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Kaolin based geopolymer properties: bromothymol blue adsorption

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Abstract

Hydrothermal stability and chemical solubility of metakaolin appear like a promising alternative for geopolymers elaboration, which have excellent properties such as high mechanical strength, long term durability and stability in alkaline and acidic solutions, fire resistance under high temperature; also the outstanding adsorption properties result in geopolymers to be a desired adsorbent.

Therefore, the adsorption of bromothymol blue was done in different concentrations to achieve optimal color degradation.

Keywords: Metakaolin, geopolymer, adsorption, bromothymol blue.

Résumé

La stabilité hydrothermale et la solubilité chimique du metakaolin dans les milieux alcalins apparaissent comme une alternative prometteuse pour l'élaboration des géopolymères, qui ont d'excellentes propriétés telles qu'une résistance mécanique élevée, une durabilité et une stabilité à long terme dans les solutions alcalines et acides, une résistance au feu à haute température; aussi les propriétés d'adsorption exceptionnelles font les géopolymères des prometteurs adsorbants.

Dans ce fait, l'adsorption du bleu de bromothymol a été faite dans différents concentrations dont le but de trouver une dégradation optimale de la couleur.

Mots clés: Métakaolin, géopolymère, adsorption, bromothymol bleu.

المخلص:

يبين الاستقرار الهيدروحراري و القدرة على التحلل في الأوساط القلوية للميتاكاولين إمكانية استغلاله كبديل حديث في صناعة الجيوبوليمار , حيث تبين لنا تمتعه بمثانة و مقاومة ميكانيكية عاليتين في الأوساط الكيميائية حمضية كانت أو قلوية , كما بيّنا تمتعه بقدرة عالية على الامتصاص تجعل الجيوبوليمار مادة ماصة بامتياز .

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الكلمات المفتاحية: ميتاكاولين, الجيوبوليمار, الامتزاز, ازرق البرومثيمول.

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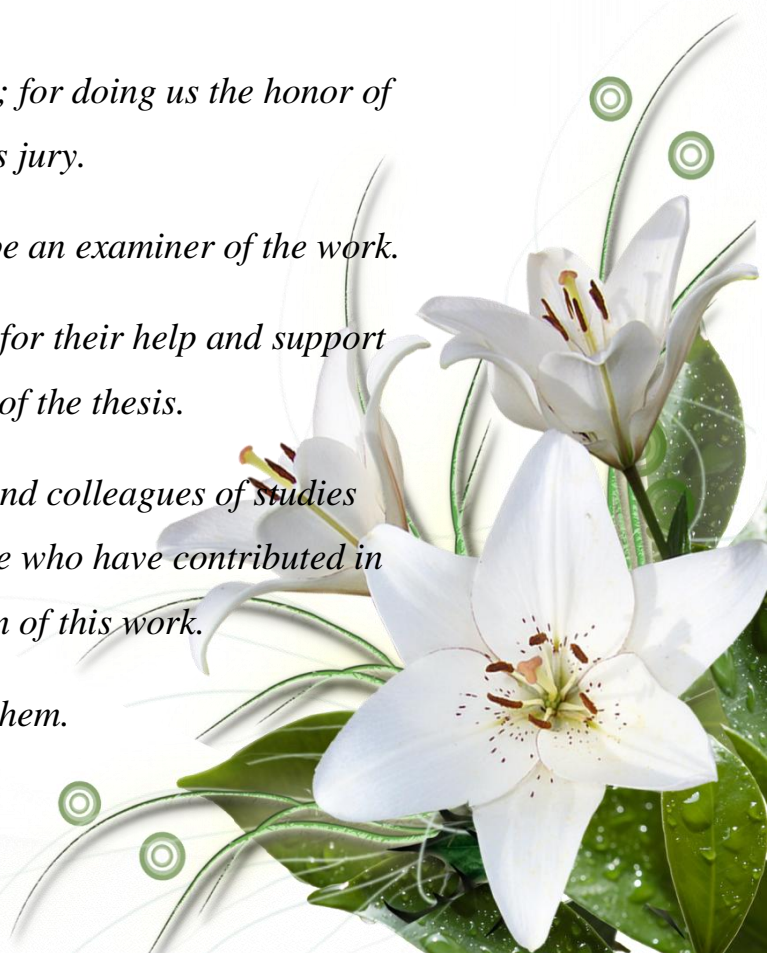
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Dedication

To my first role model, to the one who gave me infinitely, to my constant support and encouragement... to the one I held my head high in pride... to the one whom life did not give me long life... to the soul that I always wanted by my side in this moment...

"To My father Dear God rest his soul... I hope you are proud of me"



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"To My Mother "

To My companion and My Dear Brother.....


To My little princess.. A bird of paradise...My Dear Sister Salsabil, may God have mercy on her.....

To my friends Salah and Hicham

To my best friend Mina.

To my partner Amir

Thank you all





I dedicate this modest work:

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To my brother **Ramy**

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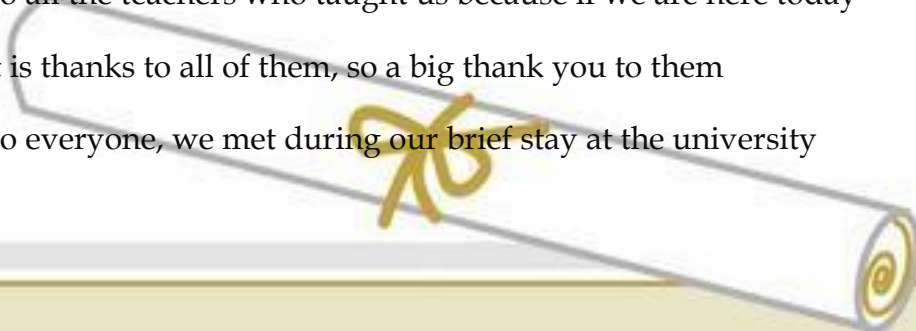
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General introduction:

Geopolymerization of alkali metakaolin is an exothermic reaction occurs at an ambient or slightly elevated temperature [1]. In the last decade, geopolymers are receiving considerable attention because of their excellent properties such as high mechanical strength, long term durability and stability in alkaline and acidic solutions, fire resistance under high temperature and also due to their interest use in diverse applications including refractory materials, biotechnology and building cements[2,3], according to Davidovits, these materials are inorganic polymers resulting from the reaction between aluminosilicate powder and alkali solution [4], these inorganic polymers are composed of tetrahedral silicate and aluminate structural units joined in a random configuration by sharing oxygen atoms [5] although different source materials can be used to prepare geopolymer binders, metakaolin has been extensively used and found to be the most practically suitable due to improvement of mechanical properties especially it can attain high compressive strength of cementation materials at an early age due to the high pozzolanic reactivity and the finer particles filling effect [6,7].

The cheap raw materials and outstanding adsorption properties result in geopolymer to be a desired adsorbent. The chemical structure of geopolymer is a negatively charged aluminosilicate framework balanced by cations (Na^+ , K^+ , or Cs^+), which can be exchanged with cations solution [8,9]. Thus, this feature provides the basis of the removal of cationic dyes.

The aim of this work is adsorption of bromothymol blue by geopolymer synthesized from metakaolin; our work revolves around 5 chapters:

Literature review

Chapter I: Kaolin and Metakaolin

Chapter II: Geopolymers

Chapter III: Dye adsorption

Experimental

Chapter IV: Geopolymer synthesis

Chapter V: Bromothymol blue Adsorption

GENERAL INTRODUCTION REFERENCES

1. Yao, X., Z. Zhang, H. Zhu, and Y. Chen. 2009. Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry. *Thermochimica Acta* 493 (1-2):49-54.
2. Salami, B.A., MagatJohari, M. A., Ahmad, Z. A., Maslehuddin, M., 2016. Impact of added water and superplasticizer on early compressive strength of selected mixture of palm oil fuel ash-based engineered on geopolymer composite, *Constr. Build. Mater* 109, 198-206.
3. Zhang, Z., J. L. Provis, A. Reid, and H. Wang. 2014. Fly ash-based geopolymers: The relationship between composition, pore structure and efflorescence. *Cement and Concrete Research* 64:30-41.
4. Görhan, G., R. Aslaner, and O. Şinik. 2016. The effect of curing on the properties of metakaolin and fly ash-based geopolymer paste. *Composites Part B: Engineering* 97:329-335.
5. V.F.F. Barbosa, K.J.D. MacKenzie, C. Thaumaturgo, Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers, *Int. J. Inorg. Mater.* 2 (2000) 309–317.
6. Kannan, V., and K. Ganesan. 2014. Chloride and chemical resistance of self compacting concrete containing rice husk ash and metakaolin. *Construction and Building Materials* 51:225-234.
7. Keleştemur, O., and B. Demirel. 2015. Effect of metakaolin on the corrosion resistance of structural lightweight concrete. *Construction and Building Materials* 81:172-178.
8. T. Luukkonen, H. Runtti, M. Niskanen, E. Tolonen, M. Sarkkinen, K. Kemppainen, J. Rämö, U. Lassi, Simultaneous removal of Ni(II), As(III), and Sb(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers, *J. Environ. Manag.* 166 (2016) 579–588.
9. K. Al-Zboon, M.S. Al-Harabsheh, F.B. Hani, Fly ash-based geopolymer for Pb removal from aqueous solution, *J. Hazard. Mater.* 188 (2011) 414–421.

Teoretical part



CHAPTER I

Kaolin and Metakaolin



In china, 1,800 years ago, the first porcelains were made from weathered materials of granite from a hill called “Kao Ling” (high hill), near Jingdezhen in Jiangxi province. In English, the term kaolin is often referred to as “china clay”.

The use of kaolin in Europe began from the 17th century, first for ceramics, before extending to the paper industry (which is the main current use), refractories, paint fillers, plastics, rubber, and fiber glass.

Kaolin essentially results from the alteration of rocks rich in feldspars, mainly acid rocks (granite, granodiorite, and pegmatite). The products of this alteration remain on site : this is the “residual kaolin”, also called “primary kaolin”. In the case where the weathering products undergo transport and then deposition, we speak of “secondary kaolin”. The latter represent the major part of the reserves[1]. .

1. Kaolin:

1.1. Definition:

The name of kaolin is derived from Chinese term ‘Kao-ling’ meaning high ridge, the name for a hill near Jauchau Fu, where this material was mined centuries ago for ceramics [2].

Fig 1 shows the typical view of kaolin. The main constituent, kaolinite is a hydrous aluminium silicate of approximate composition $2\text{H}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$.



Fig 1: Kaolin

Kaolinite is the clay minerals which provide the plasticity of the raw material and change during firing to produce a permanent material. Structurally, kaolinite consists of alumina octahedral sheets and silica tetrahedral sheets stached alternately with the theoretical composition of 46.54%SiO₂, 39.5% Al₂O₃ and 13.96%H₂O. The arrangement of atoms in the kaolinite group is shown in **Fig 2**. The kaolinite crystals are pseudo-hexagonal along with plates, some larger books, and vermicular stacks [3].

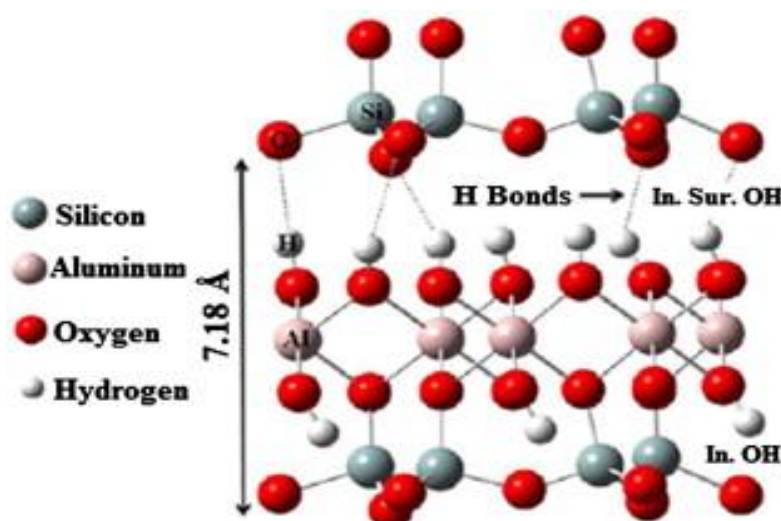


Fig 2: Schematic structural of kaolinite [4].

The physical and chemical properties of kaolin determine its use as an industrial mineral. These uses are governed by several factors including the geological condition under the kaolin formed, the total mineralogical composition of the kaolin deposit, the physical and chemical properties.

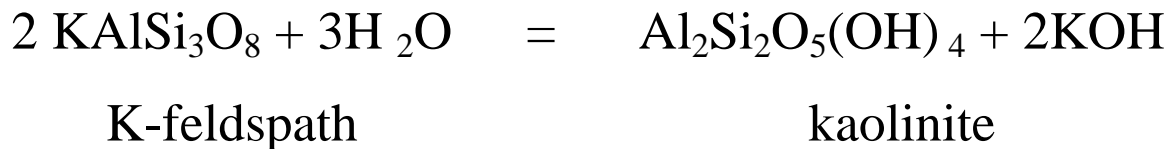
Kaolin has the particle size ranging from 0.2 to 15 μm with the specific area of 10,000–29,000 m^2/kg . The 2 μm point as the commercial control point [5]. The coarser kaolin is usually used as filler clays and the finer materials are normally used as coating products. The shape and distribution of kaolin are important factors in controlling many other properties such as equivalent diameter and determined by sedimentation method from a flocculated suspension of clay in water.

Kaolin is one of the most widely used industrial minerals; its world's total output exceeds 25 million tones [6]. Kaolin is an extremely useful mineral raw material. Its properties of white color, softness, small particle size and chemical inertness make it suitable for a number of different industrial applications. However kaolin is widely used in various industrial applications, such as production of cement, ceramics, porcelain and bricks [7, 8–9]. It is also used as filler for paint, rubber and plastics [7, 8–9]. It is a conventional raw material for coatings, fire-proof materials, chemicals, medicines, textiles and petroleum [10]. The greatest demand for kaolinite is in the paper industry where it is used to produce high-quality coated paper [11–12], pigments and aluminium industries. Kaolinite has also found applications in medicine, in toothpaste, in cosmetics and as a food additive. Currently, a

specially formulated spray has been used on fruit and vegetables while growing, to repel insects and prevent sun burn [13].

1.2. Formation:

Kaolinite is formed by the chemical weathering of feldspath. In the case of potassium feldspath, the reaction is as follows:



Kaolin deposits can be of primary or secondary origin

- **Primary kaolin** (resulting from in situ processes linked to meteoric and/or hydrothermal fluids).
- **Secondary (or sedimentary):** kaolin according to the classic source, transport and deposition model. In this memento, it is about kaolin clays.

1.2.1. Primary kaolin:

Primary deposits are residual deposits resulting from the weathering in place, of rocks rich in feldspar, by meteoric agents or by hydrothermal solutions.

Primary or residual kaolin deposits have kaolin contents that generally vary from 15 to 50%. The grade and composition of the deposit depends on several factors including the nature of the original rock, the degree and type of weathering. The alteration of granite produces kaolin which contains quartz and mica and, if the kaolinization is not complete, there will be feldspar. In general, plagioclases are the first feldspars to be kaolinized while K-feldspars weather more slowly and give kaolins which contain fine crystals of illite, sericite and hydromuscovite[14].

Most of the kaolin deposits found in Quebec are residual deposits resulting from the hydrothermal or meteoric alteration of Precambrian feldspathic rocks. These include feldspathic quartzites, quartz monzonites and anorthosites.

1.2.2. Secondary kaolin:

Secondary deposits are sedimentary deposits resulting from the transport and sedimentation of kaolinite from primary deposits. Secondary deposits are generally richer in kaolinite than primary or residual kaolin deposits. In secondary deposits, kaolinite occurs in finer crystals.

