Egypt. J. Chem. **Vol. 65**, No.12. pp. 129 – 135 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

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

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

Our strategy, which we developed a decade ago, aims to reduce pollution rates by treating the water generated from the dyeing process. Here we did the same study but using reactive dyes, by decolorizing red effluent 195 using two different types of geopolymer based on metakaolin. The factors affecting decolorization were studied such as the adsorbent dose, duration, different pH and finally the dose of dye used.

Keywords:. Reactive dyes, Geopolymer cement, Fly ash, Calcium hydroxide, Metakaolin

1. Introduction

In recent times, research has been concentrated on creating substitute cementitious materialsto decrease the emission of greenhouse gases, which can improve the achievement of a sustainable environment. The acute need for sustainability forced the researcher to look into alkali-activated binders, commonly known as "geopolymers," which can be made from materials rich in aluminosilicates through to the geopolymerization process. The technique of geopolymerization is the release of silica, alumina, and lime while an alkaline activator interacts with an aluminosilicate source material to produce an aluminate-silicate hydrate, which is then condensed and hardened[1,2]. The aluminosilicate source may come from the nature, such metakaolin and volcanic ash, or from industry, like fly ash (FA)and blast furnace slag (GGBFS)[2, 3].Additionally, when compared to conventional Portland cement, geopolymers are more environmentally friendly cementitious materials because their manufacture requires lower temperatures, which leads to a reduced CO_2 emission [4,5] as well as their resistance properties to fire and acid attack [6-8]. Geopolymers have been used in a wide range of applications, such as thermal insulation, alternative binders to Portland cement in the construction industry, and sorbents [9]. This seems to be due to their porous structure, good compressive strength, high heat resistance, and cation exchange properties. The promise of geopolymers as developing low-cost sorbents for removing colour (dyes), hazardous metals, and detergents from wastewater [10-12] has recently been the subject of numerous investigations.

Metakaolin is an amorphous aluminosilicate that is formed when kaolinitic clay is calcined and dehydroxilated at temperatures between 500 °C and 900°C. It is a highly reactive natural pozzolan. Kaolin is constituted of silica and alumina arranged alternately in tetrahedral and octahedral coordination. The mean size of metakaolin particles, which are porous, angular in shape, and platy, can vary from 1 to 20 µm. It is a pozzolanic admixture that is very reactive. based on the raw materials' deposit. The manufacturing temperature of MK is one of its eco-friendly features. MK is burned at a lower

*Corresponding author e-mail: elapaserym@yahoo.com.; (Morsy Ahmed Elapasery).

Receive Date: 07 July 2022, Revise Date: 18 July 2022, Accept Date: 24 July 2022

DOI: 10.21608/EJCHEM.2022.149781.6473

temperature, approximately 700-900 °C, than cement, which is burned at 1500 °C [13,14]. In the manufacture of geopolymers, MK has been used as a basis material and in combination with other waste materials. Recent studies recommended mixing metakaolin with industrial waste materials such as fly ash (FA), silica fume (SF), and cement kiln by-pass dust (CKD) [15-18]. Due to their superior mechanical, chemical, and thermal resistance properties, Jindal *et al.*, [2] proposed that MK-based geopolymers can be used in a variety of applications, such as a protective coating of surfaces of different types of materials, including metals, as sustainable concrete, as fireproof building materials, and as environmentally friendly materials. Making use of MK-based geopolymers as "self-cleaning" building materials is another significant application field [19]. Research demonstrated that geopolymers made from metakaolin as a basic material can be considered to be an effective adsorbent for various water pollutants, including heavy metals and dyes [20-27].In continuation of our previous work [28-31], which aims to remove the residual dyes in the dyeing baths, especially when using reactive dyes, our goal in this study is to remove the color of the reactive red 195 dye remaining in the dyeing bath by using geopolymer cement based on metakaolin.

2. Materials and Methods

2.1. Materials

Reactive red 195 was utilized for the decolorization studies. The structures of this dyes is shown (figure 1).

