table (6). For various geopolymer mix leachate solutions, the pH values increased with time until 14 days of hydration. The continuous hydration of the geopolymer paste over time and the release of alkaline species into leaching solutions are responsible for these high levels of alkalinity [29].

Table (5): Leaching percent and immobilization values of different geopolymer mixes containing various concentration of Copper chloride (670 ppm, 2700 ppm) with and without dye at different curing time (1, 3, 7 and 14 days).

Time (day)	Leaching %			Immobilization (100-leaching %)		
	SF- Cu ²⁺	SF-D-Cu ²⁺ A	SF-D-Cu ²⁺ B	SF- Cu ²⁺	SF-D-Cu ²⁺ A	SF-D-Cu ²⁺ B
1	2.71x10 ⁻⁶	0	7.86x10 ⁻⁷	99.999997	100	99.9999992
3	4.69x10 ⁻⁶	0	1.01x10 ⁻⁶	99.999995	100	99.999998
7	4.26x10 ⁻⁶	0	2.24x10 ⁻⁶	99.999995	100	99.999997
14	6.10X10 ⁻⁵	0	4.48X10 ⁻⁶	99.999993	100	99.999995

Table (6): pH's values of leachate solutions of different geopolymer mixes at different hydration ages

Geopolymer mix	pH					
	0	3 hours	1 day	3 days	7 days	14 days
SF-dye	7.40	12.75	13.08	13.24	13.38	13.58
SF- Cu ²⁺	7.40	12.67	13.44	13.54	13.47	13.50
SF- D -Cu ²⁺ A	7.40	12.38	13.35	13.45	13.48	13.48
SF-D -Cu ²⁺ B	7.40	12.39	13.36	13.49	13.48	13.52

Conclusion

In this investigation, the hydration properties of various geopolymer cements based on slag, with and without copper ions (in two concentrations), as well as reactive yellow-145 dye, were examined. They were also tested for their efficiency in removing and immobilising the copper ions and reactive yellow-145 dye. Our findings indicate the approximately complete removal of dye and copper ions by the prepared eco-friendly slag-based geopolymer pastes. Additionally, the combination of dye and copper ions enhances the mixture's compressive strength and porosity values. According to XRD and FTIR analysis, the presence of copper ions alone in the mix SF-Cu²⁺ has a negative effect on compressive strength values, whereas the nature of the hydration product formed is unaffected by the addition of copper ions and dye.

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