Following the erosion of the residual kaolin deposits, sediments are transported by waterways, washed and stripped of their impurities. This process allows finer, lighter particles of kaolinite to settle in still waters of lakes or estuaries, producing exceptionally pure kaolins (85-95% kaolinite), virtually free of sandy particles [15]. On the other hand, when the deposit of kaolinite is done in a more disturbed marine environment, the kaolin can contain a high quantity of sand.

The only secondary deposits of kaolin were found in the Schefferville area in Cretaceous sediments that originally covered the iron deposit of the Redmond mine. They were completely removed during the operation of the mine.

Some examples of kaolin deposits in the world:

Bassin des Charente (France), Cypress Hills (Alberta, Canada). Eastend, Wood Mountain, Ravenscrag (Saskatchewan, Canada). Moose River Basin (Ontario, Canada), Shubenacadie Valley (Nova Scotia, Canada), Aiken (Caroline-du-Sud, USA), Wrens, Sandersville, Macon-Gordon, Andersonville (Georgia, USA), Eufaula (Alabama, USA). Guelma, Djebel Debagh (a mountain of eastern Algeria).

1.3. Mineralogical structure of kaolinite:

The Kaolinite belongs to a dioctahedral 1:1 layer structure of clay minerals, with the general composition of $[Al_2Si_2O_5(OH)_4]$. Ka, a layered silicate mineral, consists of nanometer thick layers. The individual silicate layer is composed of one tetrahedral sheet of silica (SiO_4) and one octahedral sheet of alumina (AlO_6). The silica and alumina sheets are linked to each other covalently in layers. Adjacent layers are linked to one another with hydrogen bonds, involving oxygen atoms situated in the silica sheet and hydroxyl groups in the alumina sheet (Al-O-H.....O-Si).

There are two types of hydroxyl groups in the structure. Inner-surface hydroxyls existed on the interlayer surfaces and inner hydroxyls located inside the layers, between the two different sheets. The distance between two opposite layers, the interlayer spacing, is $d=0.71$ nm. The individual layers are further linked by dipole– dipole interactions and van der Waals forces [16, 17]. In addition, the cation exchange capacity of Ka is low ((3-15) meq/100g) [18].

As above-mentioned characteristics of Ka, the Ka layers are strongly held together by hydrogen bonding and by dipolar interaction. Therefore, intercalation, that is, the reversible insertion of a molecule or ion into layered compounds, is difficult in the case of Ka. Consequently, the Ka is not optimal nano-filler for nano-composites. To overcome these limitations, the modification of Ka is necessary for increasing the interlayer distance. Further, the intercalation of any compound is it organic or inorganic, between the layers of Ka causes a breaking up the hydrogen bonding between the layers. Therefore, guest molecules acquire the ability to arrive at the reactive aluminol groups. These groups could be reacted with organic molecules; thus, the modified Ka is possible to be used in nano-composites [19].

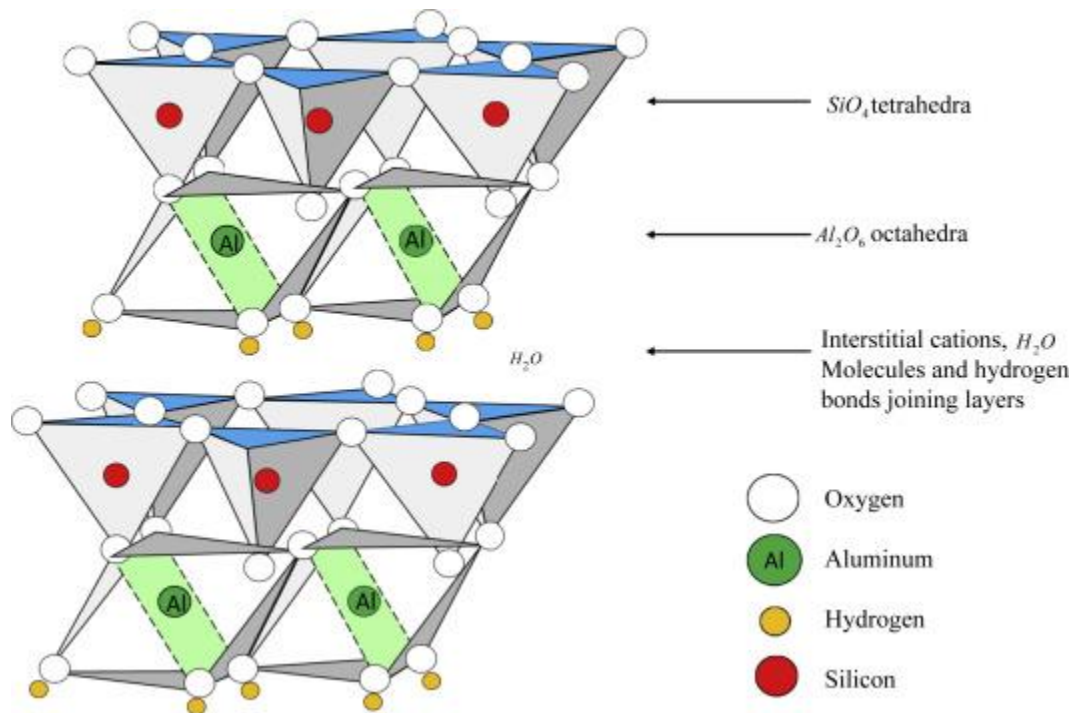


Fig 3: Mineralogical structure of kaolinite [20].

1.4. Morphology:

The morphology of the crystals is generally quite regular. These are in the form of a hexagonal plate (Fig 4 a), sometimes elongated or reduced to simple diamonds, delimited by the basal faces (001) and the lateral faces (110), (110) and (020) (Fig 4 b). [21].

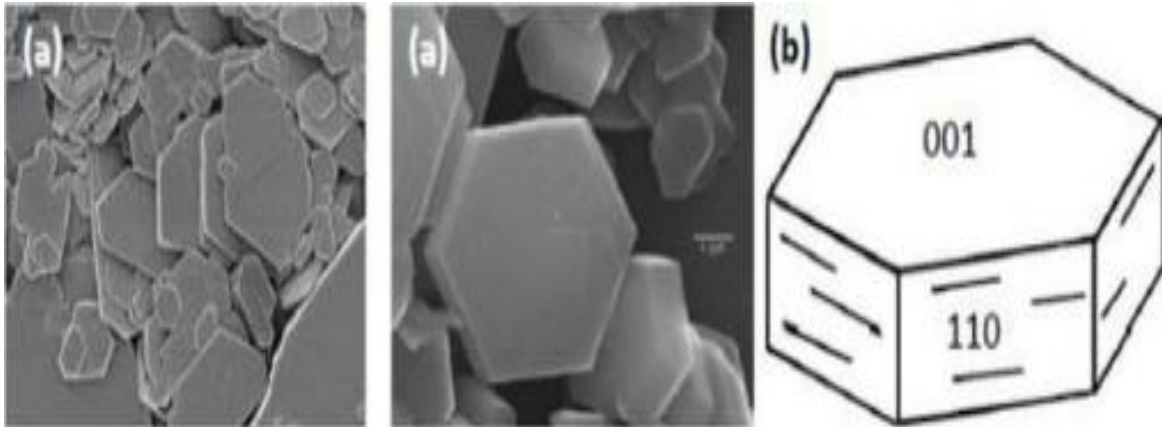


Fig 4: (a) Morphology of a very well crystallized kaolinite and (b) representation of a kaolinite plate

Example of kaolin type:

DD3 extracted from a mountain of eastern Algeria (DjebelDebagh).

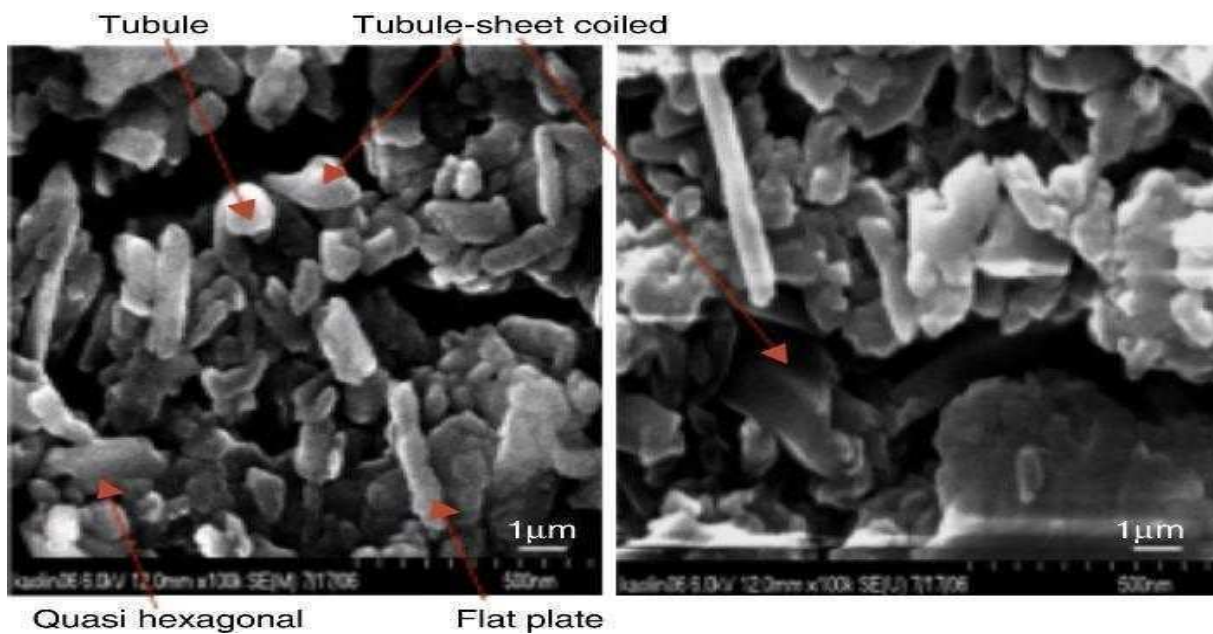


Fig 5: SEM observation of DD3 kaolin [22].

1.5. Chemical composition of kaolin:

The chemical composition of kaolin expressed as a percentage by mass (% by mass) of oxides is given in (table 1)[22].

	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	TiO ₂	P ₂ O ₅
Kaolin	50.5	31.5	0.07	0.1	0.66	0.9	1.87	2.26	0.08

Table 1: Chemical Composition (% by Mass) of Kaolin [22].

Kaolin is mainly composed of SiO₂ (50.5% by weight) and Al₂O₃ (31.5% by weight). In addition to alkali and alkaline earth metal oxides such as K₂O, MgO, Na₂O and CaO. There is also a small amount of coexisting transition metal oxides (Fe₂O₃ and TiO₂) [22].

1.6. Granulometric composition of kaolins:

Kaolins are polydispersed rocks composed of three main fractions of particles:

1. The fraction of particles smaller than 2 microns is attributed to kaolinite.
2. The fraction of particles larger than 20 microns is attributed to quartz.
3. The intermediate fraction known as dust composed of particles of 2 to 20 microns.

1.8. Kaolin properties:

- Low hardness (2 on the Mohs scale);
- High degree of whiteness;
- High alumina content (Al₂O₃) which makes it an excellent refractory;
- Very fine granularity and good opacity due to the lamellar form of kaolinite crystals.

2.1. Metakaolin:

2.1. Definition:

Metakaolin is an ultrafine inorganic, pozzolanic or latent hydraulic material which can be incorporated into concretes in order to improve certain properties or to obtain special properties according to standard NF EN 206-1.

It is obtained by calcining kaolin or kaolin clays at temperatures between 650 and 900°C. Kaolin or kaolin clays undergo a destructuring of their initial crystalline structure during calcination. This dehydration of the mineral leads to an amorphous nature of the material.



Metakaolin meets standard NF P 18-513 – Pozzolanic addition for concrete – Metakaolin – Definition, specifications and compliance criteria.

2. 2. Chemical and mineralogical compositions:

2. 2. 1. Chemical composition: Some of components:

Chemical composition	Cement (%)	Metakaolin (%)
Silica (SiO ₂)	34	54.3
Alumina Al ₂ O ₃	5.5	38.3
Calcium oxide CaO	63	0.39
Ferric oxide calcium(Fe ₂ O ₃)	4.4	4.28
Magnesium oxide (MgO)	1.26	0.08
Potassium oxide (K ₂ O)	0.48	0.50
Sodium oxide Na ₂ O	1.92	0.22
Sulphuric anhydride	1.92	0.22

Table 2: Chemical compositions of metakaolin

2. 2. 2. The mineralogical composition:

The mineralogical composition of metakaolin depends on the chemical composition of the source rock of the material and its thermodynamic path: heat treatments (calcination, deshydroxylation), chemical treatments, wet transport, etc.

The oxides are divided into the phases below [23]:

- Between 65 and 85% metakaolinite without residual hydroxyl.
- Between 5 and 25% of totally dehydroxylated muscovite.
- Between 7 and 13% quartz (SiO₂).

2.3. Main industrial uses of kaolin:

Since ancient times, kaolin has been the basic raw material for fine ceramics, due to its high melting temperature and its white color. However, over the years, the particular properties of kaolin related to its whiteness and its fineness of grinding have led to new uses:

- raw material in the manufacture of fine ceramics and refractory products (bricks, cements, mortar);
- mineral filler or additive in the manufacture of paper;
- inert filler in paints, plastics and rubber;
- source of alumina and silica in the manufacture of cement and fiberglass;
- preparation of pharmaceuticals;
- food additives and bleaching agents;
- manufacture of plaster, granules for roof coverings;
- Textile manufacturing.

2.3.1 Ceramic:

Clays are the most consumed and also the oldest materials in the ceramic industry.

A good knowledge of the relationship between the composition of clay (especially the mineralogical composition) and its physico-chemical properties is essential. The technical specifications sought for the manufacture of fine ceramics are as follows (technical sheet “Clays for fine and refractory ceramics”):

- ✓ Predominant kaolinite content; - undesired coloring elements (clays cooking white): $\text{Fe}_2\text{O}_3 < 2\%$, $\text{TiO}_2 < 2\%$.
- ✓ The presence of quartz may be desirable, except for the refractory.
- ✓ Presence of feldspars, micas, illite and calcite at levels $< 25\%$, desired for sandstone products (sandstone clays).
- ✓ Presence of smectite (content $< 5\%$), halloysite and desired organic matter (improved plasticity).
- ✓ Presence of gypsum and soluble salts prohibited [24]:.



Fig 6: Ceramics

2.3.2.Refractory:

Refractory materials are used in production processes that involve contact with corrosive substances at high temperatures.

Refractory materials must be inert with the substances with which they are in contact, they must be mechanically resistant and thermally stable ($T_{\text{fusion}} > 1500^{\circ}\text{C}$).

The main uses of fireclay relate to the manufacture of refractory bricks, chamottes (fired clay used as a "degreaser" in ceramic products) and various accessory utensils, such as crucibles, boats, retorts, and glassware pot, used in metallurgical industries [25,26]. Quartz,

ignition loss, iron compounds and alkali are minerals that play negative roles on the properties of refractory products.



Fig 7: Refractories

2.3.3. Construction materials:

Kaolin is used in the construction industry or in the manufacture of cement [27]. Kaolins calcined at low temperature, or metakaolins, have very high pozzolanic characteristics, which make them excellent additives for mortars and concretes based on Portland cement. Kaolin, as a source of alumina, replacing common clays, rich in iron, makes it possible to avoid the presence of iron for the production of white cement. Metakaolins are of particular interest to users of white cements, as well as manufacturers of mortars and technical concretes.

2.3.4. Paper:

The largest user of kaolin is the paper industry where it is used as filler material and in the sheet and as a coating on its surface. Properties that are important for paper coating are dispersion, rheology, gloss, whiteness, refractive index, softness, tackiness, film break strength, receptivity to ink, which condition the print quality. Only a few kaolins in the world can be used for paper coating due to stringent viscosity and whiteness requirements [28].