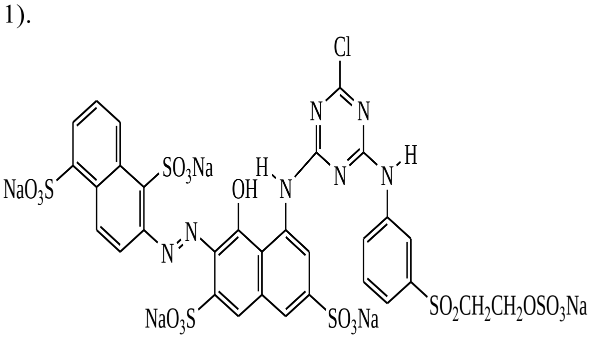

Figure 1. C.I. Reactive Red 195

2.2 Hydrolyzed Reactive Dye Preparation

The reactive dyestuff was hydrolyzed by treatment with solutions of sodium carbonate [5 g/L] and sodium hydroxide (33%) [3 mL/L] with stirring at 80°C for 2 h. At the end, it was neutralized with dilute sulfuric acid after cooling.[32]

2.3. Adsorbent preparation

2.3.1. Starting materials

Metakaolin was provided by Hemts Construction Chemical Company in Cairo, Egypt (chemical composition is shown in Table 1). According to XRF data, silica (SiO_2) and alumina (Al_2O_3), which together make up around 95% of MK, are its principal constituents. Class F fly ash (FA) was supplied by Sika Chemical Company, Burg Al-Arab, Egypt. Calcium hydroxide was obtained from EL-Goumhouria chemical company, Cairo, Egypt. Table (1) summarizes the starting materials' chemical compositions. In this work, sodium hydroxide (NaOH) and liquid sodium silicate (Na_2SiO_3) served as the alkaline activator. The NaOH flakes with 99% purity was acquired from EL-Goumhouria Chemical Company in Cairo, Egypt. Commercial liquid Sodium silicate (Na_2O 11.7 wt%, SiO_2 32.8 wt% and H_2O 55.5 wt%) was produced by Silica Egypt Company, Burg Al-Arab, Alexandria, Egypt. and silica modulus SiO_2/ Na_2O equal 2.80.

2.3. 2. Preparation of geopolymer samples

2.3.2.1 Preparation of Alkaline activator

To produce geopolymer cements, liquid sodium silicate Na_2SiO_3 and sodium hydroxide NaOH are combined as an alkaline activator. By dissolving NaOH pellets in distilled water and allowing the mixture to cool to room temperature, 10M NaOH is prepared. A set ratio of 2.5:1 is used to combine the liquid sodium silicate and sodium hydroxide solution until a clear gel is produced. The alkaline activator solution is formed 24 hours before casting

2.3.2.2. Preparation of specimens:

- As illustrated in Table 2, two different forms of geopolymer pastes are created by combining metakaolin with different ratios of both fly ash (FA) and calcium hydroxide (CH). Table 2 lists the various mixes' constituents as well as the water/solid ratio that produced standard consistency. Each mix's dry ingredients are thoroughly handled and combined to achieve perfect homogeneity.
- In order to create a homogeneous paste, raw components from each dry mix are combined with the alkaline activator solution. Fresh pastes are quickly cast into a stainless steel cube mould with a one-inch dimension. The mould is then vibrated for a short period of time to eliminate all air bubbles and improve paste compaction. A

thin-edged trowel is used to smooth the paste's surface.

- Finally, to prevent drying and allow the pastes 24 hours to set and harden at ambient temperature, or 25°C, the moulds are maintained at a nearly 100% relative humidity. Following this time, the cubes are taken out of the mould and hydrated for 7 days using tap water in a tight plastic container.
- The test cubes are taken, crushed, and added to the ethanol/acetone (1:1) stopping hydration solution. The mixture is stirred on an electrical magnetic stirrer for 30 minutes. The residue is filtered, washed with ethanol, and dried for 24 hours at 50 ^{o}C [33]. The dried samples are ground to a mean particle size of 100 µm and stored in a desiccator.

