Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Decolorization of Reactive Dyes, Part IV: Eco-Friendly Approach of Reactive Red 195 Dye Effluents Decolorization Using Geopolymer Cement Based on Slag

Morsy A. El-Apasery[1]*, Amal A. Aly[2], Doaa A. Ahmed [3]

[1] *Dyeing, Printing and Textile Auxiliaries Department, Textile Research and Technology Institute, National Research Centre, 33 El Buhouth St., Cairo 12622, Egypt*

[2] *Textile Research and Technology Institute (TRT) , Pretreatment and Finishing of Cellulosic based Textiles Department, National Research Centre, 33 El Buhouth St., Cairo 12622, Egypt*

[3] *Chemistry Department, Faculty of Women for Arts, Science and Education, Ain Shams University, Cairo, Egypt.*

Abstract

By employing two distinct kinds of slag-based geopolymers to remove the colour from the liquid wastes of reactive red 195, we were able to cleanse the water created by reactive dye dyeing processes and lower pollution rates. The decolorization-affecting variables were optimized in accordance with a variety of parameters, including the amount of dye used, the treatment time, the pH of the solution, and the amount of adsorbents employed.

Keywords:.Reactive red 195 s, Slag, Geopolymer cement, Fly ash.

1. Introduction

Around the world, cement and concrete are widely utilized as building and construction materials. A significant quantity of energy and raw materials are used in the production of Portland cement accompanied by emits a lot of CO_2 which contributes to global warming. By 2020, it is anticipated that CO2 emissions will exceed 4.8 billion tons and yearly cement production will reach 5.9 billion tons [1]. Because it is possible to use industrial or natural wastes like fly granulated ash, ground blast furnace slag (GGBFS), metakaolin, kaolinite clay, and red mud to create cost-effective, environmentally friendly cementitious materials (geopolymers) with the added benefit of low carbon dioxide emissions and low-energy-consumption, alkali activation of this waste materials has grown in importance as a field of study [2,3].The issues facing the construction sector may also be solved by these binders. As well using industrial/agricultural waste, geopolymer cements GPC cut CO2 by 80% [1,4].

Geopolymer cement is an innovative material and a real substitutional to conventional Portland cement for use in different applications. Davidovits [5] defined geopolymer as an amorphous alumino-silicate cementitious material made from natural or industrial byproducts aluminosilicates such as metakaolin, fly ash, or pulverized granulated blast furnace slag, among other industrial wastes. It is created by polymerizing aluminosilicate raw materials with alkali in an atmosphere with a high pH level. As part of the polymerization procedure, Si-Al minerals create three-dimensional polymeric chains to create rings with Si-O-Si links [1,6,7]. Pozzolanic materials must include siliceous or a mixture of siliceous and aluminous material in a very finely divided form, and they react with calcium hydroxide in the presence of moisture at normal temperatures to form compounds with performance that is comparable to that of regular Portland cements OPC. Various industrial waste materials have reportedly been employed as a source of alumina and silica for the creation of geopolymers, according to several studies [8-11]. The pozzolanic material known as ground granulated blast furnace slag "GGBFS" is generated as by-product from the production of iron

*Corresponding author e-mail: elapaserym@yahoo.com.; (Morsy Ahmed Elapasery).
Receive Date: 30 June 2022, Revise Date: 03 July 2022, Accept Date: 24 July 2022.
DOI: 10.21608/EJCHEM.2022.148302.6411

from iron ore in a blast furnace. It is duct created when iron ore and limestone flux are combined to make pig iron in the blast furnace. The principal composition of slag is alumina, silica, lime, and magnesia, whose percentages may alter depending on the composition of limestone flux, the nature of iron ore and the kind of iron being produced [12]. GGBFS has pozzolanic and binding properties in the alkaline medium. Slag also was the first cementitious materials to be alkali activated and because of it has latent hydraulic properties, slag (GGBFS) become the most proper materials for alkali activated cements [13]. Numerous studies [14-17] looked at the addition of activated slag to industrial waste products as fly ash (FA), cement kiln dust (CKD), and silica fume (SF) for production of different geopolymers cement. Geopolymer binders are environmentally-friendly material utilized as a substitute for ordinary Portland cement (OPC) binder along with the potential to reach high mechanical strength at early ages of curing, resistance to high thermally treated temperatures and resistance to chemical attack. The role of geopolymer cements protect the environment through the utilization of by-product materials in their production process and end applications in waste management [18]. Geopolymers have recently emerged as one of the most significant adsorbents may be utilized to remove pollutants (such as dyestuffs and hazardous wastes) from the environment [19]. Geopolymer cements may be used as adsorbents in recent experiments to remove various types of dyes [20–22]. The textile sector has had a high need for dyes over the past ten years, which suggests that they are probably harmful compounds.