2.3.5. Medical and cosmetic applications:

Kaolin has a long tradition of use in medical and cosmetic applications. These markets require the highest levels of purity and product specifications which, of course, come at quite a considerable cost [29].

Applications in medicine and pharmaceuticals:

Kaolin is used as a diluent and supplement in medicines and poultices, for example when mixed with morphine. The absorbent properties of kaolin can reduce the rate at which a drug is released into the body and even the actual amount absorbed by the body. The amount of kaolin varies considerably depending on the application, between 7.5% and 55% kaolin in absorbent applications, around 25% in dusting powders, and up to 55% for poultices.

Applications in cosmetics:

The main use for kaolin in beauty products is foundation. Foundations are a mixture of tinted and scented powders used to improve the appearance of the skin. The amount of kaolin in a foundation can vary from 3% in a loose powder to 10% in a heavy formulation powder.

Kaolin competes with precipitated calcium carbonate (PCC) as a filler in cosmetics, but kaolin is still considered far superior for this application. Kaolin is used in the formulation of lipsticks.

CHAPTER I REFFERENCES

- [1] DIRECTION GÉNÉRALE DES DOUANES. 25070080 - Argiles kaoliniques. Disponible sur : http://lekiosque.finances.gouv.fr/Appchiffre/LEO/frame_LEO.asp.Page17.
- [2] Hamer Frank. Clay. Watson Guptill; 1977. p. 15–36.
- [3] Murrar Haydn H. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Appl Clay Sci* 2000;17:207–21.
- [4] Caglar Bulent, ÇırakÇag ırı, Tabak Ahmet, AfsinBeytullah, ErenErdal.Covalent grafting of pyridine-2-methanol into kaolinite layers. *J MolStruct* 2013;1032:12–22.
- [5] Murray HH. Overview: clay mineral applications. *Appl Clay Sci* 1991;5(5– 6):379–95.
- [6] Nkoumbou C, Njoya A, Njoya D, Grosbois C, Njopwouo D, Yvon J, et al. Kaolin from Mayouom (Western Cameroon): industrial suitability evaluation. *Appl Clay Sci* 2009;43:118–24.
- [7] Prasad MS, Reid KJ, Murray HH. Kaolin: processing, properties and applications. *Appl Clay Sci* 1991;6(2):87–119.
- [8] Murray HH. Overview – clay mineral application. *Appl Clay Sci* 1991;5: 379–95.
- [9] Murray HH. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Appl Clay Sci* 2000;17:207–21.
- [10] Prasad MS, Reid KJ, Murray HH. Kaolin: processing, properties and applications. *Appl Clay Sci* 1991;6(4):87–119.
- [11] VehoJagl, Gomes C de SF. Characterization of Portuguese kaolins for the paper industry: beneficiation through new delamination techniques. *Appl Clay Sci* 1991;6:155–70.
- [12] Murray HH, ElzeaKogel J. Engineered clay products for paper industry. *Appl Clay Sci* 2005;29:199–206.
- [13] Schupp JR, Fallahi E, Chun I-J. Effect of particle film on fruit sunburn, maturity and quality of Fuji and Honeycrisp apples.*ISHS ActaHortic* 2004; 636:551–6.
- [14] BRISTOW, C. W., 1990. The Genesis of the China Clays of South-West England – A Multistage Story, Abstract, Clay Minerals Society 27th Annual Meeting, Columbia, MO, page 27.

CHAPTER I REFERENCES

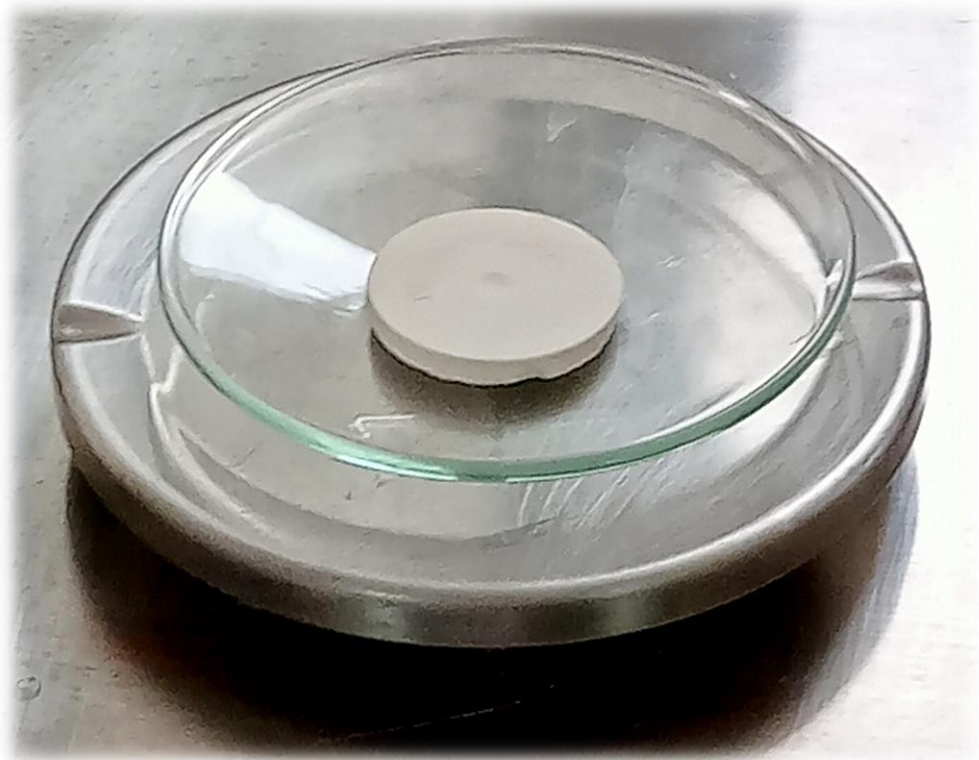
- [15] PRASAD, M.S., REID, K.J. et H. H. MURRAY, 1991. Kaolin : processing, properties and applications. Applied Clay Science, 6, 87-119.[olin.jsp](#)
- [16]Uwins, P. J.; Mackinnon, I. D.; Thompson, J. G.; Yago, A. J. Clays and clay minerals 1993, 41, 707-717.
- [17] Ke, Y.; Stroeve, P. Polymer-Layered Silicate and Silica Nanocomposites; Elsevier: Amsterdam, the Netherlands 2005.
- [18] Carroll, D., Geological Society of America Bulletin 1959, 70, 749-779.
- [19] Dedzo, G. K., Detellier, C. Applied Clay Science 2016, 130, 33-39.
- [20] O. Rivera ; o. Pavez, J. Li Kao, A. Nazer, Metallurgical characterizations ok kaolin from Atacama, Chile, Rem Revista Escola de Minas, 2016.
- [21] LACHTER Boutheyna, KHAN Mohamed Salah Kaolin, DD3 de Djebel Debagh Guelma : Caractérisation et utilisation dans la l'élaboration d'un ciment composé. Université du 08 Mai 1945 de Guelma, Septembre 2020.
- [22] Y. Dong, X. Feng, D. Dong, S. Wang, J. Yang. «Elaboration and characterization of tubular macroporous ceramic support for membranes from kaolin and dolomite »ay 2007
- [23] Garcia-Diaz E (1995)., Réactivité pouzzolanique des métakaolinites : corrélations avec les caractéristiques minéralo-gitologiques des kaolinites, Thèse de Doctorat de l'École des Mines de Saint-Etienne.
- [24] DIRECTION GÉNÉRALE DES DOUANES. 25070080 - Argiles kaoliniques. Disponible sur : http://lekiosque.finances.gouv.fr/Appchiffre/LEO/frame_LEO.asp page 75.
- [25] Pasquet J.F, "Le kaolin, mémento roches et minéraux industriels", Chapitre I. Généralités sur les argiles, les kaolins et leurs applications industrielles 33, BRGM, 1988.
- [26] Helgeson H.C, Garrels R.M, Mackenzie F.T. " Evaluation of irreversible reactions in geochemical processes involving mineral and aqueous solutions: II applications Geochim. Cosmochim". Acta, 33, 1969. 455-481upérieure de mines de Saint-Etienne (France), le 23 Septembre 2012.
- [27] Eppler A.R. "Glazes and glass coatings»; The American Ceramic Society. Published, 2000.
- [28] Bormans P., "ceramics are more than clay alone". Cambridge international science publishing, 2004

CHAPTER I REFFERENCES

[29] Cases J.M, Cunin P, Grillet Y., Poinson C, Yvon J., "Methodes of analysing morphology of kaolinites : relations between crystallographic and morphological properties " Clay Minerals, Vol.21, 1986, pp. 55-68.

CHAPTER II

Geopolymers



1.1. What is it?

Geopolymers (GPs) are aluminosilicate inorganic polymers, cured at ambient temperatures from a liquid precursor. The strained nature of the 5-coordination aluminum cation polyhedral is identified as the reason why metakaolin-based geopolymer ceramics are made from solution, rather than with high temperature diffusion. The microstructure of alkali based geopolymers is nano-porous and nano-particulate. This enables carbothermal reduction and carbothermal nitridation under flowing argon or nitrogen, in the presence of excess carbon to produce nano-particles of silicon carbide (SiC), silicon nitride (Si₃N₄) or SiAlON from geopolymers. Crystallized geopolymer composites have been developed having tailor able thermal expansion coefficients. Intrinsic mechanical properties as well as those of geopolymer composites are summarized for composites containing ceramic, polymeric as well as biological reinforcements. Amorphous glass frit-containing geopolymer composites undergo amorphous self-healing upon heating above the melting point of the glass. Amorphous self-healed geopolymer (ASH-G) refers to composites below ~950°C where the geopolymer is still amorphous, while ASH-C denotes amorphous self-healed ceramic where the geopolymer matrix has crystallized. [1]

1.2. A History of Geopolymers:

Geopolymers recently emerged as a new class of inorganic aluminosilicate polymeric materials. These materials were synthesized for the first time in 1940 by A. O. Purdon [2] and again in the late 1950's by Glukhovsky [3]. The term geopolymer was introduced by Davidovits [4] in the early 70's to denote their inorganic nature (—geo) and structural similarity to organic polymers (—polymers), and is commonly used nowadays [5, 6].

These inorganic polymers are processed by polycondensation of aluminum and silicon monomeric or oligomeric species in metal alkali-activated solutions [4]. The GP precursors can be obtained from different aluminosilicate sources such as clays, Metakaolin, and industrial waste (fly-ash or furnace slug). Alkali hydroxide solutions are added to the aluminosilicate source to activate the dissolution and polymerization process. The activating solutions are based on aqueous solutions of alkali hydroxides and the most commonly used metal alkaline activators are Na and K [6]. However, other metals from group I and II of the periodic table as well as NH₄⁺, and H₃O⁺ may also be utilized for synthesis [7, 8].

The silicon content of the final product can be manipulated by the addition of SiO₂ to the alkaline aqueous solution. After mixing, K-silicate and Na-silicate solutions with aluminosilicate sources, the material is placed in molds and cured usually at temperatures

below 100 °C for various periods of time [9]. According to Davidovits, the resulting GP structure can be characterized as a 3-D matrix of tetrahedrally coordinated Si and Al species. The negatively charged aluminum anions are balance by the positively charged metal cations in the 3-D network structure of geopolymers [4].

1.3. The mechanism to form a geopolymer:

The Geopolymerization mechanism is not fully understood and varies depending on the precursors and activation solution. However, the general reaction can be separated into three different steps with overlapping phases [10].

1. Deconstruction, dissolution of the solid state.
2. Polymerization.
3. Stabilization.

Deconstruction:

In an alkaline environment, aluminum oxide and silicium oxide are dissolved from the solid precursor and form aluminate ($\text{Al}(\text{OH})_4^-$) and silicate ($[\text{SiO}_x(\text{OH})_y]_z^-$). The major silicate species are $[\text{SiO}(\text{OH})_3]^-$ and $[\text{SiO}_2(\text{OH})_2]_2^-$, with the concentration ratio of $[\text{SiO}_2(\text{OH})_2]_2^-$ to $[\text{SiO}(\text{OH})_3]^-$ increasing with pH [11].

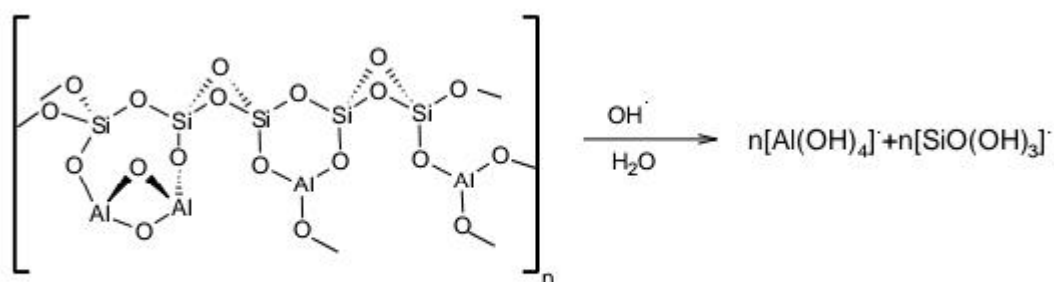


Fig 8: Reaction of deconstruction

Polymerization:

After dissolution of the solid species, aluminates and silicates are formed. The following condensation reaction between aluminate and silicate is a nucleophilic substitution reaction. An example of this reaction between $[\text{Al}(\text{OH})_4]^-$ and $[\text{SiO}(\text{OH})_3]^-$ is shown below.

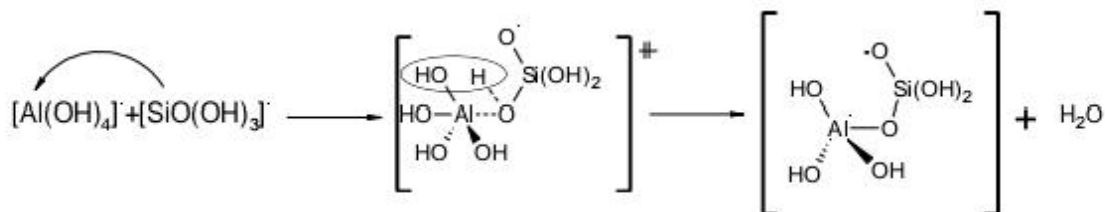


Fig 9: The reaction $[Al(OH)_4]^-$ and $[SiO(OH)_3]^-$

The monomers in a nucleophilic substitution react to form an aluminatesilicate oligomeric; from which an amorphous polymer is produced. This polymer forms a gel which subsequently hardens [12].

Stabilization:

The oligomers undergo a further condensation reaction and release the water which was consumed during the hydrolysis. With this gelation, the system starts to rearrange and reorganize, resulting in a three-dimensional aluminosilicate network that is relatively resistant to dissolution in water [13].

2. Synthesis and Properties of Geopolymers:

2.1. Geopolymers Synthesis:

GP materials are usually synthesized using an aluminosilicate raw material and an activating solution which is mainly composed of alkalis of sodium or potassium and water-glass [14]. A GP contains a variety of semi-crystalline or amorphous phases and it is a three-dimensional aluminosilicate mineral polymer, furthermore, the network structure of GP consists of $Si(OH)_4^-$ and $Al(OH)_4^-$ linked alternately by sharing oxygen [15,16].

In recent years, researchers have done a lot of research on the GP material synthesis for further improving its performance. J.J.Trochez used a spent fluid catalytic cracking catalyst as precursor to prepare GPs, and the study found that increased SiO_2/Al_2O_3 was beneficial to the formation of GPs, but the mechanical strength was reduced [17]. In addition, there are many researches on the preparation process of GPs. Jean Noël Yankwa Djobo studied the effects of different preparation process conditions on the reactivity of volcanic ash [18].

Results showed that the reactivity of volcanic ash in alkaline solution is lower than that of other aluminosilicate, but the reaction activity increases slightly with the increase of concentration and curing temperature. Prinya Chindaprasirt has found that the use of outdoor

heat exposure (OHE) for curing polypropylene (PP) fiber-reinforced GP composite can achieve the purpose of saving energy [19]. Solar energy is sustainable and renewable energy for OHE-curing of GP composites leading to strong bridging properties between the PP fiber and the matrix, and strong composites.