2.3.2.3. Water of consistency:

Vicate apparatus is used to determine the standard water's consistency in accordance with ASTM specifications [34]. The amount of liquid needed to create a paste with a standard consistency is the same amount needed to create a paste that allows the vicat plunger (10 mm in diameter) to settle to a point 5 to 7 mm from the bottom of the vicat mould

2.4 Adsorption experiments

A certain weight of the adsorbent (0.01- 0.2 g) and 100 mL of dye solution (5-100 ppm) was shaken in the water bath at 140 rpm and 30°C. By filtration we could obtained a supernatant of the samples solutions. By using SHIMADZU spectrophotometer we could estimated the absorbance [at a maximum wavelength (λ_{max} = 504 nm)] with computing concentration of the calibration curve. The Removal efficiency % which indicated the amount of dye adsorbed onto the adsorbent was calculated via the equations [35],

$$qe = (Co - C) V/W \quad (1)$$

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

$$\text{Removal efficiency \%} = 100 (qe / Co) \quad (2)$$

3. Results and discussion

3.1. Characterization of the adsorbent

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

Table (1): Chemical oxide composition of the raw materials as evaluated by XRF, mass %.

Oxides, %	MK	FA
SiO_2	64.80	63.10
Al_2O_3	30.10	26.54
K_2O	----	0.09
MgO	----	0.52
CaO	0.52	2.33
Fe_2O_3	0.55	5.40
Na_2O	0.10	----
SO_3	0.13	----
P_2O_5	0.06	----
TiO_2	2.70	----
Cl^-	----	0.85
Loss on ignition	0.73	----
Total	99.69	98.83

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

Mix Name	MK	FA	CH	Na_2SiO_3 %	NaOH %	L/S ratio
MF1	80	20	----	25	10	0.49
MC1	80	---	20	25	10	0.56

3.2 Factors affecting on the adsorption

3.2.1 Effect of pH

It is noteworthy that figure 2 shows the change in the removal efficiency %when using the dye effluents of reactive red 195 dye under the pH of the adsorption bath. In order to determine the optimum pH value of the metakaolin based – geopolymer mix on the dye treated with metakaolin, it was determined conducted at different pH (2-10). The results from figure 2 show that the maximum removal efficiency % was at pH 3 and pH 2 for both geopolymer cements based on metakaolin MF1 and MC1, respectively. The maximum values were 53% for MF1 and 54% for MC1.

3.2.2 Effect of adsorbent dose

We found that figure 3 reveals the effect of absorbent 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 geopolymer cement, for 120 min using the dye effluents for reactive red 195 with concentration (10 ppm) was at pH 3 for MF1 geopolymer mix and pH 2 for MC1 geopolymer mix. The results of figure 3 show a decreasing in the removal efficiency % by increasing the weight of the absorbent. The maximum removal efficiency % was 53.2% at 0.01 g/100 mL for the MF1 geopolymer mix and it was 54.4% at 0.01 g/100 mL for the MC1 geopolymer mix.

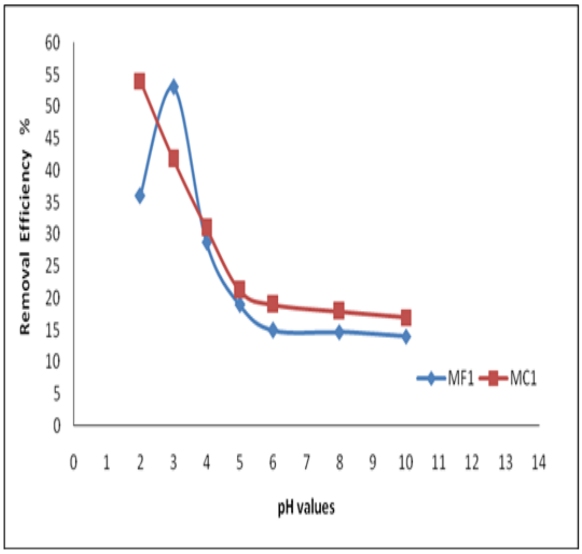

Figure 2. Effect of pH on dye removal efficiency % (Time 120 min, Temperature 30^{o}C, weight of adsorbent 0.01g, concentration of dye 10 ppm)