During the dyeing process, 35 to 45 percent of the dye is thought to linger in the waste water. Reactive dyes are the most popular dyes because they have several benefits such a stable structure, vibrant colour, and functionality in mild settings. Several chemical and physical decolorization processes such as precipitation, adsorption, oxidation, reduction, coagulation, and electrolysis are utilized to remove the dye [23-28]. The adsorption procedure is the best method for handling tiny quantities of wastewater [29–37].

The aim of this study is to remove the color of the reactive red 195 dye 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.

2. Materials and Methods

2.1. Materials

Reactive Red 195 was utilized for the decolorization studies. The structures of this dyes is shown in figure 1.

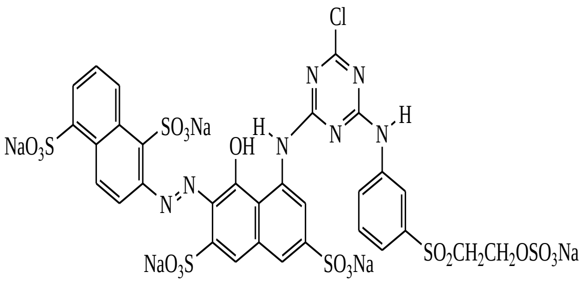

Figure 1. C.I. Reactive Red 195

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 [30].

2.3 Adsorbent preparation

2.3.1 Starting materials

Materials used in this investigation were: granulated blast furnace slag (GBFS) obtained from the Egyptian iron & steel of Helwan Company with Blaine surface area 4700±50 cm2/g. Fly ash (FA) is provided from Sika Egypt Company, Obour, Egypt with surface area 300 to 500 m2/Kg. Sodium silicate liquid (SSL) is provided from Silica Egypt Company, Burg Al-Arab, Alexandria, Egypt and Sodium hydroxide (NaOH) pellets is provided from EL-Goumhouria chemical company, Cairo, Egypt with purity 99%. The chemical composition of liquid sodium and the utilized materials are given in Table (1).

2.3.2. Geopolymer Synthesis

2.3.2.1. Alkaline activator

The alkali activator (AA) is prepared by mixing sodium silicate liquid (SSL) and sodium hydroxide (NaOH) pellets with mechanically stirring according to ratio show in table (2). The temperature of the mixture is initially high so it left till reach to room temperature in few minutes before proceeding.

2.3.2.2. Preparation of specimens:

The mix compositions of the prepared samples are shown in Table (2). The paste specimens are prepared by adding the prepared activator to dry mixes and mixed them on a smooth and non- absorbent surface for about 5 minutes. The pastes are then cast into stainless steel molds of one-inch dimension (cubic-shaped mold). The mold is vibrated for 1 minute to ensure no air/voids are present in the specimens. Finally, the molds are held at a nearly 100% relative humidity for preventing drying and giving enough time (24 hrs) to the pastes to set and harden at ambient temperature, i.e. 25 °C. After molding the cubes demolded and kept under relative humidity 100% for 7 days of hydration specimens.

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 ºC for 24 hrs. Then dried samples were ground to obtain a mean particle diameter of 100 µm and stored in a desiccator.

2.3.3. Water of consistency:

The standard water of consistency are determined according to ASTM specification using Vicate apparatus [36]. 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 (10mm in diameter) to a point 5 to 7 mm from the bottom of the vicatmould.

2.4 Adsorption experiments

Specific amount of the adsorbent were shaking at 30 ^{o}C and140 rpm with 100 mL of dye solution. The supernatant of the samples solutions were separated by filtration. Absorbance at maximum wavelength (λ_{max} = 504 nm for reactive red 195 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 structure and chemical characterization of geopolymer based on slag were listed in tables 1 and 2.

