KAOLIN BASED ADSORBENT FOR ENVIRONMENTAL APPLICATIONS

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Declaration form

DECLARATION

I hereby, declare that this manuscript, entitled "*Kaolin based adsorbent for environmental applications",* is the result of my own work except for quotations and citations which have been duly acknowledged.
I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.

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Abstract

Kaolin is an abundant clay material that can be used for the adsorption of methylene blue dye, the water pollutant generated by the textile industry. Current research in this area is performed by studying different kaolin materials in a powder form, while the shaped adsorbents are not widely considered. The deficiency in the studies about the shaped adsorbents could be the convenience of utilizing the powder materials for experiments and the absence of a detailed recipe for the preparation of shaped adsorbents and catalysts. In this work, the preparation of the shaped kaolin adsorbent by extrusion is explored, and its adsorption ability of methylene blue is studied. The parent kaolin powder was exposed to thermal, acid, and base treatment. The adsorption capacity of the kaolin powder increased from 9.25 mg/g to 26.47 mg/g after the treatment. The first part of the thesis was dedicated to finding the best combination of the treatment parameters and pellet preparation parameters, and the second part was dedicated to adsorption studies. The pellets prepared from the activated kaolin and extrusion with 1.5% PVA solution binder demonstrated the best mechanical and adsorption properties among all tested alternatives. The kaolin was characterized after each treatment and pellet formation by SEM, XRD, FTIR, TGA, and BET analyses. The composition of the parent kaolin was identified by the XRF method. The adsorption experiments performed by activated kaolin pellets lasted for 2 days, and the maximum adsorption capacity was equal to 20.09 mg/g. The experimental data were fit to Langmuir equilibrium isotherm, with an R^2 value of 0.9991 and a predicted maximum adsorption capacity of 21.58 mg/g. The kinetic experiments were done for 10 hours and samples were taken each 30 minutes. Obtained experimental results demonstrated pseudo-first-order kinetic behavior, with the R^2 equal to 0.9722.

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Chapter I - Introduction

1.1. An overview of the master thesis topic.

Catalysts and adsorbents are crucial components of chemical reactions and adsorption processes, which are used on both laboratory and industrial scales. In most cases, catalysts are produced in a powder form, consequently, the mass transfer limitations can be neglected. Catalysts and adsorbents in powder form are suitable for laboratory experiments, however, shaped catalysts and adsorbents are required for industrial applications. Most scientific works are focused on the catalysts and adsorbents in powder form, and the research area of shaped industrial catalysts and adsorbents is limited.

Catalyst shaping is individual for every industry and the actual preparation procedure is kept secret from the public. The main focus of shaping catalysts and adsorbents is the production of granules with chemical and physical properties specific to the particular process. Mechanical strength, specific surface area, pore size distribution and distribution of active sites are crucial characteristics of shaped granules. Additionally, utilized catalysts and adsorbents should be easily separated from the product and removed from the reaction vessels. Shaped chemicals are convenient for the separation and further transport of deactivated catalysts or adsorbents for regeneration and are expected to preserve their form.

Commonly used catalysts and adsorbents in the industry are metals, like iron, platinum, or nickel, which act as catalyst active components, while zeolites and activated carbon are used as catalytic supports. They are efficient but require higher costs than other alternatives like clay materials. The potential of the clay materials like kaolin for industrial applications requires thorough investigation, as it is a cheap and accessible material, as there are kaolin-providing companies in Kazakhstan. The assessment of the adsorption ability of shaped kaolin adsorbents can demonstrate the future perspectives of using kaolin in various environmental applications.

1.2. Aims, objectives, and structure of the thesis.

This master thesis work is aimed to discover the potential of shaped adsorbents made from clay materials. The main objectives of this master thesis are:

- To develop a recipe for a catalyst/adsorbent made from kaolin and processed by extrusion;
- To assess the adsorption performance of prepared kaolin extrudates;
- To investigate the effects of the different experimental parameters during adsorption experiments and different preparation parameters during extrusion on the performance of the extrudates.
- To search for techniques of improvement of the kaolin by various treatments to enhance its adsorption capability.
- To discover the kaolin pellet that can both showcase good adsorption capacity and maintain its shape during the experiments.

The roadmap to achieving this goal includes searching for the recipe for preparing the shaped catalysts or adsorbents and evaluating their performance in possible applications available on the lab scale. The kaolin powder will be the primary raw material, and the extrusion process will be implemented for the preparation of the shaped materials. The most convenient way for the initial evaluation of the material performance is the determination of the adsorption capacity, therefore, the adsorption of well-known chemicals, like methylene blue, from the water is going to be studied. The initial milestone of the thesis would be the evaluation of the extrudate materials made from kaolin and its modifications and the next step would involve the equilibrium and kinetic studies of one particular kaolin extrudate during the adsorption of the methylene blue dye.