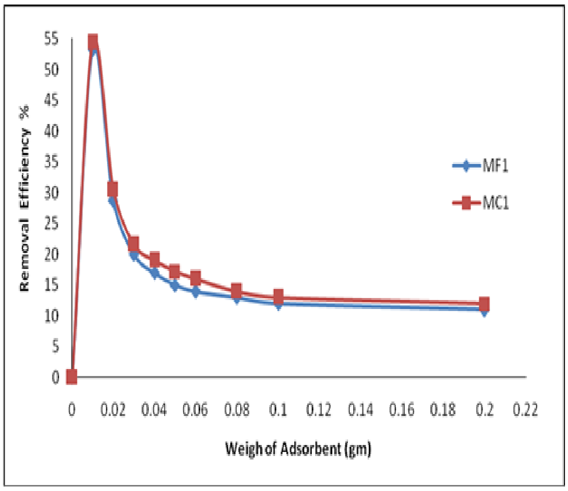

Figure 3. Effect of adsorbent weight on the removal efficiency % (Time 120 min,Temperature 30^{o}C,concentration of dye 10 ppm, pH 3 for MF1 and pH 2 for MC1)

3.2.3 Effect of time

It should also be noted here that in order to determine the optimum duration of interaction of reactive red 195 dye with the geopolymeric cement materials the removal of the dye was carried out for different periods of time (60-300 min). The results of figure 4 show a decreasing in the removal efficiency % by increasing the time. The maximum removal efficiency % was 59.8% at 60 minutes for the MF1 geopolymer mix and it was 67.4% at the same time for the MC1 geopolymer mix

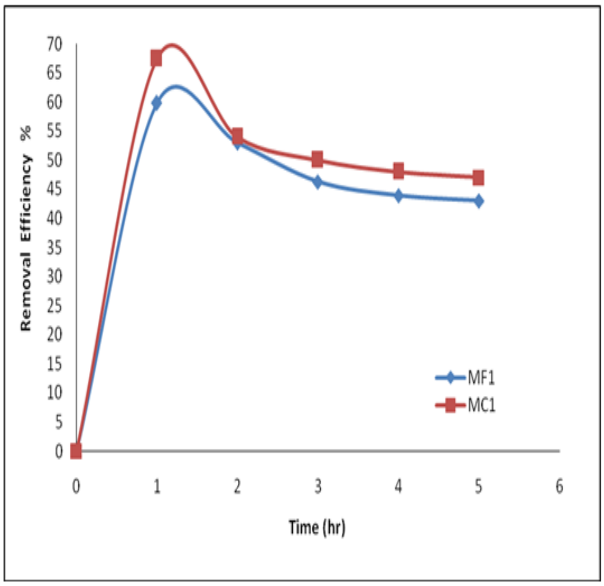

Figure 4. Effect of time on the removal efficiency % (Weight of adsorbent 0.01 g, Temperature 30 ^{o}C, concentration of dye 10 ppm, pH 3 for MF1 and pH 2 for MC1)

3.2.4 Effect of dye concentration

We also found figure 5 reveals that the effect of dye concentration on the removal efficiency % when using constant weight for MF1 and MC1 cured geopolymer cement mixes with both optimum pH and optimum time. The adsorption of decolorization from the dye under investigation was examined with different concentrations of the dye (5 - 100 ppm). The dye effluents concentration (5 ppm) giving maximum removal efficiency % (75%) at pH 3 for MF1 geopolymer mix and (84.5 %) at pH 2 for MC1 geopolymer mix.

Adding calcium hydroxide ($Ca(OH)_2$) to raw MK results in a slightly different reaction in which a network structure and a C-S-H gel form, according to previous research [36]. A calcium silicate hydrate (CASH) precipitate, which is produced when silicon and aluminium react with $Ca(OH)_2$ in a solution, speeds up the decomposition of metakaolin. Granizo *et al.*[36] found that when the fraction of metakaolin increases in the presence of $Ca(OH)_2$, a large amount of amorphous aluminosilicate (C-S-H and C-A-S-H) gels form. Calcium hydroxide generally speeds up geopolymerization and enhances the performance of geopolymer products. Additionally, the pore structure of geopolymer samples could be modified by the addition of calcium hydroxide. [37]