Table (1): Chemical oxide composition of starting materials in n percentage (%)

Oxides%	GGBFS	FA	SSL
SiO_2	32.86	63.10	32.8
Na_2O	0.29	----	11.7
K_2O	0.15	0.09	----
Al_2O_3	7.02	26.54	----
Fe_2O_3	1.14	5.40	----
SO_3	2.50	----	----
CaO	42.56	2.33	----
MgO	11.58	0.52	----
Cl^-	----	0.85	----
Loss in ignition	0.93	----	----
H_2O	----	----	55.5
Total	99.03	98.83	100

Table (2): The investigated geopolymer cement mixes composition and liquid/solid (L/S) ratios.

Mix No	Mix Name	GGBFS	FA	NaOH %	Na_2SiO_3 %	L/S ratio
1	S	100	----	10	15	0.43
2	SF1	90	10	15	15	0.53

3.2 Factors affecting on the adsorption

3.2.1 Effect of pH

The change in the dye removal efficiency % when using the dye effluent of reactive red 195 dye under the pH of the adsorption bath is illustrated in Figure 2. In order to determine the optimum pH value of the slag based- 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 dye baths effluents, the dye removal efficiency % increases with increasing pH from pH 2 to pH 3 and then decreases. Secondly, for the dye effluent of reactive red 195 dye, the maximum removal efficiency % was at pH 3 when using geopolymer mixes S and SF1 and its maximum value was73.3% for both.

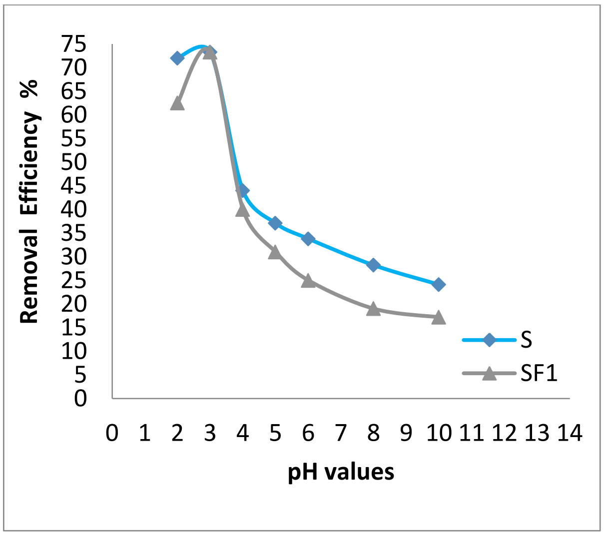

Figure 2. Effect of pH on dye removal efficiency % (Time 120 min, Temperature 30°C, weight of adsorbent 0.01g, concentration of dye 10 ppm)

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 geopolymer mixes S andSF1, for using the dye effluent of reactive red 195 dye. The dye concentration was (10 ppm) at pH 3 and the duration time was 120 min. The results of figure 3 show a decrease the removal efficiency % of the dye by increasing the weight of the adsorbent. The maximum degree at (0.01 g / 100 mL) for treatment mixes S and SF1 where the decolorization peaks of the maximum value reached 73.3% for both.

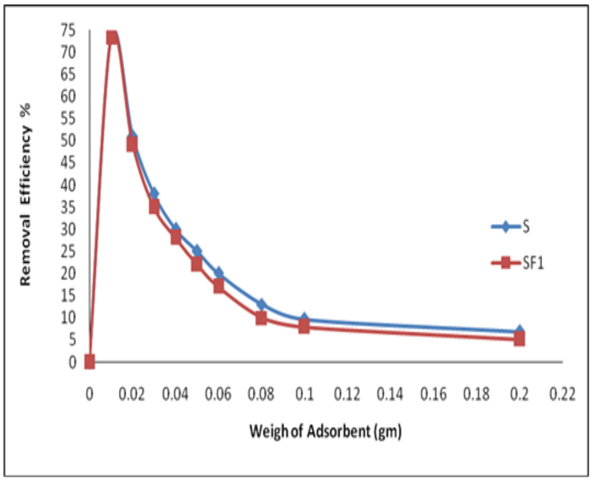

Figure 3. Effect of adsorbent weight on the removal efficiency % (Time 120 min, Temperature 30°C, concentration of dye 10 ppm, pH 3 for geopolymer mixes S and SF1)

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 slag based-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 mix is 73% at 120 min and 73.6% for SF1 geopolymer mix.