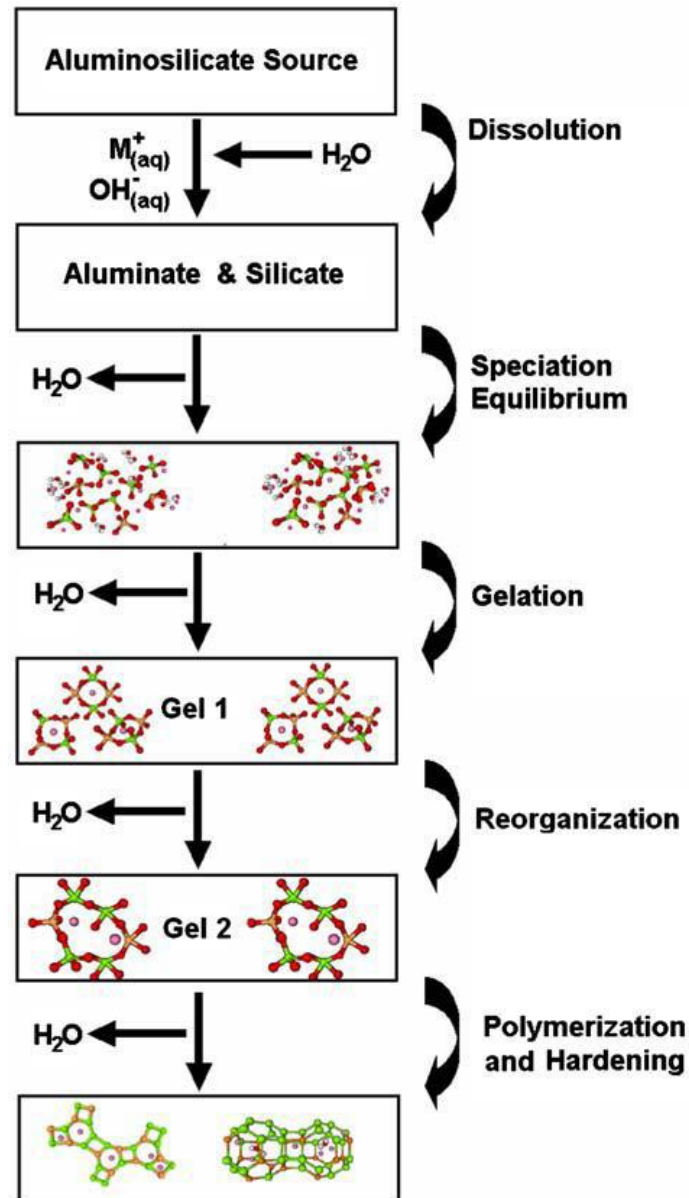


Fig 10: Conceptual model for nano structural evolution of geopolymers by duxon et al

2.2. The Properties of Geopolymers:

2.2.1. Environmental friendliness:

GPs, an environmental protective silicon aluminates inorganic material, whose products can significantly reduce the carbon footprint in their preparation and application process; and in the nature world, various containing silicon and aluminum oxide can be used to synthesize GP. For instance, GP concrete is a building material with high application potential. It can reduce the amount of CO₂emissionsto a large extent, and the maximum can be 86% lower than that of Standard Ordinary Portland cement [21].

2.2.2. Rapid hardening and high strength:

GP has the characteristics of high early strength and fast setting time .In recent years; researchers have done a lot of research on GP owing to its high mechanical strength. Du revealed that using SiC can obviously enhance the compressive strength of GP composites. When the content of SiC is 10wt%, the compressive strength of GP composites can reach 155MPa, which is equivalent to increasing 100% on the basis of unfilled GP [10].

2.2.3. High temperature resistance and heat insulation:

The oxidation reaction and decomposition reaction of the GP products between 1000-1200 °C are not possible, and they are stable under high temperature. The linear shrinkage at 400°C and 800°C are0.2% to 1% and 0.2% to 2%, respectively, and the original strength above 60% can be maintained [22]. This shows better mechanical strength at elevated temperature.

2.2.4. Good corrosion resistance and durability:

GPs show good stability in acidic solutions and in various organic solvents. In 5wt. % hydrochloric acid and sulfuric acid solution, the decomposition rate of GP were only 1/13 and1/12 of it of Portland cement, respectively. GP can form compact structure with high strength and excellent impermeability.

2.2.5. Strong interfacial bonding ability:

At the interface between the traditional Portland cement and the aggregate, the transition zone of calcium hydroxide enrichment and preferred orientation is easy to occur, resulting in weak interfacial bonding force. And for GP, the transition zone does not appear due to the reason that the hydration reaction of calcium silicate does not exist, and the final product is a three-dimensional network of gel, which combined with the aggregate interface.

2.2.6. Immobilizing toxic metal ions:

Mallows and others believe that metal ions are also involved in the formation of GP structures, so that metal ions in the system can be more effectively fixed.

3. The Application of GPs:

The excellent properties of GPs determine their broad application and development prospects, and the main applications are as follows.

3.1. Innovative GP Binder and Sustainable Repair Material:

Utilization of GP binder has been extensively investigated for its low shrinkage, high early strength, sulfate attack and corrosion, high resistance to thawing and freezing. Used in civil engineering, it can greatly shorten the stripping time, speed up the template operation cycle, and improve the construction speed. One-part GP mixtures is a new type of geopolymeric binders, which can be used to simplify the process of activating GPs in silicate solution. At the temperature of 950°C, Peng has performed thermal treatment of low-quality kaolin, and the strength of the corresponding binders is up to 47MP, which could reach comparable strength with two-part mix systems [23]. Nasvi revealed that GP cement is suitable for storage wells under deep down-hole stress conditions and carbon capture owing to its good acid resistance, high mechanical strength, durability and low permeability [24].

GP cement is regarded as potential replacement of Portland cement. This is mainly based on the properties and sustainability criteria.

3.2. GP-Type Coatings:

The GP can be connected into the network structure of film material through the aluminum tetrahedral and silicon tetrahedral, so as a kind of inorganic coating, with non-toxic environmental protection, low cost, fireproof and waterproof etc. Various proportions of β -SiC were used to prepare the GP-type paints by A. Khosravanihaghighi, and the results show that, by increasing the proportion of nano-SiC, the porosity is reduced, and the corrosion resistance and wear resistance are improved [25]. In addition, reflective heat insulation GP coating was synthesized from metakaolin and sodium silicate solutions as main initial raw material, and talcum powder, hollow glass microspheres and sericite powder are added as fillers [26].

The properties of two hybrid type GP concrete composed of alkaline-activated metakaolin and fly ash has been studied by Ana Maria Aguirre-Guerrero, and it was treated as protective coatings against chloride-induced corrosion in its application [27].

3.3. Novel Ceramic Materials:

Compared with the hydrothermal and the sol-gel methods, GP technology provides a new method for the direct synthesis of final structural ceramics. GPs can form a structure comparable to those of high temperature sintered ceramics, and the low temperature GP ceramic is convenient for forming products of various complex shapes and has good overall performance.

3.4. Sealing Materials for Industrial Toxic Waste Residue:

Harmful heavy metals can be produced from modern industry, agriculture, disposal of waste and others. GP technology can transform industrial solid waste containing aluminosilicates into useful products thanks to the flexibility and capability to immobilize and stabilize the wastes inside the GP network. Metals such as Co, Cu, Pb, Cd, Ni, Zn, Pd, As, Ra and U can be incorporated in the 3 dimensional GP network decreasing the mobility of the heavy ions through metal hydroxide precipitation, ion substitution or physical encapsulation [28].

3.5. GP Based Self-Cleaning Concrete Materials:

Severe air pollution is mainly caused by industrial production, natural disasters, engineering construction and automobile exhaust, etc. Thus building facilities will become dirty when exposed to the pollute air. This problem has forced the industries to develop alternative materials for supporting the sustainable development. GP based self-cleaning concrete material is green alternative for solving the problem owing to their unique properties; And the self-cleaning performance of GP based concrete are studied by introduction of photo-catalytic materials such as ZnO and TiO₂ [29].

3.6. GP Biological Materials:

GP composite has the advantages of non-toxic, biocompatibility, good drug carrying capacity and sufficient mechanical strength, etc., which can be used as oral drug delivery carrier. Metakaolin-based Na GP has been reported as an appropriate carrier for the powerful synthetic the sedative drug zolpidem and opioid analgesic drug fentanyl [30].

Further more, the ion exchange property of GP has been developed into germicidal material with potential application prospect of water purification, and it has a great application prospect in water-scarce countries.

3.7. Anti-corrosive coating for marine concrete:

Zhang et al. [31] reported the potential of geopolymer as anti-corrosive coating for marine concrete. These authors studied the bonding strength, the durability in concentrated seawater, the permeability and the volume stability under the ambient conditions, also

performed trial coating on concrete surface at Hangzhou Bay (Shanghai) and examined the hardening behavior of geopolymer coating layer.



Fig 11: The use of geopolymer as anti-corrosive coating for marine

3.8. The Applications of Other Fields:

GPs have a wide variety of applications in other field sowing to its excellent properties. For example, there are some of the following:

- Thermal shock refractories;
- Fire-resistant materials, thermal insulation, foams;
- Environmentally friendly adhesive for wood based panels and modern biotechnology;
- High-tech carbon fiber materials used inside and outside of aircraft;
- Dielectric materials for electronic packaging and molecular sieve catalysts material.

CHAPTER II REFERENCES

- [1] <https://www.sciencedirect.com/topics/materials-science/geopolymer>
- [2] A. O. Purdon, "The action of alkalis on blast furnace slag," *Journal of the Society of Chemical Industry*, vol. 59, pp. 191-202, 1940.
- [3] V. D. Glukhovskiy, G.S. Rostovskaja, and G.V. Rumyna, "High strength slag-alkaline cements," *Communications of the 7th International Congress on the Chemistry of Cement*, vol. 3, pp. 164-168, 1980.
- [4] J. Davidovits, "Geopolymers - inorganic polymeric new materials," *Journal of Thermal Analysis*, vol. 37, pp. 1633-1656, Aug 1991.
- [5] F. Pacheco-Torgal, J. Castro-Goines, and S. Jalali, "Alkali-activated binders: A review Part 1. Historical background, terminology, reaction mechanisms and hydration products," *Construction and Building Materials*, vol. 22, pp. 1305–1314, 2008.
- [6] J. Davidovits, *Geopolymer Chemistry and Applications*, 2nd ed. Saint-Quentin, France: InstitutGeopolymer, 2008.
- [7] L. Weng and K. Sagoe-Crentsil, "Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I—Low Si /Al ratio systems," *Journal of Materials Science*, vol. 42, pp. 2997-3006, 2007.
- [8] K. Sagoe-Crentsil and L. Weng, "Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part II. High Si/Al ratio systems," *Journal of Materials Science*, vol. 42, pp. 3007-3014, 2007.
- [9] P. Duxson, "Geopolymer technology: The current state of the art," *Journal of Materials Science*, vol. 42, pp. 2917-2933, 2007.
- [10] (Provis and van Deventer, 2007b, Yao et al., 2009)
- [11] (Weng et al., 2005, Panias et al., 2007)
- [12] (Provis et al., 2005a).
- [13] (Fernández-Jiménez et al., 2006, Provis and van Deventer, 2007a).
- [14] Du F P, Xie S S, Zhang F et al 2016 *Composites Part B Eng.***105**93
- [15] Balcikanli M, Ozbay E 2016 *Compos Part B Eng.***91**243
- [16] Izquierdo M, Querol X, Davidovits J, Antenucci D, Nugteren H, Fernández-Pereira C 2009 *J. Hazard. Mater***166** 561
- [17] Trochez J J, Gutiérrez RM, Rivera J, Bernal S A 2015 *Materiales de Construcción***65**46
- [18] Djobo J N Y, Elimbi A, Tchakouté H K, Kumar S 2016 *J Mater Sci***51**10301
- [19] Chindaprasirt P, Rattanasak U 2017 *Clean Techn Environ Policy***19**1985

CHAPTER II REFERENCES

- [20] Duxson, P., A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo and J. S. J. van Deventer (2007a). "Geopolymer Technology: the Current State of the Art." *Journal of Materials Science* **42**(9): 2917-2933.
- [21] McLellan B C, Williams R P, Lay J, Riessen A V, Corder G D 2011 *J. Clean. Prod***19**1080
- [22] Wang E, Wen N, Sun H 2005 *Multipurpose Utilization of Mineral Resources***2** 30
- [23] Peng M X, Wang ZH, Shen S H, Xiao Q G 2015 *Mater. Struct***48**699
- [24] Nasvi M C M, Rathnaweera T D, Padmanabhan E 2016 *Geomech. Geophys. Geo-energ. Geo-resour***2**245
- [25] Khosravanihaghighi A, Pakshi M 2017 *J Aust Ceram Soc***53**909
- [26] Zhang Z T, Wang K T, Mo B H, Li X F, Cui X M 2015 *Energy and Buildings***87**220
- [27] María Aguirre-Guerrero A M, Robayo-Salazar R A, Gutiérrez R M D 2017 *Appl Clay Sci***135**437
- [28] Guo X, Hu W, Shi H 2014 *Constr. Build. Mater* **56** 81
- [29] Norsaffirah Zailan S, Mahmed N, Bakri Abdullah M M A, Sandu AV 2016 *Mater Sci Eng***133**012026.
- [30] Jämstorp E, Strømme M, Bredenberg S 2012 *J. Pharm. Sci***101**1803.
- [31] Zhang, Z., Yao, X., Zhu, H., 2010b. Potential application of geopolymers as protection coatings for marine concrete II. Microstructure and anticorrosion mechanism, *Appl. Clay Sci.* 49, 7–12.

CHAPTER III

Dye adsorption



Introduction:

Industrial developments in recent years have left their impression on the environmental society. Many industries like the textile industry used dyes to color their products and thus produce wastewater containing organics with a strong color, where in the dyeing processes the percentage of dye lost wastewater is 50% of the dye because of the low levels of dye-fiber fixation [1]. Discharge of these dyes in to effluents affects the people who may use these effluents for living purposes such as washing, bathing and drinking [2]. Therefore it is very important to verify the water quality, especially when even just 1.0 mg/L of dye concentration in drinking water could impart a significant color, making it unfit for human consumption [3]. Furthermore dyes can affect aquatic plants because they reduce sunlight transmission through water. Also dyes may impart toxicity to aquatic life and may be mutagenic, carcinogenic and may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system [4–5].

The removal of color from waste effluents becomes environmentally important because even a small quantity of dye in water can be toxic and highly visible [6]. Since the removal of dyes from waste water is considered an environmental challenge and government legislation requires textile wastewater to be treated, therefore there is a constant need to have an effective process that can efficiently remove these dyes [7].

In spite of the availability of many techniques to remove these pollutants from wastewaters as legal requirements, such as coagulation, chemical oxidation, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation, these methods are not very successfully due to suffering from many restrictions [8]. Among all of these methods adsorption has been preferred due to its cheapness and the high-quality of the treated effluents especially for well-designed sorption processes [9]. Adsorption by activated carbon is an important way to clean up effluents and wastewater [10], where it used to polish the influent before it is discharged into the environment [11].

However adsorption by activated carbon has some restrictions such as the cost of the activated carbon, the need for regeneration after exhausting and the loss of adsorption efficiency after regeneration [12]. Therefore adsorption by agricultural by-products used recently as an economical and realistic method for removal of different pollutants has proved to be an efficient at removing many types of pollutants such as heavy metals [13,14], COD [15,16], phenol [17,18], gasses [19] and dyes [20–21,22].

In order to increase the adsorption capacity of the adsorbent, researchers have followed different activation methods and they usually used the Langmuir isotherm to indicate the effectiveness of the activation process. Activation methods involve physical activation such as carbonization of material and chemical activation such as using chemical activating agents. Real textile wastewater is a mixture of dyes, organic compounds, heavy metals, total dissolved solids, surfactants, salts, chlorinated compounds, chemical oxygen demand and biological oxygen demand [23, 24].