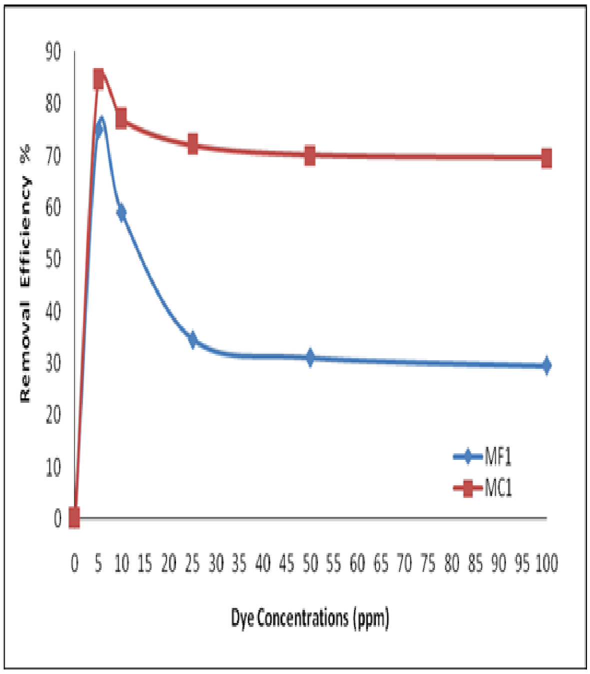

Figure 5. Effect of dye concentration on the removal efficiency % (Weight of adsorbent 0.01g ,Temperature 30 °C, pH 3 for MF1 and pH 2 for MC1, time 60 min)

4. Conclusion

In continuation of our previous study, we would like to point out the importance of using metakaolin-based geopolymer mixes to remove the reactive red 195 dye effluent. The factors that affect the percentage of dye removal were studied, including the adsorbent dose, pH, treatment time, and dye doses.

References

1- Khale D, Chaudhary R , "Mechanism ofgeopolymerization and factors influencing its development: a review", J Mater Sci.,2007, https://doi. org/ 10. 1007/ s10853- 006- 0401-4

2- Jindal B.B., Alomayri Th., Hasan A., Kaze C. 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

3- Ye N., Yang J., Ke X., Zhu J., Li Y., Xiang C., Wang H., Li L., Xiao Bo, "Synthesis and characterization of geopolymer from bayerred mud with thermal pretreatment". J Am Ceram Soc., 2014, https:// doi.org/ 10. 1111/ jace. 12840

4- Duxson, P., Lukey, G.C., Separovic, F., Van Deventer, J.S.J., "Effect of alkali cations on aluminum incorporation in geopolymeric gels." Ind. Eng. Chem. Res. ,2005, 44, 832–839. https://doi.org/10.1021/ie0494216

5- Toniolo, N., Boccaccini, A.R.,." Fly ash-based geopolymers containing added silicate waste. A review. Ceram. Int., 2017, 43, 14545–14551. https://doi.org/10.1016/j.ceramint.2017.07.221

6- 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.

7- 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.

8- Burciaga-Díaz, O., Magallanes-Rivera, R., Escalante-García, J., "Alkali-activated slag-metakaolin pastes: strength, structural, and microstructural characterization". Journal of Sustainable Cement-Based Materials, 2013,2, 111-127

9- Shikuku V., Tome S., Hermann D.T., Tompsett G.A., Timko M.T., "Rapid Adsorption of Cationic Methylene Blue Dye onto VolcanicAsh‑metakaolin Based Geopolymers", Silicon,2021, https://doi.org/10.1007/s12633-021-01637-9

10- Li L, Wang S, Zhu Z "Geopolymeric adsorbents from flyash for dye removal from aqueous solution". J Colloid In-terfaceSci, 2006, 300, 52–59

11- Siyal AA., Shamsuddin R., Rabat NE., Zulfiqar M., Man Z., Low A., "Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution.", J Cleaner Prod,2019, 229, 232–243

12- Tan TH, Mo KH, Ling TC, Lai SH "Current development of geopolymer as alternative adsorbent for heavy metal removal", Environ Technol Inno, 2020, 100684. https:// doi. org/ 10. 1016/j. eti. 2020.100684

13- Daman K. "Panesar, in Developments in the Formulation and Reinforcement of Concrete", Supplementary cementing materials"(Second Edition), (2019)

14- Johnson U. Alengaram, "Valorization of industrial byproducts and wastes as sustainable construction materials"; in Handbook of Sustainable Concrete and Industrial Waste Management, 2022

15- Rovnaník, P., Šafránková, K., "Thermal behaviour of metakaolin/fly ash geopolymers with chamotte aggregate", Materials, 2016, 9, 535.