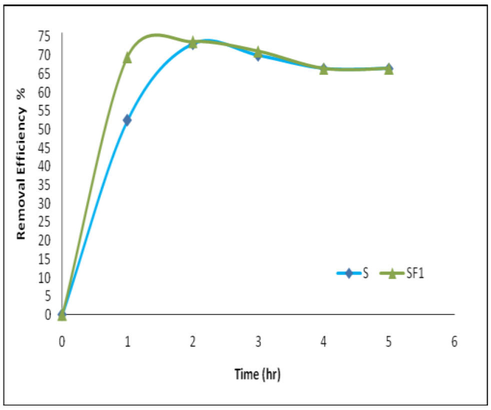

Figure 4. Effect of time on the removal efficiency % (Weight of adsorbent 0.01g, Temperature 30°C, concentration of dye 10 ppm, pH 3 for geopolymer mixes S and SF1)

3.2.4 Effect of Dye concentration

It is of value to report here that figure 5 shows the effect of dye concentration on the removal efficiency % when using a fixed weight of the two treated slag based-geopolymer 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 (5 – 100 ppm). The dye concentration (5 ppm) was at pH 3 and 120 min for S mix giving the maximum removal efficiency percentage 82.6%. Also the same concentration of the dye achieved the goal at the same conditions of time and pH for SF1 geopolymer mix, with removal efficiency percentage 91.3%.

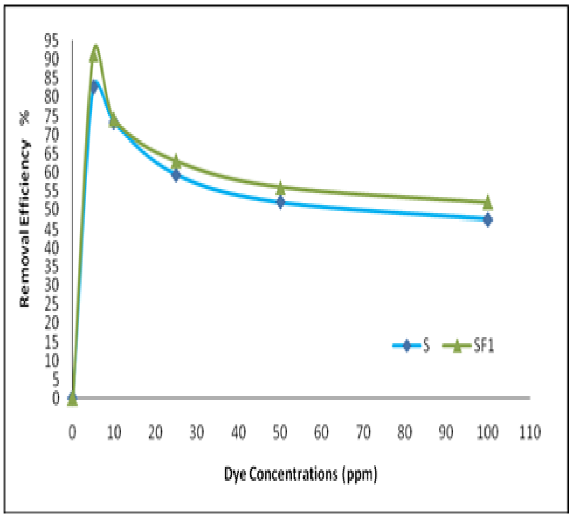

Figure 5. Effect of dye concentration on the removal efficiency % (Weight of adsorbent 0.01g, Temperature 30^{o}C, pH 3, time 120 min)

4. Conclusion

This study can be seen as demonstrating the suitability of using two different slag-based geopolymer cement mixes for removal of reactive Red 195 wastewater. We investigated factors that affect the removal efficiency percentages of dye effluents such as adsorbent dose, pH, treatment time, and dye dose. The results indicate that the maximum absorption capacity of the reactive red 195 dye under investigation in geopolymer cement mix SF1 was superior to geopolymer cement mix S. The presence of fly ash in addition to slag (SF1) increases the adsorption properties of slag based geopolymer cement.

References

1-Singh, N. B., &Middendorf, B., "Geopolymers as an alternative to Portland cement: An overview", Construction and Building Materials, 2020, 237, 117455-117469

2-Abdel-Gawwad H., Abo-El-Enein S.,"A novel method to produce dry geopolymer cement powder", Housing & Building National Research Center journal, 2016, 12, 13-24.

3-NobouassiaBewa, C., Tchakouté, H.K., Fotio, D., Rüscher, C.H., Kamseu, E., Leonelli, C., "Water resistance and thermal behavior of metakaolin-phosphate-based geopolymer cements", Journal of Asian Ceramic Societies, 2018, 6, 271-283.

4-Salimi, M., Ghorbani, A., "Mechanical and compressibility characteristics of a soft clay stabilized by slag-based mixtures and geopolymers", Applied Clay Science, 2020, 184, 1-15.