Therefore some studies tested the agricultural wastes as adsorbents for these pollutants. Ahmad and Hameed [16] studied the reduction of color and COD using bamboo activated carbon, and they found that the maximum reduction of color and COD were 91.84% and 75.21%, respectively. Anionic and cationic surfactants may effect on the dye adsorption depending on the dye type. The adsorption of the basic dyes can be enhanced in the presence of anionic surfactant, on other hand the adsorption of anionic dyes can be enhanced in the presence of cationic surfactant. The negative ion of surfactant may be adsorbed on the adsorbent by van der waals interaction and then the anionic dye can be adsorbed by anionic exchange. Although high concentrations of surfactants may cause aggregation or dye solubilization thus decreases the dye adsorption [25, 26].

1. Adsorption:

The term adsorption refers to the accumulation of a substance at the interface between two phases (liquid-solid interface or gas-solid interface). The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent [27]. Adsorption can be classified into two types; chemical sorption and physical sorption. Chemical adsorption or chemisorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface, which is generally due to the exchange of electrons [28] and thus chemical sorption generally is irreversible. Physical adsorption or physisorption is characterized by weak Van der Waals intra particle bonds between adsorbate and adsorbent and thus reversible in most cases [28]. Adsorption on most of the adsorbent including agricultural by-products is controlled by physical forces with some exception of chemisorption. The main physical forces controlling adsorption are Van der Waals forces, hydrogen bonds, polarity, dipole-dipole π - π interaction, etc. [29].

This Process provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step

before its application [27]. As for environmental remediation purpose, adsorption techniques are widely used to remove certain classes of chemical contaminants from waters, especially those that are practically unaffected by conventional biological wastewater treatments [27, 28]. Adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce the harmful substances [30]. Factors that influence the adsorption efficiency include adsorbate adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH and contact time [30,28] etc.

1.2. Factors Affecting Adsorption of Dye:

There are many factors affecting dye adsorption such as solution pH, temperature, initial dye concentration, etc. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment process. In this section, some of the factors affecting adsorption of dyes are discussed below:

Effect of initial dye concentration :

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In General, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration [31]. Zhang et al. [32] studied the adsorption of Methyl Orange by Chitosan/Alumina interface and it was found that when the Methyl Orange concentration increased from 20 mg/L to 400 mg/L, the percentage of dye removal decreased from 99.53% to 83.55% with the same MB concentration range. Yagub et al. [33] studied the effect of initial dye concentration on the adsorption of methylene blue (MB) by pine leaves and they noticed that as the initial dye concentration increase from 10 to 90 mg/L, the percentage removal of dye decreased from 96.5 to 40.9% on increasing the initial dye concentration from

10 to 90 mg/L after 240 minutes. Fig 2 showed that the amount of CR dye adsorption increased with increase initial dye concentration.

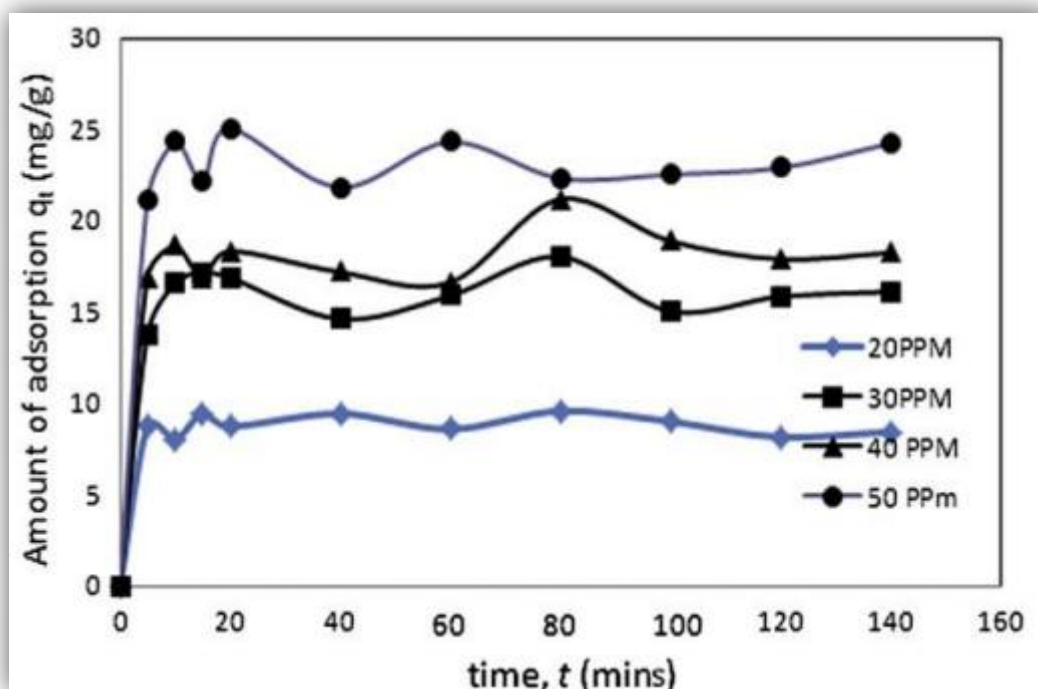


Fig 12: Effect of Initial MB Dye Concentration on the adsorption of CR onto raw pine cone [34].

✚ Effect of Temperature :

Effect of temperature is another significant physio-chemical process parameter because temperature will change the adsorption capacity of the adsorbent [35]. If the amount of adsorption increases with increasing temperature then the adsorption is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption [36].

✚ Effect of Amount of Adsorbent :

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of

sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for ability of a dye adsorption to be adsorbed with a smallest amount of adsorbent, so as to recognize the capability of a dye from an economical point of view [36].

2. Adsorption Principles:

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, bimolecular or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by the other atoms and thus, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

- **Physisorption:** It is a type of adsorption in which the adsorbate adheres to the surface through Van der Waals (weak intermolecular) interactions.
- **Chemisorption:** It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area. Separation occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid [37].

3. Dye adsorption:

3.1. Classification of dyes:

In the dye molecules there are two important components: chromophores which are responsible for producing the color and auxochromes which enhance the affinity of the dye toward the fibers [38]. Generally, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes [39], where azo derivatives are the major class of dyes that are used in the industry today [40]. Table 1 shows the typical dyes used in textile dyeing operations. Dyes can be classified

into cationic, anionic and nonionic dyes. Cationic dyes are basic dyes while the anionic dyes include direct, acid and reactive dyes [41]. Recently, numerous studies have been reported

Dye class	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, applied in weakly acidic dye baths ; very bright dyes
Direct	Water-soluble, anionic compounds ; can be applied directly to celluloses without mordants (or metals like chromium and copper)
Disperse	Not Water-soluble
Reactive	Water-soluble, anionic compounds ; largest due class
Sulfur	Organic compounds containing sulfur or sodium sulfide
Vat	Water-insoluble ;Water-insoluble; oldest dyes; more chemically complex

Table 3: Typical dyes used in textile dyeing operations [39].

Acid dyes :

It is a sodium salt of a sulfonic, carboxylic or phenol organic acid. It is soluble in water and possesses affinity for amphoteric fibers. It is used for nylon, wool, paper, leather, food, cosmetics etc.

Basic dyes :

They yield colored cations in solution and this is the reason for calling them cationic dyes. This type of dye finds uses in paper, modified nylons and polyesters, medicine etc.

Direct dyes :

These are water soluble anionic dyes. These are used for dyeing of cotton and rayon, paper, leather etc.

Disperse dyes :

These are substantially insoluble nonionic dyes. These are used mainly on polyester and also applied on nylon, cellulose, acrylic fibers etc.

Sulfur dyes :

These types of dyes have intermediate structures. They form a relatively small group of dyes, but the low cost and good wash fastness properties make it very important from the economic point of view. Its main uses are for cotton and rayon.

Reactive dyes :

They have a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The prime reason to make them classified among the most permanent of dyes is the covalent bond that attaches reactive dyes to natural fibers. They find their uses for cotton, wool and nylon.

Solvent dyes :

These type of dyes are generally non-polar or little polar and thus, are water insoluble. They are used for plastics, gasoline, lubricants, oils etc.

Vat dyes :

This type of dye is water insoluble and incapable of dyeing fibers directly. But, reduction in alkaline liquor produce the water soluble alkali metal salt of the dye, which, in this leucoform, has an affinity for the textile fiber. These are used mainly for cotton, wool and nylon.

3.1.1. Cationic dyes:

Cationic dyes are widely used in acrylic, wool, nylon and silk dyeing. These dyes include different chemical structures based on substituted aromatic groups [42]. This group of dyes is considered as toxic colorants and can cause harmful effects such as allergic dermatitis, skin irritation, mutations and cancer [43]. These dyes are also called basic dyes and depend on a positive ion, which are generally hydrochloride or zinc chloride complexes [44]. Cationic dyes carry a positive charge in their molecule, further more it is water soluble and yield colored cations in solution. Cationic functionality is found in various types of dyes, mainly in cationic azo dyes and methane dyes, also in anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, various polycarbocyclic and solvent dyes. The anthraquinone dyes are expensive and weak while the azo dyes have good properties, strength us reducing cost [45]. Basic dyes are highly visible and have high brilliance and intensity of colors [41]. Cationic dyes were used intensely as a model in dye adsorption studies such as Crystal violet [46], Methylene blue [47,48], Basic blue 41 [49] and Basic red 46 [50]. Methylene blue is an important basic dye and widely used in the textile industry. Acute exposure to Methylene blue may cause increased heart rate, shock, vomiting, cyanosis, quadriplegia, heinz body formation and tissue necrosis in humans [51]. Many researchers have studied the adsorption of Methylene blue dye using agricultural solid wastes such as peanut hull [52], castor seed

shell [53], coconut shell [54], guava leaf [55], neem leaf [56] and gulmohar plant [57], where the dye adsorption capacities were 123.5, 158, 277.9, 295, 351, 186.22 mg/g respectively. All these wastes showed good adsorption capacities for Methylene blue dye adsorption.

3.1.2. Anionic dye:

Anionic dyes depend on a negative ion [44]. Anionic dyes includes many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g. azoic, anthraquinone, triphenylmethane and nitro dyes) but possess as a common feature, water solubilizing, ionic substituents. The anionic dyes also include direct dyes, and from the chemicals and point the group of anionic azo dyes includes a large proportion of the reactive dyes [45]. Most of the reactive dyes including a reactive group and interact with cotton, wool, etc to form covalent bonds. There lease of reactive dyes into the environment is undesirable, because they have a low degree of fixation due to the hydrolysis of reactive groups in the water phase [58]. Acid dyes are used with silk, wool, polyamide, modified acrylic and polypropylene fibers. Acid dyes have good water solubility; on the other hand they have a harmful effect on human beings since they are organic sulphonic acids [59]. Many researchers have studied the adsorption of anionic dyes using different adsorbents such as the removal of Acid scarlet, Acid turquoise blue and Indigo carmine by organo-bentonite [5], Reactive brilliant red, Acid fuchsine, Orange IV and Methyl orange by ammonium-functionalized MCM-41(member of the mesoporous molecular sieves M41S family) [60], Reactive Yellow 4 (RY4) by apatitic tricalcium phosphate and apatitic octocalcium phosphate [61], Red reactive 141 by wood-shaving bottom ash [22], Brilliant yellow using sepiolite [62], Acid black 26, Acid green 25 and Acid blue 7 by pine cone [63] and Acid blue 80 by bagasse ash [64]. In the last few years agricultural solid wastes have been used intensely as low-cost, available adsorbents for the adsorption of anionic dyes such as mango seed [65], soy meal [66], bag7asse [67,66] and bamboo [68].

4. Dye bromothymol blue (BTB)

Triphenylmethane dye bromothymol blue (**BTB**), which belongs to the family of anionic dyes. **BTB** is a chemical compound often used as a colored indicator of **pH**, and it has halochromic properties. The acid form is yellow (**pH<7**) and the basic form is blue (**pH>7**). It is widely used in biomedical, biological, and chemical engineering applications.

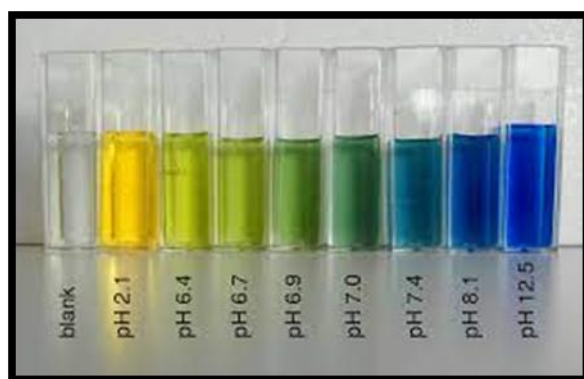


Fig 13: Different colors of bromothymol blue at marked pH conditions

The degradation of this dye has been studied by many researchers. H. Ayoub et al [69] carried out photo degradation of the dye (BTB) using TiO_2 as a catalyst. In their work, L. Cao et al [70] and M. S. E. Farida et al [71] studied the adsorption of BTB on QCF (quaternized cellulose fibers) and on bentonite carbon composite, respectively. M. Ghaedi et al [72] and H. Tavakkoli et al [73] used gold nanoparticles loaded activated carbon (Au-NP-AC) and nanoparticles of perovskite type for the elimination of BTB. Y. Zheng et al [74] studied the photo catalytic performance of MgO in the degradation of BTB. A. Ameri et al [75] carried out a photo catalytic bleaching of BTB using biogenic selenium nanoparticles.

CHAPTER III REFERENCES

- [1] N. Mohan, N. Balasubramanian, C.A. Basha, Electrochemical oxidation of textile wastewater and its reuse, *J. Hazard. Mater.* 147 (2007) 644–651.
- [2] M.K. Sharma, R.C. Sobti, Rec effect of certain textile dyes in *Bacillus subtilis*, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 465 (2000) 27–38.
- [3] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, *Waste Manage.* 27 (2007) 1129–1138.
- [4] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Patabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, *J. Biores. Technol.* 87 (2003) 129–132.
- [5] D. Shen, J. Fan, W. Zhou, B. Gao, Q. Yue, Q. Kang, Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems, *J. Hazard. Mater.* 172 (2009) 99–107.
- [6] M.S. Chiou, P.-Y. Ho, H.-Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, *J. Dyes Pig.* 60 (2004) 69–84.
- [7] J.W. Lee, S.-P. Choi, R. Thiruvengkatachari, W.-G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, *J. Dyes Pig.* 69 (2006) 196–203.
- [8] M.T. Sulak, E. Demirbas, M. Kobya, Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran, *J. Biores. Technol.* 98 (2007) 2590–2598.
- [9] R. Qadeer, Adsorption behavior of ruthenium ions on activated charcoal from nitric acid medium, *Colloids Surf. A: Physicochem. Eng. Aspects* 293 (2007) 217–223.
- [10] Y. Al-Degs, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, G.M. Walker, Competitive adsorption of reactive dyes from solution: equilibrium isotherm studies in single and multi solute systems, *Chem. Eng. J.* 128 (2007) 163–167.
- [11] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Polyethyleneimine impregnation on activated carbon: effects of impregnation amount and molecular number on textural characteristics and metal adsorption capacities, *J. Mater. Chem. Phys.* 112 (2008) 417–422.

