707 Egypt. J. Chem. Vol. 65, No. 11. pp. 55 - 60 (2022)

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

Decolorization of Reactive Dyes, Part III: Eco-Friendly Approach of Reactive 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*

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

Abstract

Our strategy aims to reduce pollution rates by treating the water generated from the dyeing operations using reactive dyes, by removing the color from yellow effluent 145 using two different types of geopolymer based on metakaolin. Factors affecting decolorization are optimized according to many criteria including adsorbent dose, duration, different pH, and dose of dye used.

Keywords:. Reactive dyes, Geopolymer, Metakaolin

1. Introduction

Portland cement manufacturing is the major cause of global warming-induced by emissions of carbon dioxide. Each 1-ton of ordinary Portland cement results in about 1-ton of carbon dioxide being loaded into the environment and this gas is the major contributor to the greenhouse effect and global warming [1, 2]. One of major advancement in recent years is substitute Portland cement (OPC) by the new class of alkali-activated based cement and concrete material which using industrial wastes and enhanced environmental and strength performance. This new alkali–activated binders which first name as geopolymer by Davidovits, J., in 1999 [3], provides an environmental-friendly alternative to ordinary Portland cement (OPC) and concrete [4]. Geopolymers are a product of the chemical reaction between aluminosilicate and alkali-polysialate in a relatively highly alkaline medium. They have amorphous to semi-crystalline structures with nanoparticle size depend on curing temperatures. Geopolymers are regarded as a green alternative construction materials due to their merits over Portland cement such as low energy consumption, low shrinkage [5], excellent mechanical strength[6], less CO_2 emission [7, 8] and have superior resistance to fire[5, 9].To date, the investigations carried out have used the following raw materials: blast furnace slag, metakaolin, fly ash, kaolinite clay, and red mud to production geopolymer cement. Many recent studies carried out in developing alkali-activated geopolymer binders show that this new binder is expected to become an alternative to Portland cement [10–16]. Metakaolin (MK) is a supplementary cementitious material having highly pozzolanic properties as a result of their amorphous structure and high surface area. It is a thermally activated aluminosilicate material derived from the calcinations of kaolin clay with a temperature range from 700-800^{o}C [17]. MK has been used as a base material and in combination with other waste materials in the preparation of geopolymers. Several studies suggested the combination of metakaolin with industrial waste products for example fly ash (FA) [18], silica fume (SF) [19] and cement kiln by-pass dust (CKD) [20].

*Corresponding author e-mail: elapaserym@yahoo.com.; (Morsy Ahmed Elapasery).
Receive Date: 20 June 2022; Revise Date: 22 June 2022; Accept Date: 22 June 2022.
DOI: 10.21608/ejchem.2022.146023.6356.
©2022 National Information and Documentation Center (NIDOC).

Jindal *et al.* [21] suggested that MK‑based geopolymers can be employed in several applications such as a protective coating of surfaces of different types of materials due to their suitable corrosion resistance abilities, as sustainable concrete, thermal resistance and fireproof building materials. Another significant application area regarding MK-based geopolymers is utilizing as “self-cleaning” construction materials [22].

Different studies showed that geopolymers manufactured from metakaolin as a raw material can be evaluated as a good adsorbent for different water wastes such as heavy metals and dyes [22-31].

The ideal process for treating small amounts of wastewater is the adsorption process [32-42]. We focused in this investigation to eliminate the color of the reactive yellow dye 145 residual in the dyeing bath instead of dumping this hazardous waste without treatment by using metakaolin - based geopolymer cement as a new approach that is environmentally safe.

2. Materials and Methods

2.1. Materials

Reactive yellow 145 was utilized for our investigation through this work. Chemical structure of reactive yellow 145 is publicized (figure 1).

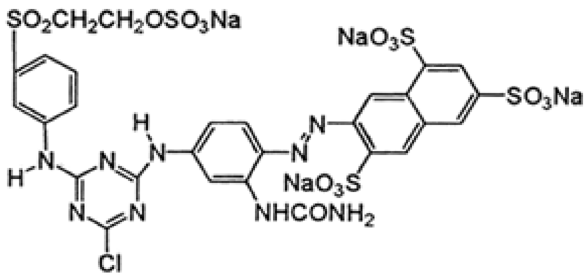

Figure 1. C.I. Reactive Yellow 145

2.2 Preparation of Hydrolyzed Reactive Dye

The reactive dyestuff was hydrolyzed by adding a 3 mL/L NaOH solution (33%) and a 5 g/L sodium carbonate solution, and heating them at 80°C for 120 min. while stirring. Finally, diluted H_2SO_4 was used to neutralise the hydrolyzed colour after it had been cooled [33].