5-Davidovits, J. "Chemistry of geopolymeric systems", terminology, Geopolymer. sn, 1999, pp. 9-39.

6-Rahmawati, C., Aprilia, S., Saidi, T., &Aulia, T. B., "Current development of geopolymer cement with nanosilica and cellulose nanocrystals.", Annual Conference on Science and Technology Research, Medan, Indonesia, Conference Series: Journal of Physics, 2021, 1783, 12056-12066.

7-Khale D and Chaudhary R.,"Mechanism of geopolymerization and factors influencing its development: a review., ", Journal of materials science, 2007, 42 (3), 729-746.

8-Singh, S. P., Tripathy, D. P., &Ranjith, P. G., "Performance evaluation of cement stabilized fly ash–GBFS mixes as a highway construction material" , Waste management, 2008, 28, 1331-1337.

9-Jindal B. B., Alomayri T., Hasan A. &KazeC. R.,"Geopolymer concrete with metakaolin for sustainability: a comprehensive review on raw material's properties, synthesis, performance, and potential application", Environmental Science and Pollution Research, 2022, https://doi.org/10.1007/s11356-021-17849-w

10-Kassem N.N., Kishar E.A. & Ahmed D.A.,"Effect of Elevated Temperatures on The Performance of MetakaolinGeopolymer Pastes Incorporated by Cement kiln dust" , Egyptian Journal of Chemistry , 2021, 64(4), pp. 1911 – 1926.

11-Selim F., Ahmed D.A &KisharE.A.,"Effect of Alkali Concentration on Physico -Chemical and

Mechanical Properties of Slag Based Geopolymer Cement" ,Journal of Scientific Research in Science, 2021, 38, (1): 210-232

12-Amer, I., Kohail, M., El-Feky, M. S., Rashad, A., & Khalaf, M. A., "Characterization of alkali-activated hybrid slag / cement concrete" ,Ain Shams Engineering Journal, 2021, 12, 135-144.

13-Singh, S. P., Tripathy, D. P., &Ranjith, P. G.,"Performance evaluation of cement stabilized fly ash–GBFS mixes as a highway construction material", Waste management, ,2008, 28, 1331-1337.

14-Phoo-ngernkham, T., Maegawa, A., Mishima, N., Hatanaka, S., &Chindaprasirt, P. "Effects of sodium hydroxide and sodium silicate solutions on compressive and shear bond strengths of FA – GBFS geopolymer", Construction and Building Materials,2015, 91, 1–8.

15-KisharE.A. ; Ahmed D.A.; Nabil N.,"Geopolymer Cement Based on Alkali Activated Slag", Journal of scientific research in science, 2017, 34(1), 538-552

16-Mahmoud A.;Kishar E.; Ahmed D.,"Resistance of alkali-activated slag to sulphate attack and elevated temperatures", Journal of scientific research in science , 2018, 35(1), 315-329

17-Elyamany H. E.; Abd Elmoaty M. A.; and Diab A.A, "Properties of slag geopolymer concrete modified with fly ash and silica fume" Canadian Journal of Civil Engineering, 2022, 49(2), https://doi.org/10.1139/cjce-2019-0757

18-Bouguermouh K, Bouzidi N, Mahtout L, Hassam T, Mouhoub S and Perez-VillarejoL.,"Stabilization of flotation wastes resulting from the treatment of Pb/ Zn ore based on geopolymer. ", Materials Letters, 2018, 227, 221-224

19-Siyal A.A., Shamsuddin R. M., Khan I., RabatallN.,ZulfiqarM.,Man Z., Siame J. , Khairun A.; " A Review on Geopolymers as Emerging Materials for the Adsorption of Heavy Metals and Dyes", Journal of Environmental Management, 2018, 224, DOI: 10.1016/j.jenvman.2018.07.046

20-El Alouani M., Alehyen Sh., El Achouri M., and Taibi M.; "Preparation, Characterization, and Application of Metakaolin-Based Geopolymer for Removal of Methylen Blue from Aqueous Solution" Journal of Chemistry, 2019, Volume 2019, Article ID 4212901 https://doi.org/10.1155/2019/4212901