- [12] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), *Chem. Eng. J.* 132 (2007) 267–278.
- [13] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, *J. Hazard. Mater.* 141 (2007) 77–85.
- [14] M.K. Aroua, S.P.P. Leong, L.Y. Teo, C.Y. Yin, W.M.A.W. Daud, Real-time determination of kinetics of adsorption of lead(II) onto palm shell-based activated carbon using ion selective electrode, *J. Biores. Technol.* 99 (2008) 5786–5792.
- [15] M.H.El-Naas, S.Al-Zuhair, M.A.Alhaija, Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon, *J. Hazard. Mater.* 173 (2010) 750–757.
- [16] A. Ahmad, B. Hameed, Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon, *J. Hazard. Mater.* 172 (2009) 1538–1543.
- [17] N.H. Phan, S. Rio, C. Faur, L. Le Coq, P. Le Cloirec, T.H. Nguyen, Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications, *Carbon* 44 (2006) 2569–2577.
- [18] N. El Hannafi, M.A. Boumakhla, T. Berrama, Z. Bendjama, Elimination of phenol by adsorption on activated carbon prepared from the peach cores: modelling and optimization, *Desalination* 223 (2008) 264–268.
- [19] M.A. Ahmad, W.M.A. Wan Daud, M.K. Aroua, Adsorption kinetics of various gases in carbon molecular sieves (CMS) produced from palm shell, *Colloids Surf. A: Physicochem. Eng. Aspects* 312 (2008) 131–135.
- [20] C.H. Weng, Y.-T. Lin, T.-W. Tzeng, Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder, *J. Hazard. Mater.* 170 (2009) 417–424.
- [21] M. Arulkumar, P. Sathishkumar, T. Palvannan, Optimization of orange G dye adsorption by activated carbon of *Thespesia populnea* pods using response surface methodology, *J. Hazard. Mater.* 186 (2011) 827–834.
- [22] P. Leechart, W. Nakbanpote, P. Thiravetyan, Application of ‘waste’ wood-shaving bottom ash for adsorption of azo reactive dye, *J. Environ. Manage.* 90 (2009) 912–920.

CHAPTER III REFFERENCES

- [23] K.P. Sharma, S. Sharma, Sharma Subhasini, P.K. Singh, S. Kumar, R. Grover, P.K. Sharma, A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests, *Chemosphere* 69 (2007) 48–54.
- [24] S. Sen, G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bed reactor, *Water Res.* 37 (2003) 1868–1878.
- [25] R. Devi, V. Singh, A. Kumar, COD and BOD reduction from coffee processing wastewater using Avacado peel carbon, *J. Biores. Technol.* 99 (2008) 1853–1860.
- [26] L. Zhu, J. Ma, Simultaneous removal of acid dye and cationic surfactant from water by bentonite in one-step process, *Chem. Eng. J.* 139 (2008) 503–509.
- [27] Dabrowski, A., Adsorption--from theory to practice. *Advances in Colloid and Interface Science*, 2001. 93(1-3): p. 135.
- [28] Allen, S. and B. Koumanova, Decolourisation of water/wastewater using adsorption. *Journal of the University of Chemical Technology and Metallurgy*, 2005. 40(3): p. 175-192.
- [29] Ali, H., Biodegradation of synthetic dyes—a review. *Water, Air, & Soil Pollution*, 2010. 213(1): p. 251-273.
- [30] Crini, G., Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource technology*, 2006. 97(9): p. 1061-1085.
- [31] Nandi, B., A. Goswami, and M. Purkait, Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies. *Applied Clay Science*, 2009. 42(3-4): p. 583-590.
- [32] Chowdhury, S., S. Chakraborty, and P. Saha, Biosorption of Basic Green 4 from aqueous solution by *Ananas comosus* (pineapple) leaf powder. *Colloids and Surfaces B: Biointerfaces*, 2011. 84(2): p. 520-527.
- [33] Dawood, S. and T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Research*, 2012. 46(6): p. 1933-1946.

- [34] Ibrahim, S., et al., Adsorption of anionic dyes in aqueous solution using chemically modified barley straw. *Water science and technology: a journal of the International Association on Water Pollution Research*, 2010. 62(5): p. 1177.
- [35] Yagub, M.T., T.K. Sen, and H. Ang, Equilibrium, Kinetics, and Thermodynamics of Methylene Blue Adsorption by Pine Tree Leaves. *Water, Air, & Soil Pollution*, 2012. 223(8): p. 5267-5282.
- [36] Liu, W., et al., Kinetics and thermodynamics characteristics of cationic yellow X-GL adsorption on attapulgite/rice hull-based activated carbon nanocomposites. *Environmental Progress & Sustainable Energy*, 2012. 32(3): p. 655-662.
- [37] Bulut, Y. and H. Aydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 2006. 194(1): p. 259-267.
- [38] Zhang, J., Q. Zhou, and L. Ou, Kinetic, Isotherm, and Thermodynamic Studies of the Adsorption of Methyl Orange from Aqueous Solution by Chitosan/Alumina Composite. *Journal of Chemical & Engineering Data*, 2012. 67: p. 412-419.
- [39] Argun, M.E., et al., Activation of pine cone using Fenton oxidation for Cd (II) and Pb (II) removal. *Bioresource technology*, 2008. 99(18): p. 8691-8698.
- [40] Salleh, M.A.M., et al., Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination*, 2011. 280(1): p. 1-13.
- [41] W.L.McCabe, J.C.Smith, P.Harriot, *Unit operations of chemical engineering*, McGraw-Hill, Singapore (2005).
- [42] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal — a review, *J. Environ. Manage.* 90 (2009) 2313–2342.
- [43] A. Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review, *J. Hazard. Mater.* 167 (2009) 1–9.
- [44] E. Forgacs, T. Cserhádi, G. Oros, Removal of synthetic dyes from wastewaters: a review, *Environ. Int.* 30 (2004) 953–971.
- [45] G. Mishra, M. Tripathy, A critical review of the treatment for decolorization of textile effluent, *Colourage* 40 (1993) 35–38.

- [46] E. Eren, B. Afsin, Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated sepiolite surfaces, *J. Dyes Pig.* 73 (2007) 162–167.
- [47] E. Eren, Investigation of a basic dye removal from aqueous solution onto chemically modified Unye bentonite, *J. Hazard. Mater.* 166 (2009) 88–93.
- [48] O.D. Tyagi, M.S. Yadav, M. Yadav, *A Textbook of Synthetic Dyes*, 67, Anmol-PVT. LTD., 2002.
- [49] K. Hunger, *Industrial Dyes, Chemistry, Properties, Applications*, Wiley-VCH, Weinheim, Germany, 2003, pp. 1–10.
- [50] E. Eren, O. Cubuk, H. Ciftci, B. Eren, B. Caglar, Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study, *Desalination* 252 (2010) 88–96.
- [51] E.N. El Qada, S.J. Allen, G.M. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.* 135 (2008) 174–184.
- [52] A. Al-Futaisi, A. Jamrah, R. Al-Hanai, Aspects of cationic dye molecule adsorption to palygorskite, *Desalination* 214 (2007) 327–342.
- [53] N. Atar, A. Olgun, Removal of basic and acid dyes from aqueous solutions by a waste containing boron impurity, *Desalination* 249 (2009) 109–115.
- [54] F. Deniz, S.D. Saygideger, Removal of a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf, *Desalination* 268 (2011) 6–11.
- [55] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interface Sci.* 286 (2005) 90–100. [56] D.Özer, G. Dursun, A. Özer, Methylene blue adsorption from aqueous solution by dehydrated peanut hull, *J. Hazard. Mater.* 144 (2007) 171–179.
- [57] N.A. Oladoja, C.O. Aboluwoye, Y.B. Oladimeji, A.O. Ashogbon, I.O. Otemuyiwa, Studies on castor seed shell as a sorbent in basic dye contaminated wastewater remediation, *Desalination* 227 (2008) 190–203.

- [58] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *J. Dyes Pig.* 51 (2001) 25–40.
- [59] V. Ponnusami, S.Vikram, S.N. Srivastava, Guava (*Psidium guajava*) leaf powder: novel adsorbent for removal of methylene blue from aqueous solutions, *J. Hazard. Mater.* 152 (2008) 276–286.
- [60] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder, *J. Dyes Pig.* 65 (2005) 51–59.
- [61] V. Ponnusami, V. Gunasekar, S.N. Srivastava, Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: multivariate regression analysis, *J. Hazard. Mater.* 169 (2009) 119–127.
- [62] A. Tabak, E. Eren, B. Afsin, B. Caglar, Determination of adsorptive properties of a Turkish Sepiolite for removal of Reactive Blue 15 anionic dye from aqueous solutions, *J. Hazard. Mater.* 161 (2009) 1087–1094.
- [63] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, *J. Dyes Pig.* 69 (2006) 128–136.
- [64] Q. Qin, J. Ma, K. Liu, Adsorption of anionic dyes on ammonium-functionalized MCM-41, *J. Hazard. Mater.* 162 (2009) 133–139.
- [65] H. El Boujaady, A. El Rhilassi, M. Bennani-Ziatni, R. El Hamri, A. Taitai, J.L. Lacout, Removal of textile dye by adsorption on synthetic calcium phosphate, *Desalination* 275 (2011) 10–16.
- [66] D. Bingol, N. Tekin, M. Alkan, Brilliant Yellow dye adsorption onto sepiolite using a full factorial design, *Appl. Clay Sci.* 50 (2010) 315–321.
- [67] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies, *Desalination* 268 (2011) 117–125.
- [68] M. Valix, W.H. Cheung, G. McKay, Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption, *Chemosphere* 56 (2004) 493–501.

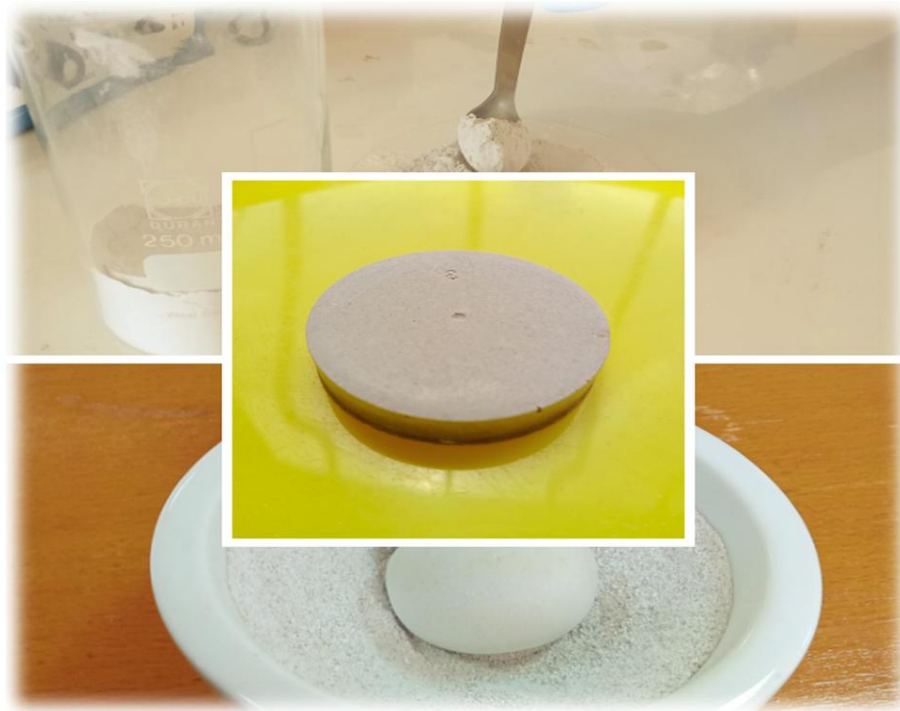
- [69] H. Ayoub, M. Kassir, M. Raad, H. Bazzi, A. Hijazi, Effect of Dye Structure on the Photodegradation Kinetic Using TiO₂ Nanoparticles, *J. Chem. Eng. Mater. Sci.* 5 (2017) 31–45, doi: <https://doi.org/10.4236/msce.2017.56004>.
- [70] L. Cao, T. Liang, X. Zhang, W. Liu, J. Li, X. Zhan, L. Wang, In-Situ pH-Sensitive Fibers via the Anchoring of Bromothymol Blue on Cellulose Grafted with Hydroxypropyltriethylamine Groups via Adsorption, *Polymers* 10 (2018) 709–722, doi: <https://doi.org/10.3390/polym10070709>.
- [71] M. S. E. Farida El-Dar, M. Hamed Ibrahim, A. B. Heba Farag, M. Zakaria Abdelwahhab, M. E. H Shalabi, Preparation, Characterization of Bentonite Carbon Composite and Design Application in Adsorption of Bromothymol Blue Dye, *J. Multidiscip. Eng. Sci. Technol.* 3 (2016) 3758–3765, url: <https://pdfs.semanticscholar.org/3acf/345cc02278a608cdc5f7983ae24ccce5466e.pdf>.
- [72] M. Ghaedi, E. Nazari, R. Sahraie, M. K. Purkait, Kinetic and isotherm study of Bromothymol Blue and Methylene blue removal using Au-NP loaded on activated carbon, *Desalin. Water. Treat.* 52 (2014) 5504–5512, doi: <https://doi.org/10.1080/19443994.2013.822156>.
- [73] H. Tavakkoli, Z. Zaman, A. Ghaemi, Gd_{0.5} Y_{0.5}CrO₃ Perovskite-Type Oxide Nanopowder: A Novel Adsorbent to Remove Organic Dye from Aqueous Media, *J. Chem. Res.* 40 (2016) 53–61, doi: https://doi.org/10.3184/17475191_6X14501064417178.
- [74] Y. Zheng, L. Cao, G. Xing, Z. Bai, J. Huang, Z. Zhang, Microscale flower-like magnesium oxide for highly efficient photocatalytic degradation of organic dyes in aqueous solution, *RSC Adv.* 9 (2019) 7338–7348, doi: <https://doi.org/10.1039/C8RA10385B>.
- [75] A. Ameri, M. Shakibaie, A. Ameri, M. A. Faramarzi, B. Amirheidari, H. Forootanfar, Photocatalytic decolorization of bromothymol blue using biogenic selenium nanoparticles synthesized by terrestrial actinomycete *Streptomyces griseobrunneus* strain FSHH12, *Desalin. Water. Treat.* 57 (2016) 21552–21563, doi: <https://doi.org/10.1080/19443994.2015.1124349>

Experimental part



CHAPTER IV

GEOPOLYMERS SYNTHESIS AND PROPERTIES



1. Materials and Methods:

1.1. Materials used:

Laboratory oven: Laboratory ovens are standard equipment found in most clinical, forensic, electronics, material processing, and, research laboratories. Laboratory ovens provide uniform temperature and precise temperature control for heating, baking, evaporating, sterilizing and other industrial laboratory functions.

Oven temperature ranges from ambient to above 300°C[1]. (**Memmert**)



Fig 14: Laboratory Oven (Memmert)

Analytical balance: Analytical balances are highly sensitive lab instruments designed to accurately measure mass. Their readability has a range between 0.1mg - 0.01mg. Analytical balances have a draft shield or weighing chamber to prevent the very small samples from being affected by air currents. They're meant to detect very fine increments, so the slightest vibrations or breeze can impact the results. As such, analytical balances should be used in a dedicated room with as few disturbances as possible. Analytical balances need to be monitored carefully and calibrated frequently. Most analytical balances have both automatic internal motorized calibration and calibration with external weights.[2] (**Nahita**)



Fig 15: Analytical balance (Nahita)

Hotplate Stirrer: The hotplate stirrer (or hot plate stirrer or hot plate magnetic stirrer) is used for mixing and heating aqueous solutions for a great variety of chemical reactions such as synthesis.[3] (**Heidolph**)



Fig 16: Hotplate stirrer (Heidolph)

1.2. Reactives used:

- Potassium hydroxide (KOH) (**Biochemchemopharma**, Mw =56.11g/mol)
- Hydrochloric acid (HCl) (**Honeywell Fulka**, MW =36.46g/mol)
- Silicon dioxide (SiO₂)(**Riedel-deHaen**)
- Water glass (prepared in the laboratory)
- Bromothymol blue

1.3. Raw Material Used

The commercial Metakaolin MK (**Metastar 501**) was obtained from IMERYS(SiO₂: 50.44%, Al₂O₃: 43.92%, TiO₂: 1.00%, Fe₂O₃: 0.46%, MgO: 0.09%, NaO: 0.15%, SO₃: 0.19, Cl: 0.01%)

Metakaolin was characterized by X-ray diffraction (XRD) using a Brucker D8 T2T advance diffract meter equipped with a Cu-K_α source, with a scan step of 2° min⁻¹, from 3 to 75° 2θ values.