2.3. Adsorbent preparation

2.3. 1. Starting materials

•The materials used in this study are metakaolin (MK), fly ash (FA), in addition to calcium hydroxide (CH).

•The alkaline activator in this study was sodium hydroxide (NaOH) and liquid sodium silicate (Na_2SiO_3).

•Metakaolin (MK) is supplied by Hemts Construction Chemical Company, Cairo, Egypt. Its chemical composition obtained from X-ray fluorescence (XRF) analysis is presented at Table 1. The XRF results exhibited that the major constituents of MK are silica (SiO_2) and alumina (Al_2O_3) that represent about 95%..

•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% Na_2O, 32.8 wt% SiO_2, and 55.5 wt% H_2O and silica modulus SiO_2/ Na_2O 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 (MK, FA, and CH) 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 are given in Table (2).MF1 & MC1 geopolymer pastes are fabricated by mixing metakaolin with different ratios of Fly Ash (FA) and calcium hydroxide (CH) as shown in Table (2).

The alkali activator (AA) is prepared by mixing of liquid sodium silicate (SSL) and sodium hydroxide (SH) (10M NaOH) with fixed ratio then stirred them until a clear gel is obtained. 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 fresh prepare 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 Vicate Apparatus [39]. 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 vicat mold.

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 50ºC for 24 hrs. Then dried samples were ground to obtain a mean particle diameter of 100 µm and stored in a desiccator.

2.5 Adsorption experiments

A specific amount of the adsorbent was shaken with 50 mL of dye solution at 30 oC and 140 rpm. Filtration was used to separate the sample solutions' supernatant.

When utilizing SHIMADZU spectrophotometer to assess absorbance at maximum wavelength (λ_{max} = 475 nm for yellow 145 dye), concentration was calculated using the calibration curve. By using a mass balance relationship, the amount of dye that was adsorbed onto the adsorbent, qe (mg/g), was estimated.

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

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

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

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 starting materials by XRF, mass%.

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

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

Mix No	Mix Name	MK	FA	CH	Na_2SiO_3 %	NaOH %	L/S ratio
1	MF1	80	20	----	25	10	0.49
2	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 yellow 145 dye under the pH of the adsorption bath. In order to determine the optimum pH value of the geopolymer mixes based on metakaolin treated with the dye, it was determined conducted at different pH (2-10). The results from figure 2 show that with all wastewaters, the removal efficiency % decreases with increasing pH. The maximum removal efficiency % was at pH 2 for both geopolymer mixes (MF1 and. MC1). The maximum values were 49.2% for MF1 and 53% for MC1.

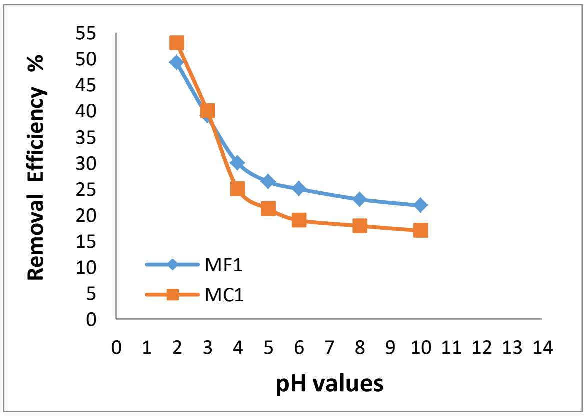

Figure 2. Effect of pH on dye removal efficiency % (Time 120 min, Temperature30°C, weight of adsorbent 0.01g, concentration of dye 10 ppm).

3.2.2 Effect of adsorbent dose

It is important to report here that figure 3 reveals the outcome 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 yellow 145. The dye concentration (10 ppm) was at pH 2 for MF1 and MC1. The results of figure 3 show an increase in the removal efficiency % by increasing the weight of the absorbent until it reaches the maximum value and then decrease.

The maximum removal efficiency % was 57.1% at 0.1 g/100 mL for the MF1 and it was 82.5% at 0.05g/100 mL for the MC1.

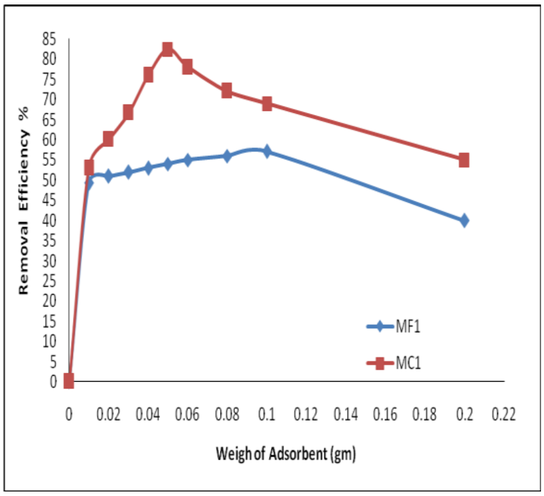

Figure 3. Effect of adsorbent weight on the removal efficiency % (Time 120 min, Temperature 30 °C, concentration of dye 10 ppm, pH 2)

3.2.3 Effect of time

It should also be noted here that in order to determine the optimal duration of interaction of reactive 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 that the removal efficiency % increases by prolonging the adsorption time until it reached a period of 180 minutes achieving the maximum removal efficiency% was 65.4% for geopolymer mix MF1 while, the goal was 99.2% at 240 minutes for geopolymers mix MC1.