16- Villaquirán-Caicedo, M.A., de Gutiérrez, R.M., Sulekar, S., Davis, C., Nino, J.C., "Thermal properties of novel binary geopolymers based on metakaolin and alternative silica sources" , Applied Clay Science, 2015, 118, 276-282.

17- Abo-El-Enein, S., Heikal, M., Amin, M., Negm, H., "Reactivity of dealuminated kaolin and burnt kaolin using cement kiln dust or hydrated lime as activators" , Construction and Building Materials, 2013, 47, 1451-1460.

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

19- Kaya-Özkipera K., Uzunbcd A., Soyer-Uzuna S., " Red mud- and metakaolin-based geopolymers for adsorption and photocatalytic degradation of methylene blue: Towards self-cleaning construction materials", Journal of Cleaner Production, 2021, 288, 125120

20- Rasakiae S.A. , Bingxuea Z., Guarecucob R., Thomascd T., Minghuia Y., "Geopolymer for use in heavy metals adsorption, and advanced oxidative processes: A critical review" Journal of Cleaner Production,2019, 213, 42-58

21- Yu Z., Song W., Li J., Li Q., "Improved simultaneous adsorption of Cu(II) and Cr(VI) of organic modified metakaolin-based geopolymer" , Arabian Journal of Chemistry, 2020, 13(3), 4811-4823

22- Lertcumfu N., Jaita Ph., Rujijanagul G., Tunkasiri T., "Characterization of Metakaolin-Based Materials for Dye Adsorption from Aqueous Solution" , Solid State Phenomena, 2018, 283, https://doi.org/10.4028/www.scientific.net/SSP.283.88

23- Kara I. , Tunc D.Y. , Akar S. T., "Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions", Applied Clay Science, 2017, DOI: 10.1016/j.clay.2017.01.008

24- Medria V., Papaa E. Mora M., Vaccariab A. , Murria A.N., Piottec L., Melandria C., Landia E., "Mechanical strength and cationic dye adsorption ability of metakaolin-based geopolymer spheres", Applied Clay Science, 2020, 193, 105678

25-Victor O. Shikuku, Tome S., Hermann D.T., Tompsett G.A., Timko M.T. "Rapid Adsorption of Cationic Methylene Blue Dye onto Volcanic Ash-metakaolin Based Geopolymers" ,Silicon , 2022, https://doi.org/10.1007/s12633-021-01637-9

26- 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.

27- Al-Etaibi, A.M.; El-Apasery,M.A. " Acomprehensive review on the synthesis and versatile applications of biologically active pyridone-based disperse dyes." Int. J. Environ. Res. Public Health, 2020, 17, 4714.

28- Aly A. A., Mahmoud S. A. and El-Apasery M.A. "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- Elapasery M.A.; Ahmed D.A.; Aly A.A., "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

30-. Elapasery M.A.; Ahmed D.A.; Aly A.A., "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

31- Elapasery M.A.; Ahmed D.A.; Aly A.A., "Decolorization of Reactive Dyes, Part IV: Eco-Friendly Approach of Reactive Red 195 Dye Effluents Decolorization Using Geopolymer

Cement Based on Slag", Egyptian Journal of Chemistry, 2022. In press

32 - 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) PP. 227 – 234.

33- Chen X., Meawad A., Struble L.J., "Method to Stop Geopolymer Reaction", Journal of the American Ceramic Society, 2014, 97(10)DOI: 10.1111/jace.13071.

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

35 - Hashem, A., Okeil, A., Fikry, M., Aly, A., Aniagor, C.O. "Isotherm and Kinetics Parametric Studies for Aqueous Hg(II) Uptake onto N-[2-(Methylamino)Ethyl]Ethane-1,2-Diaminated Acrylic Fibre" , Arabian Journal for Science and Engineering, 2021, 46(7), 6703–6714.

36- Granizo, M.L., Alonso, S., Blanco-Varela, M.T., Palomo, A., “Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction” ,Journal of the American Ceramic Society, 2002, . 85, 225-231.

37- Maa B., Luob Y., Zhou L., Shao Z., Liang R., Fu J., Wang J., Zang J., Hu Y., Wangb L., “The influence of calcium hydroxide on the performance of MK-based geopolymer” Construction and Building Materials, 2022, 329, 127224