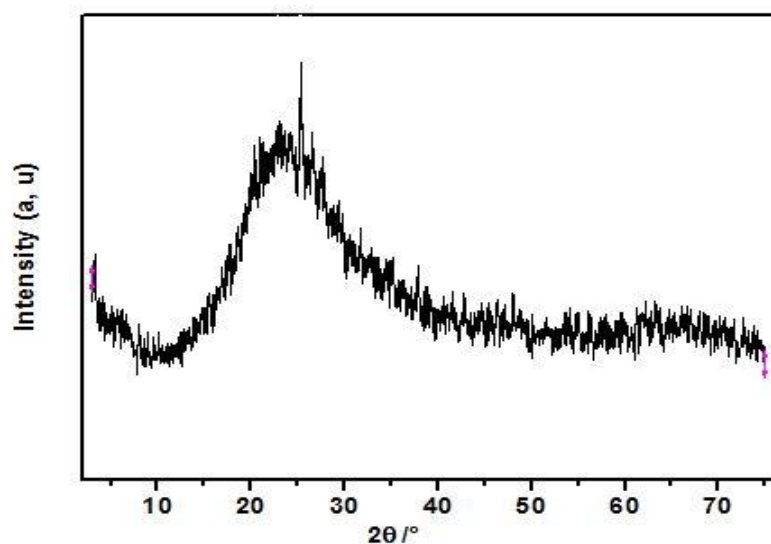


Fig 17: XRD of commercial metakaolin

XRD pattern of metakaolin sample is completely amorphous owing to the presence of broad hump structure.

2. Metakaolin pretreatment:

➤ Oven drying:

This step is used to reduce the moisture content in the solid samples and powders of Metakaolin powder to facilitate grinding and sieving.

➤ Grinding:

Grinding reduces the grain size of the material. A porcelain mortar was used for this used for this operation.



Fig 18: Grinding of metakaolin

➤ Sieving:

This operation allows to eliminate the agglomerates and to obtain a well determined granulometry determined granulometry. The clay obtained by grinding was sieved through a 0.355 mm mesh sieve. (ANAYSENESIEB, Retsch)



Fig 19: Sieve(ANAYSENESIEB, Retsch0.355mm)

3. Synthesis of geopolymers samples:

3.1. Preparation of the activation solution “water glass”:

The first step in the synthesis of geopolymers is the preparation of the activation solution "water glass".

water glass is an aqueous solution of strongly basic caustic potash (the solution of potassium hydroxide was obtained by dissolving in distilled water, soda pellets having purity of 99% until saturation with $\text{pH}=14$) with silica solution (SiO_2) // the ratio $\text{SiO}_2/\text{KOH} = 1.05$ (95.45g SiO_2) / (90.90g KOH)

The mixture was left under magnetic stirring for 24 hours to allow cooling and equilibration of the species.



Fig 20 ,Fig 21: Preparation of the activation solution “water glass”

3.2. Formulation of geopolymers:

Geopolymers was synthesized following these steps:

Firstly, 60 g of dry metakaolin powder was added to 69.6 ml the alkaline solution (water glass) in a mass ratio (alkaline solution/metakaolin) = 1.16.

Then, the mixture was mixed for 10 minutes to ensure dissolution between the powder and solution, resulting the formation of geopolymer precursor paste.

Finally, the mixture obtained is placed in cylindrical polystyrene bottles which are kept closed in an oven at $70\text{ }^{\circ}\text{C}$ for 24 hours.

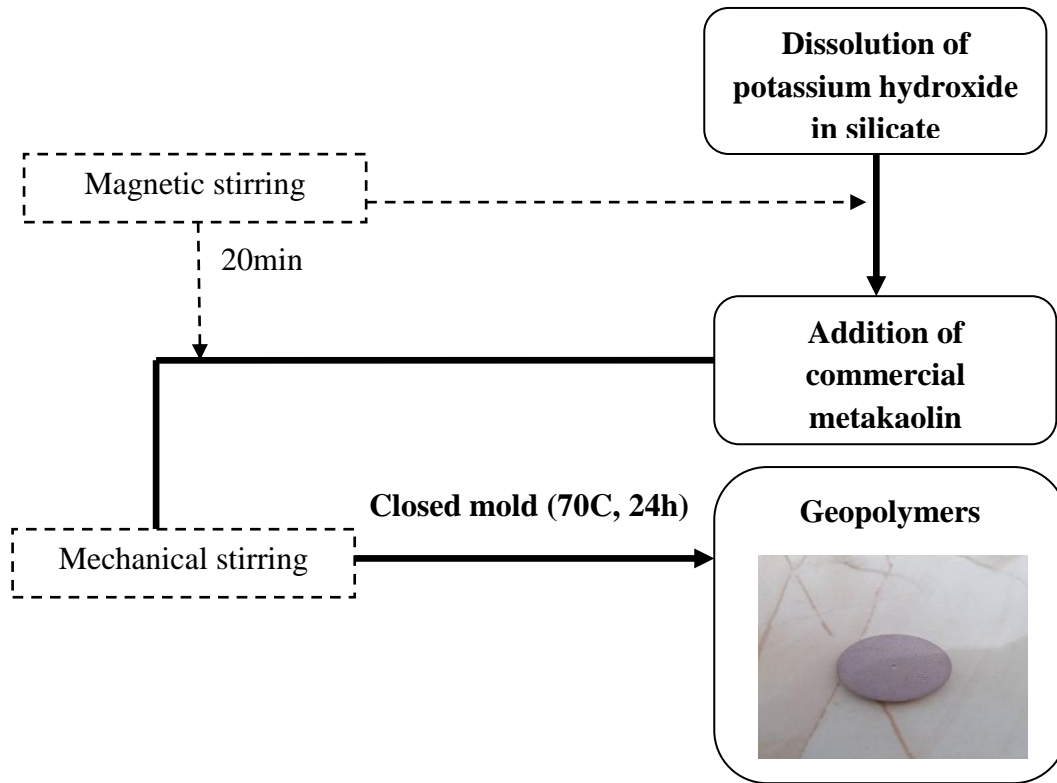


Fig 22: Diagram of the synthesis protocol of geopolymeric materials

4. Geopolymers properties

4.1. Chemical resistance:

4.1.1. Preparation of acidic solution and alkaline solution:

A. Acidic solutions (HCl):

To perform experiments, a stock solution of HCl was prepared with volume $V_f = 20\text{mL}$ and concentration $C_f = 10^{-1}\text{mol/L}$:

$$C_0 \times V_0 = C_f \times V_f$$

$$C_0 = \frac{\mu \times d \times \tau}{M} = \frac{1000 \times 1.19 \times 36.46}{100 \times 36.46} = 11.9 \text{ mol/L}$$

$$V_0 = \frac{C_f \times V_f}{C_0} = \frac{0.02 \times 0.1}{11.9} = 1.68 \times 10^{-4} \text{L} = 0.168 \text{mL}$$

C_0 : The initial concentration of HCl

C_f : The concentration selected to perform the experiment

V_0 : The initial volume of HCl

V_f : The final volume of HCl

μ : water density =1 kg/L

d: commercial HCl density =1.19

τ : mass percentage of commercial HCl= 36.46%

M: molar mass =36.46g/mol

So, we put 0.168 ml of HCl and complete the volume to 20 ml with distilled water to obtain the stock solution with 1mol/L.

Then we prepare 3 new solutions from the mother solution C_2 , C_3 , C_4 by taking 1 ml of the stock solution ($C=1\text{mol/L}$) and complete the volume to 10 ml with distilled water to obtain 3 diluted solutions.

- $C_1 = C_f = 1 \text{ mol/L}$
- $C_2 = C_1 / 10 = 10^{-1} \text{ mol/L}$
- $C_3 = C_2 / 10 = 10^{-2} \text{ mol/L}$
- $C_4 = C_3 / 10 = 10^{-3} \text{ mol/L}$

B. Alkaline solution (KOH):

To prepare potassium hydroxide solution at concentration of 10^{-1}mol/L , we follow the following steps:

$$\begin{aligned} &\triangleright n = C \times V \quad \text{and} \quad n = \frac{m}{M} \\ \implies &\triangleright C = \frac{m}{M \times V} \quad m = C \times V \times M \\ &\triangleright m = 10^{-1} \times 20 \times 10^{-3} \times 40 = 0.08\text{g} \end{aligned}$$

Dissolve 0.08 g of (KOH) in 20 ml of distilled water to obtain the stock solution.

Then we prepare 3 new diluted solutions C_2 , C_3 , C_4 from the bulk solution by taking 1ml of stock solution and complete the volume to 10 ml with distilled water.

- $C_1 = C = 10^{-1} \text{ mol/L}$

- $C_2 = C_1 / 10 = 10^{-2} \text{ mol/L}$
- $C_3 = C_2 / 10 = 10^{-3} \text{ mol/L}$
- $C_4 = C_3 / 10 = 10^{-4} \text{ mol/L}$

4.1.2. Acidic and alkaline resistance:

Geopolymers were floated at acidic and alkaline at different concentration for 24 h. The weight was measured before and after living them in solutions. These experiments were done as claimed by Singh et al[4].

The deterioration of geopolymers was identified in terms of mass loss, with the increase in exposure period loss in mass was observed with a higher percentage in the case of acidic medium comparing with alkaline solution.

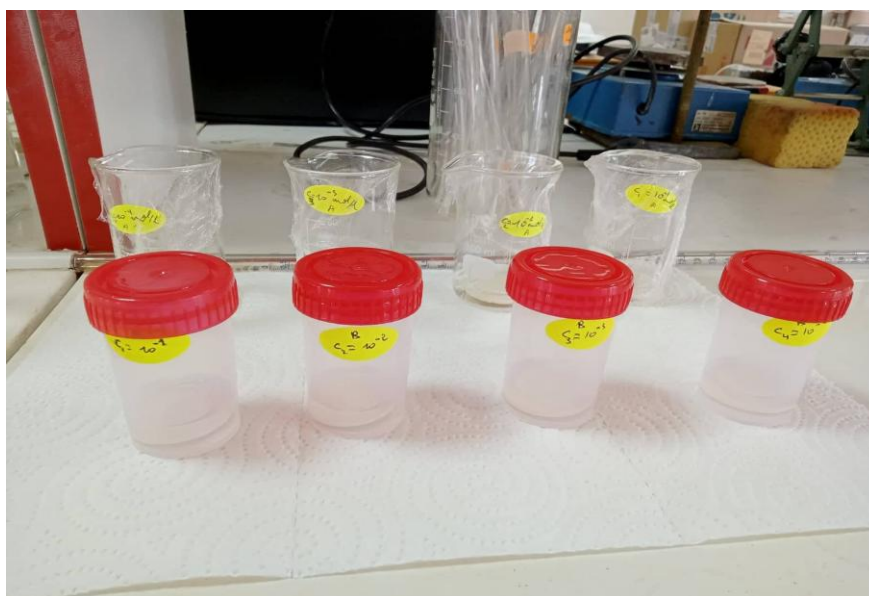




Fig 23: Geopolymers in different alkaline and acidic solutions

Geopolymer after acidic attack	C(mol/l)	Weight before(W_b) (g)	Weight after(W_a) (g)	Dissolved Quantity(g)= $W_a - W_b$
	$C_1=1$	1.487	1.240	-0.247
	$C_2=10^{-1}$	2.801	2.381	-0.42



	$C_3=10^{-2}$	1.357	1.152	-0.205
	$C_4=10^{-3}$	1.551	1.289	-0.262

Table 4: Results of geopolymers samples in different concentrations of acidic medium

At different concentrations of acidic environments mass loss over time is average 0.2 for almost concentrations: (Table 4)

White layers were deposited on the surface of geopolymer specimen, may due to gypsum crystal formation [4].





Geopolymer after alkaline attack	C (mol/l)	Weight before (g)	Weight after (g)	Dissolved Quantity(g)= W_a-W_b
	$C_1=10^{-1}$	1.461	1.311	-0.1551
	$C_2=10^{-2}$	1.064	0.881	-0.183
	$C_3=10^{-3}$	1.542	1.411	-0.131
	$C_4=10^{-4}$	1.431	1.347	-0.084

Table 5: Results of geopolymers samples in different concentrations of alkaline medium

We notice that in an alkaline medium the resistance is stronger than in an acid medium environment, less corrosion of the geopolymer is observed than in acid environment.

In alkaline medium white spots which appeared to be calcium hydroxide $\text{Ca}(\text{OH})_2$ developed on the attacked end of the specimen. NaOH salts were deposited on the surface [5]

4.2. Water uptake:

We studied the resistance of GP samples in an aqueous ambient temperature 22 and at pH 7 and we obtained the results shown in the following table:

The percent of water absorption for these samples were determined by **Eq. (1)**.

$$\% \text{ Water Absorption} = \frac{\text{Wetweig ht} - \text{Dryweig ht}}{\text{Dryweig ht}} \times 100 [4]. \quad (1)$$

Results and discussions:

Table 6 shows the results of water absorption in (%) for geopolymer sample after 1 hour, 2 hours, and 24 hours.

From table 6, it was observed that the (%) of water uptake reduced after 1 hour until 24 hours where the average absorption were 1.93%, 0.63 % and 0.45% respectively. The sample for water absorption decreased after 1 hour until 24 hours indicate that constant exposure to water allows the concrete to continuously hydrate; this causes further expansion of the geopolymers. As the paste expands, the void ratio decreases while causes permeability and absorptivity to decrease [4]

Geopolymer	Weight before (g)	Weight after (g)	Percentage (%)
GP _{1h}	7.646	7.794	1.93
GP _{2h}	5.796	5.833	0.63
GP _{24h}	8.652	8.691	0.45

Table 6: Results of water absorption (%) of a geopolymer sample

4.2. Porosity:

The porosity tests were conducted according to ASTM D7063/D7063M-11 [6]. The percent of porosity for these samples were determined by **Eq. (2)**.

$$\% \text{ Porosity} = \frac{W_u - W_k}{W_u - W_a} \times 100 \quad (2)$$

Where:

- . W_u = mass of specimen in air.
- . W_k = mass of dry specimen
- . W_a = mass of specimen under water

Results and discussions:

Table 7 shows the results of porosity in (%) for geopolymer sample after 1 hour, 2 hours, and 24 hours in water.

From table 7, the percent of porosity also showed a reduction for the sample tested after first hour until hour 24 from 15.54%, 13.51%, and 10.25%.

Geopolymer	$W_a(g)$	$W_k(g)$	$W_u(g)$	Porosity (%)
GP _{1h}	7.646	7.623	7.794	86.54
GP _{2h}	5.796	5.791	5.833	88.09
GP _{24h}	8.652	8.648	8.691	90.69

Table 7: Results of porosity (%) of a geopolymer sample

The geopolymer paste samples at 24h showed the highest percentage of water absorption and porosity while the geopolymer paste samples at 1h showed the lowest water absorption. This is due to the structure of samples becomes denser, harder and improved crystallinity from 24h until 1h. The pore size decreases and the structure became denser. The porosity and permeability also decreased hence the durability potentially be improved. [5]

CHAPTER IV REFFERENCES

- [1] <https://www.laboratory-supply.net/blog/laboratory-ovens/>
- [2] <https://www.adamequipment.com/aeblog/what-are-analytical-balances>
- [3] https://www.rampfesthudson.com/what-is-a-stirrer-used-for-in-chemistry/#What_is_a_hot_plate_stirrer_used_for
- [4] N. Singh, S. Vyes, R.P. Pathak, P. Sharma, N.V. Mahure, S.I. Gupta, Effect of aggressive chemical environmental on durability of green geopolymers concrete, international journal of engineering and innovative technology , 2013.
- [5] Brock William Tomkins, chemical resistance of geopolymer concrete against H₂SO₄ and NaOH, University of Southern Queen Island, 2011.
- [6] ASTM D7063/D7063M-11, Standard Test Method for Effective Porosity and Effective Air Voids of Compacted Bituminous Paving Mixture Samples, ASTM International, United States, 2011.