3.2.4 Effect of dye concentration

We found that figure 5 shows the effect of dye concentration on the removal efficiency % when using constant weight for MF1 and MC1 cured geopolymer 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) at pH 2 for both MF1and MC1 geopolymer mix, giving maximum decolorization. The maximum removal efficiency % was 75% for MF1 and 100 % for MC1 geopolymer cements**.**

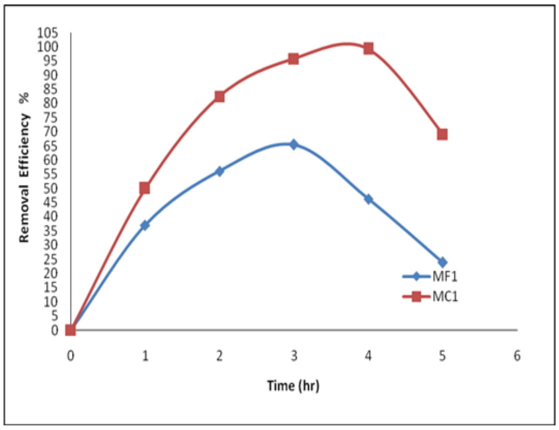

Figure 4. Effect of time on the removal efficiency % (Weight of adsorbent 0.05g for MC1 and 0.1 g for MF1, Temperature 30 ºC, concentration of dye 10 ppm, pH 2)

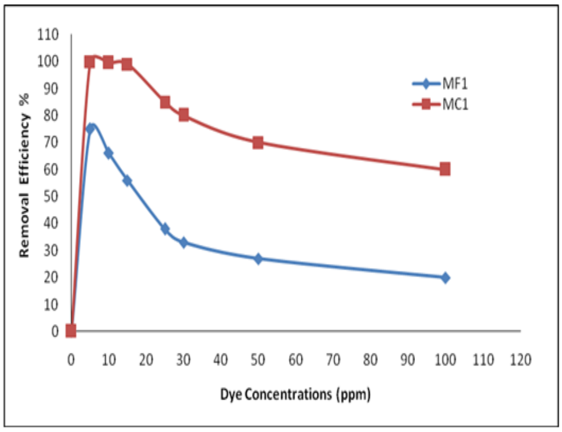

Figure 5. Effect of dye concentration on the removal efficiency % (Weight of adsorbent 0.05g for MC1 and 0.1 g for MF1 , Temperature 30 ^{o}C, pH 2, time 4hrs for MC1 and 180 min for MF1)

The geopolymer specimens with supplementary calcium hydroxide exhibited a more compact structure, a higher bulk density and an enhanced compressive strength performance[40]. $Ca(OH)_2$ react with silicon and aluminium in soln and form CASH precipitation which accelerated dissolution of the metakaolin. According to Granizo et al., [41] increase of metakaolin proportion in the presence of $Ca(OH)_2$ leads to large formation of an amorphous aluminosilicate (C-S-H and C-A-S-H) gels due to the increase in the reactant species. In general, calcium hydroxide accelerates the geopolymerization process and has a positive effect on the performance of geopolymer products [41].

4. Conclusion

The current investigation is the second part, so we can now confirm that the current study is an indication of the use of geopolymer cement based on metakaolin for reactive yellow 145 dye effluents waste. Factors affecting the percentage of dye removal were studied, including adsorbent dose, pH, treatment time and dye dose. According to our results, the maximum adsorption capacity of reactive yellow 145 dye using geopolymer mix MC1 was better than using geopolymer mix MF1, due to the fact that calcium hydroxide speeds up the geopolymerization process and has a favorable impact on the geopolymer's ability to adsorption dye.

References

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

2.CaballeroL.R., Paiva M.d.D.M., Fairbairn E.d.M.R., Toledo Filho R.D.,"Thermal, Mechanical and Microstructural Analysis of Metakaolin Based Geopolymers" Materials Research, 2019, 22.

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

4.Provis J. L., (2018)"Alkali-activated materials", Cement and Concrete Research, 114, 2018, Pages 40-48

5.Zhang Y.J., Li S., WangY.C., "Microstructural and strength evolutions of geopolymer composite reinforced by resin exposed to elevated temperature" Journal of Non-Crystalline Solids, 2012, 358, 620-624.