21-Malekia A., Mohammad M., Emdadia Z., Asimb N., Azizia M., Safaeib J., "Adsorbent materials based on a geopolymer paste for dye removal from aqueous solutions" , Arabian Journal of Chemistry, 2020, 13(1) , 3017-3025

22-Fitriani E., and Purbasari A., (2021) "Application of low-cost mesoporousgeopolymer for dye waste removal", International Conference on Chemical and Material Engineering, doi:10.1088/1757-899X/1053/1/012002

23-Morsy Ahmed Elapasery; Doaa abdelmonem Ahmed; Amal A Aly. Decolorization of Reactive Dyes, Part II: Eco-Friendly Approach of Reactive Dye Effluents Decolorization Using Geopolymer Cement Based on Slag, Egyptian Journal of Chemistry, 2022. In press

24-Morsy Ahmed Elapasery; Doaa abdelmonem Ahmed; Amal A Aly . Decolorization of Reactive Dyes, Part III: Eco-Friendly Approach of Reactive Dye Effluents Decolorization Using Geopolymer Cement Based on Metakaolin, Egyptian Journal of Chemistry, 2022. In press

25-Feng X.; Yan Sh.; Jiang Sh.; Huang K. ; Ren X.; Du1 X.; Xing P., "Green Synthesis of the Metakaolin/slag Based Geopolymer for the Effective Removal of Methylene Blue and Pb (II)", Silicon, 2021, https://doi.org/10.1007/s12633-021-01439-z,

26- Al-Etaibi, A. M.; El-Apasery, M. A. Ultrasonic Dyeing of Polyester Fabric with Azo Disperse Dyes Clubbed with Pyridonones and Its UV Protection Performance, *Chemistry*, **2021**, 3 (3), 889-895.

27-Al- Degs, Y.; Khraisheh, M.A.M.; Allen, S.J.; Ahmad, M. N. Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Res., 2000, 34, 927-935.

28-Amal A. Aly, Safia A. Mahmoud and Morsy A. El-Apasery , "Decolorization of reactive dyes, Part I: Eco-friendly approach of reactive dye effluents decolorization using cationized sugarcane bagasse", Pigment & Resin Technology, 47 (2), 2018, 108-115.

29- Hashem, A., Aly, A.A., Aly, A.S., Hebeish, A. Derivation of quaternized products from cotton stalks and palm tree particles Journal of the Textile Association, 2004, 65(1) ,. 35 – 39.

30-Khalil, M.I., Aly, A.A. Use of cationic starch derivatives for the removal of anionic dyes from textile effluents Journal of Applied Polymer Science, 2004, 93 (1), 227 - 234.

31-Hashem, A., Aly, A.A., Aly, A.S., Hebeish, A. Quaternization of cotton stalks and palm tree particles for removal of acid dye from aqueous solutions Polymer - Plastics Technology and Engineering 2006, 45 (3), 389 - 394

32-A. Hashem ,Chukwunonso O. Aniagor , E.S. Abdel-Halim , A. Amr , S. Farag , A.A. Aly, Instrumental characteristics and acid blue 193 dye sorption properties of novel lupine seed powder , Cleaner Chemical Engineering, 2022, 2 ,10001.

33-Aly A. Hebeish, Amal A. Aly Synthesis, Characterization and Utilization of Starch Hydroxypropyl Sulphate for Cationic Dye Removal. International Journal of Organic Chemistry, 2014, (4) 208-217.

34-Hashem, A.; Aly, A. A.; Aly, A. S. Preparation and utilization of cationized sawdust Polymer - Plastics Technology and Engineering, 2006, 45(3), 395-401.

35-Aly, A. A.; Hebeish, A. Development of starch-based cationic adsorbents for removal of anionic dyes from aqueous systems International Journal of Scientific Research, 2015, 4(8), 4-12.

36-Designation, A., 2008. C191: Standard test method for normal consistency and setting time of Hydraulic Cement ". Annual Book of ASTM Standards, 172-174.

37-Al-Etaibi, A.M.; El-Apasery, M.A. Microwave-Assisted Synthesis of Azo Disperse Dyes for Dyeing Polyester Fabrics: Our Contributions over the Past Decade. Polymers 2022, 14, 1703.