CHAPTER V

Bromothymol blue adsorption



1. Bromothymol structure:

- **Type:** Anionic dye
- **Nature:** Acid
- **IUPAC name:** 2-bromo-4-[3-(3-bromo-4-hydroxy-2-methyl-5-propan-2-ylphenyl)-1,1-dioxo-2,1λ⁶-benzoxathiol-3-yl]-3-methyl-6-propan-2-ylphenol
- **Chemical formula :** C₂₇H₂₈Br₂O₅
- **molecular weight:** 624.38 g/mol
- **λ_{max} :** 620 nm
- **Structure:**

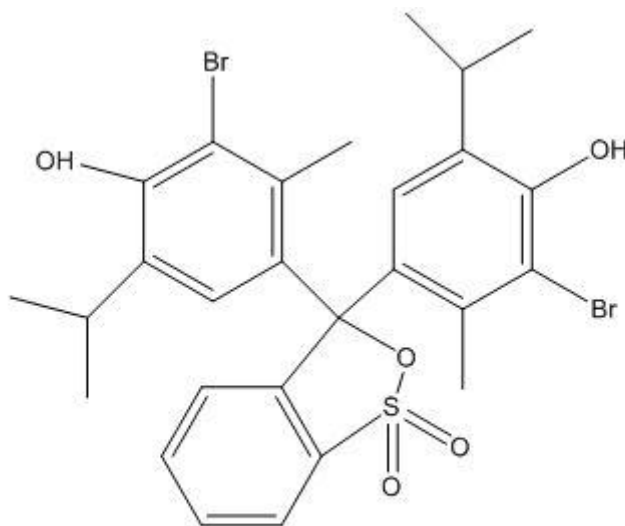


Fig 24: Bromothymol blue structure created by ChemDraw

2. Bulk solution preparation:

To realize different sorption experiments, 4 dye stock solutions were prepared.

$$m = C \times M \times V$$

M (Molar mass) = 624.38 g/mol

V : volume L

C : Concentration mol/L

- $V_1=0.5$ L has a concentration $C_1=10^{-4}$ mol/L

$$m_1 = C_1 \times M \times V_1$$

$$m_1 = 0.03 \text{ g}$$

- $V_2=0.5$ L has a concentration $C_2=3 \cdot 10^{-4}$ mol/L

$$m_2 = C_2 \times M \times V_2$$

$$m_2 = 0.09 \text{ g}$$

- $V_3=0.2$ L has a concentration $C_3=3 \cdot 10^{-3}$ mol/L

$$m_3 = C_3 \times M \times V_3$$

$$m_3 = 0.39 \text{ g}$$

- $V_4=0.2$ L has a concentration $C_4=10^{-2}$ mol/L

$$m_4 = C_4 \times M \times V_4$$

$$m_4 = 1.24 \text{ g}$$

The obtained mixture was homogenized by stirring.

A UV-Visible scan of the solutions allowed us to determine the maximum wavelength and the maximum absorbance.

The method consists in using two preparations:

The first one which is introduced in the reference cell contains; distilled water to draw the baseline.

Once the maximum wavelength is determined, we measured the absorbance of different concentrations C_1, C_2, C_3, C_4 prepared of the stock solution at a given concentration in order to establish a calibration curve.

When establishing the calibration lines, we sought to have $A < 1$. Thus, we ensure that the concentration of the analyzed samples remains sufficiently low to correctly apply the Beer-Lambert law.

These solutions are analyzed with the UV-Visible spectrophotometer type PhotolabSpektral **Fig 25** below.

Then we establish the calibration line representing the absorbance "A" at a given wavelength as a function of the concentration "C" using origin8 software.



Fig 25 : UV-Visible spectrophotometer type PhotolabSpektral

3. Calculation of adsorption percentage:

The percentage of dye adsorbed is given by the following isotherm formula:

$$P (\%) = (C_0 - C_t) * 100 / C_0$$

Where:

C_0 and C_t : Initial and instantaneous concentrations of metal (mg/L), respectively,

P: Percentage of metal fixation.

4. The Beer-Lambert law:

Can be expressed as:

$$A = C_t \cdot L \cdot \epsilon = C \cdot k$$

$$\Rightarrow C_t = \frac{A}{k}$$

With:

C: Concentration ($\text{mol} \cdot \text{L}^{-1}$)

L: Adsorption optical path length (cm)

M: Molar mass ($\text{g} \cdot \text{mol}^{-1}$)

ϵ : Specific molar absorbance coefficient ($\text{L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$)

k: Slope ($\text{L} \cdot \text{mol}^{-1}$)

Concentration (mol/L)	3×10^{-3}	10^{-2}
Absorbance	0.5	1.7

Table 8: Absorbance of bromothymol blue in differents concentration

5. Batch adsorption:

The study of dye adsorption on Geopolymer allows us to examine the influence of contact time on their retention and to determine the percentages of adsorbate (the dye) brought into contact.

A specimen of geopolymer is put in contact with 10ml of solution of initial concentration of the dye $C_0 = 10^{-2}$ mol/L. at room temperature and free pH. Aliquots of 1ml of the solution were taken at appropriate time intervals and immediately assayed by a UV-Visible spectrophotometer (PhotolabSpektral WTW) at a wavelength λ maximum 620 nm of the dye.

6. Adsorption capacity (percentage):

Adsorption capacities (%) are constructed by measuring the concentration of adsorbate (dye) in the medium before and after adsorption. For this, data are performed using 10^{-2} initial concentration solution under normal conditions.

$$\triangleright C = 10^{-2} \text{ mol/l}$$

Time (min)	30	50	120	480	1440
Absorbance	1.610	1.558	1.459	1.206	1.192
Residual dye Concentration C_t (mol/L)	9.39×10^{-3}	9.08×10^{-3}	8.49×10^{-3}	7.02×10^{-3}	6.95×10^{-3}
Adsorption %	6.1	9.2	15	29.8	30.5

Table 9: The evolution of the adsorption percentage as a function of time

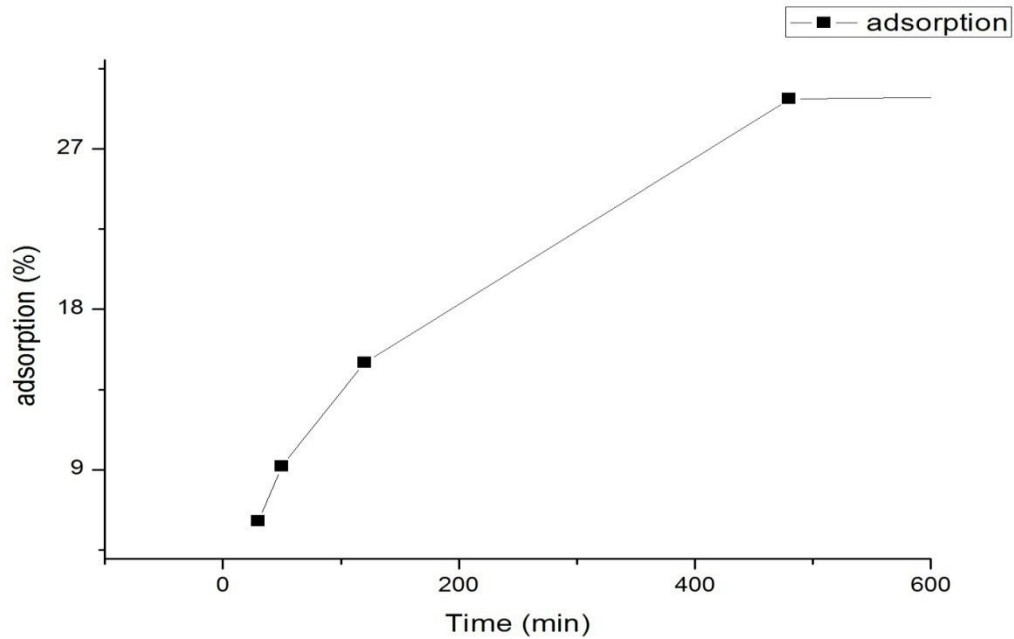


Fig 26: Adsorption percentage as function of time

The figure **Fig 26** represents the evolution of the adsorption percentage of dye bromothymol blue at increasing time for concentration 10^{-2} . It is clear from the graph that the percentage increased with increasing time showing a peak at about 480 min and then it reaches equilibrium for the remainder of the run time. This phenomenon can be interpreted that when time increases, adsorption of the dye in the sites of geopolymer increases until it reaches saturation.

7. Contact time effect:

The figure **Fig 27** presents the evolution of the adsorbed quantity and the percentage of adsorption as a function of time. The absorbance was examined by varying the time ranging from 5 min to 24h at initial dye concentration $3 \cdot 10^{-4}$, $3 \cdot 10^{-3}$, 10^{-4} , 10^{-2} .

Time(min)	5	15	30	50	80	120	240	1440
Absorbance ($C=3 \cdot 10^{-4}$ mol/L)	0.587	0.591	0.682	0.585	2.832	0.678	1.754	0.615
Absorbance ($C=3 \cdot 10^{-3}$ mol/L)	0.958	1.843	1.096	0.92	1.013	0.884	1.010	0.673
Absorbance ($C=10^{-4}$ mol/L)	2.435	0.866	0.912	1.414	2.487	2.786	1.035	0.902

Absorbance ($C=10^{-2}$ mol/L)	1.416	2.155	1.610	1.558	1.619	1.459	1.710	1.192
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Table 10: Absorbance in different contact times

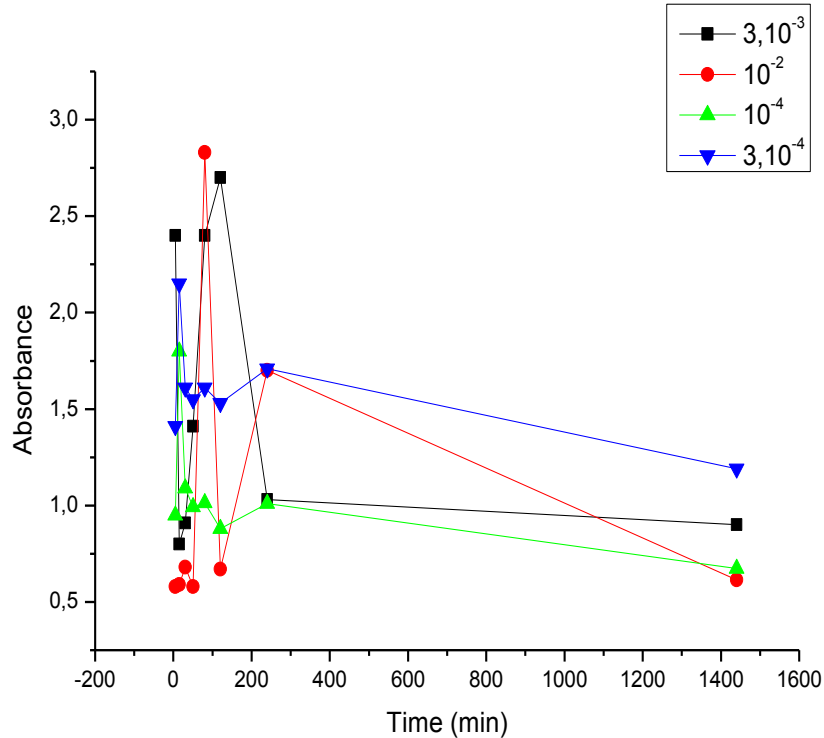


Fig 27: Effect of contact time on the absorbance of bromothymol blue dye

We notice that the kinetics of adsorption of dye on the synthetic geopolymer present the same trends characterized by a strong adsorption from the first minutes of contact dye-geopolymer, followed by a slow increase until reaching an equilibrium time.

This indicates that the adsorbents active sites/surfaces were vacant/unoccupied with enough concentration of dyes in the solution [1]. However, after 200min contact time (optimal), the removal efficiently almost remains constant up to 24h suggested that the lack of availability of active sites on the adsorbent surface in that the adsorbate tends to desorb into the liquid phase [2]. Thus, it can be concluded that the optimal contact time for the prepared dye solutions onto the prepared adsorbent is 200min at given experimental conditions.

8. Effect of initial dye concentration:

The figure **Fig 28** represents the effect of initials dye concentrations on the absorption.

Absorbance ($C=3.10^{-4}$ mol/L)	0.587	0.591	0.682	0.585	2.832	0.678	1.754	0.615
Absorbance ($C=3.10^{-3}$ mol/L)	0.958	1.843	1.096	0.92	1.013	0.884	1.010	0.673
Absorbance ($C=10^{-4}$ mol/L)	2.435	0.866	0.912	1.414	2.487	2.786	1.035	0.902
Absorbance ($C=10^{-2}$ mol/L)	1.416	2.155	1.610	1.558	1.619	1.459	1.710	1.192

Table 11: Effect of initials concentrations of dye BTB

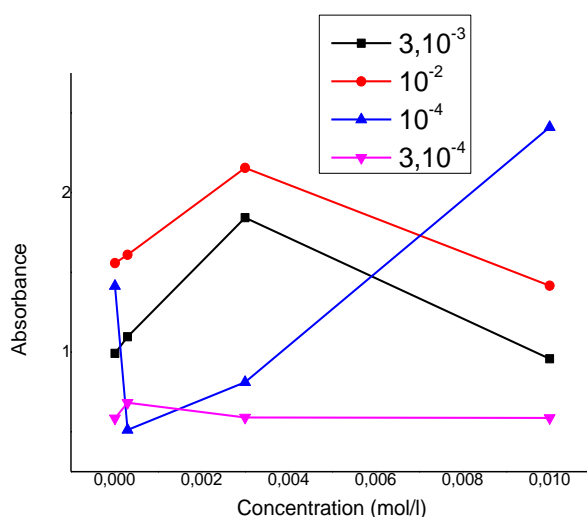


Fig 28: Effect of bromothymol blue initials concentrations on absorption

In the case of: 3.10^{-3} , 3.10^{-4} and 10^{-2} mol/L as the concentration of dye ions increases, the adsorption of dye ions increases. This is due to the limited number of active sites in an adsorbent. Adsorbents have sufficient active sites which are significantly diminished as compared to dye ions. But in the case of 10^{-4} mol/L concentration we note that the adsorption is reduced to the smallest value, and then it rises to the highest value at the end.

CHAPTER V REFERENCES

- [1] A.H. Jawad, A.S. Abdulhameed, Mesoporous Iraqi red kaolin clay as an efficient adsorbent for methylene blue dye: adsorption kinetic, isotherm and mechanism study, *Surface. Interfac.* 18 (2020), 100422, <https://doi.org/10.1016/j.surfin.2019.100422>.
- [2] P.S. Yap, V. Priyaa, Removal of crystal violet and acid green 25 from water using kaolin, *IOP Conf. Ser. Mater. Sci. Eng.* 495 (2019), <https://doi.org/10.1088/1757-899X/495/1/012052>.

CONCLUSION

Conclusion:

The present work shows:

- Synthesis of geopolymers from commercial metakaolin, where the resulting material has chemical resistance either in acidic or alkaline environments. The deterioration of geopolymers was identified in terms of mass loss, with the increase in exposure period loss in mass was observed with a higher percentage in the case of acidic medium comparing with alkaline solution. We notice that in an alkaline medium the resistance is stronger than in an acid medium environment, less corrosion of the geopolymer is observed than in acid environment.
- A limited color removal from dye solutions using geopolymers was investigated. The obtained results showed that geopolymers exhibits effective adsorption in aqueous solution, elimination of bromothymol blue dye was done in different initial concentrations at room temperature and free pH, where the adsorption percentage increased with increasing dye concentration. Thus, it can be concluded that the optimal contact time for bromothymol blue dye adsorption in the synthesized geopolymer is 280 min at given experimental conditions.