6.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

7.NobouassiaBewaC., Tchakouté H.K., Fotio D., RüscherC.H., Kamseu E., LeonelliC., "Water resistance and thermal behavior of metakaolin-phosphate-based geopolymer cements". Journal of Asian Ceramic Societies ,2018, 6, 271-283.

8.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.

9.YaoX., ZhangZ., Zhu H., Chen Y., "Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry" ,Thermochimica Acta,2009, 493, 49-54.

10.Revathi T., Vanitha N., JeyalakshmiR., BaskarS., Jegan M.,KannanRajkumar R.R., "Adoption of alkali-activated cement-based binders (geopolymers) from industrial by-products for sustainable construction of utility buildings-A field demonstration", Journal of Building Engineering, 2022, 52 (15) , 104450

11.Mavroulidou M., Gray C. , Gunn M.J.& Pantoja-Muñoz L.,"A Study of Innovative Alkali-Activated Binders for Soil Stabilisation in the Context of Engineering Sustainability and Circular Economy" ,Circular Economy and Sustainability,2021, https://doi.org/10.1007/s43615-021-00112-2

12.Rosales J., AgrelaF.,Díaz-LópezJ.L.,& Cabrera M., "Alkali-Activated Stainless Steel Slag as a Cementitious Material in the Manufacture of Self-Compacting Concrete" Materials (Basel), 2021, 14(14): 3945.

13.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), 1911 – 1926.

14. Selim F.,Ahmed D.A., Kishar E.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.

15.Amranab M., AlFakihc A., Chu S.H., Fediuke R., Harunaf S., AzevedogA.,Vatinh N,. "Long-term durability properties of geopolymer concrete: An in-depth review"Case Studies in Construction Materials, 2021, 15, e00661.

16.BeskopylnyA.N., Stel'makhS.A. ,Shcherban E. M. , Mailyan L.R., MeskhiB. , El'shaevaD. and Varavka V.,"Developing Environmentally Sustainable and Cost-Effective Geopolymer Concrete with Improved Characteristics" Sustainability 2021, 13, 13607 , https://doi.org/10.3390/su132413607

17.Rasekh, H., Joshaghani, A., Jahandari, S., Aslani, F., Ghodrat, M., "Rheology and workability of SCC" Self-compacting concrete: materials, properties and applications, 2021, 31-63.https://doi.org/10.1016/B978-0-12-817369-5.00002-7

18.Rovnaník, P., Šafránková, K.,"Thermalbehaviour of metakaolin/fly ash geopolymers with chamotte aggregate", Materials, 2016, 9, 535.https://doi: 10.3390/ma9070535

19.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.

20.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.
21.Jindal B.B.,Alomayri T., 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
22.Kaya-ÖzkiperaK. ,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.
23.RasakiaeS.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.
24.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.
25.LertcumfuN.,Jaita P., 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
26. Sananmuang, R., Cha-un, N., "Physical characteristics and adsorption propertiesfor reactive dyes of char and activated carbon prepared mangosteen peel and tamarind seed." Naresuan Univ. J., 2007, 15(1), 9-16.
27. Mall, I. D.; Srivastava, V. C.; Agarwal, N. K. "Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash kinetic study and equilibrium isotherm analyses", Dyes and Pigments, 2006, 69, 210-223.
28. Mane, V. S.; Mall, I. D.; Srivastava, V. C. "Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution", Dyes and Pigments, 2007, 73, 269-278.
29. Wong, S.Y.; Tan, Y. P.; Abdullah, A. H.; Ong, S. T.,"The Removal of Basic and Reactive Dyes Using Quartenised Sugar Cane Bagasse", Journal of Physical Science, 2009, 20(1), 59-74.
30. Aysha, T.; El-Sedik, M.; Mashal.; H. M.; El-Apasery, M. A.; Machalický , O.; Hrdina; R. "Synthesis, characterisation, and applications of isoindigo/Pechmann dye heteroanalogue hybrid dyes on polyester fabric", Coloration Technology, 2015, 131(4), 333-341.
31. 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.
32. 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, 2018, 47 (2), 108-115.
33. 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
34. 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) PP. 389 - 394 .
35. Hashem A., 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 ,100011
36- 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
37. Hashem, A.; Aly, A. A.; Aly, A. S.,"Preparation and utilization of cationized sawdust Polymer - Plastics Technology and Engineering", 2006, 45(3), 395-401.
38. Aly, A. A.; Hashem, 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.
39. Designation, A., C191: "Standard test method for normal consistency and setting time of Hydraulic Cement". Annual Book of ASTM Standards, 2008, 172-174.
40. 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.
41. 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.
42. 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