The presented thesis consists of 5 chapters, which include an introduction, literature review, materials and methods, results and discussion, and conclusion. The introduction and literature review chapters declare the problem statement and goals of the thesis and provide general information about the past research works dedicated to the shaping, kaolin, and adsorption of methylene blue. The materials and methods chapter presents the overview of all materials, extrudate preparation techniques, and adsorption experiments, as well as the characterization methods used to analyze the adsorbents. The graphical representation and interpretation of the experimental results are discussed in the results and discussion chapter. The thesis ends with the conclusion chapter, where the main findings and future work potentials are summarized.

1.3. The scope of the research.

Based on the literature review, there is a scarcity of research focused on shaped catalysts and adsorbents, which use kaolin clay as the main component. Additionally, the studies about the shaped catalysts and adsorbents mainly pay major concern to the mechanical characteristics of the extrudates, while the other characteristics, like adsorption, are not studied. The current work is done by testing the adsorption capability of the kaolin extrudates and their modifications. The methylene blue dye was chosen as a substance to be adsorbed due to availability of the studies related to the adsorption of methylene blue by various kaolin powders. All experiments performed for this thesis can be divided into two major parts. The first part is dedicated to testing kaolin in different forms (powder and extrudate) and different modifications (heat, acid, and base treatments) for the adsorption of methylene blue. In the second part, the most promising kaolin extrudate was picked and subjected to adsorption experiments focused on the identification of the effects of the solution pH, adsorbent dose, and initial methylene blue concentration on the adsorption capacity. Kinetic and equilibrium studies were performed and acquired data were fitted to well-known kinetic and equilibrium models.

Chapter II - Literature Review

2.1. Shaping of adsorbents and catalysts.

Adsorbents and catalysts are an essential part of processes and reactions taking place in industries. Adsorbents are used to remove undesirable components from the liquid or gases, while the purpose of catalysts is to increase the reaction rate so that the reaction will proceed faster. Scaling-up adsorbents and catalysts to utilize them on an industrial scale are important and sophisticated since most industrial catalysts are unique and formed by trial and error, making the production of those catalysts confidential. Most academic publications on heterogeneous catalysts focus on the microscopic level of catalytic engineering, where the catalyst's sizes are measured in nanometers. The sizes of industrial reactors are in meters, which requires the size of the catalysts to be in millimeters, creating the necessity in understanding the catalytic behavior on a macroscopic level. The intrinsic kinetics and transport phenomena processes are crucial in catalytic engineering, and catalyst shaping has a wide field of research [1].

During the shaping, the catalyst powder is transformed into various forms, like pellets, tablets, and extrudates of different shapes. The main techniques of shaping are extrusion, tableting, and agglomeration. Extrusion is a process, where the wet ceramic or other substance is molded and shaped continuously until the feed is supplied. The extrudates go through a die of different diameters, and the product is commonly called spaghetti-like extrudate due to its appearance. The effects of additives, like binders and peptisizers, on the performance of the shaped catalysts or adsorbents are studied to ensure better activity [2].

Porous materials with high specific surface areas, like zeolites, metal-organic frameworks (MOF), and porous polymers, are mainly shaped as industrial adsorbents and catalysts and utilized in various applications. Applications of shaped materials include air separation, carbon capturing, purification of natural gas, biodiesel production, alkylation of aromatic compounds, cracking of hydrocarbons, etc. Another important criterion for industrial catalysts and adsorbents is thermal stability, as industrial processes proceed at high temperatures [3].

Despite the fact of high interest in zeolites and MOFs, their comparatively high price generates a search for more cheap and more available alternatives. The ability to withstand high temperatures, ease of shaping, relative strength [4], and availability of domestic source makes kaolin powder an interesting option for research. The literature review of the existing applications and production recipes of catalysts and adsorbents will be discussed.

2.2. Review of the studies on the shaping of the catalysts and adsorbents.

Zeolites that are used in industry are mostly used in the form of H-ZSM-5, which is the high-silica pentasil type of zeolite and several studies were performed with this material. Catalytic conversion of glycerol to bio-based aromatics was investigated by utilizing H-ZSM-5 with different types of binders, which were aluminum oxide (Al_2O_3), kaolinite, and silicon dioxide (SiO_2). The main goals of the application of the binders during the extrusion process are the improvement of mechanical and thermal properties, elimination of possible poisoning, and diminishing the coking characteristics of a catalyst. 9 g of H-ZSM-5 and 1 g of a binder were mixed with the water, which varied from 4.3 to 5.5 g. The amount of the added water is adjusted by physically observing the state and viscosity of the powder. The final extrudates were 2 mm in diameter and 5-10 cm in length. Prepared extrudates were dried and calcinated to improve the integrity of the pellets. The combination of H-ZSM-5 with Al_2O_3 binder, where the binder content was 10 wt% demonstrated the best result in the conversion of glycerol. Additionally, the catalyst lifetime was increased due to the ability of Al_2O_3 to store higher amounts of coke, so that the main active catalyst is not coked [5].

Another application of shaped H-ZSM-5 is in the production of gasoline from dimethyl ether. The powder form H-ZSM-5 demonstrated promising results in the conversion of dimethyl ether to hydrocarbons in the range of gasoline, therefore the performance of the shaped catalysts was investigated. Alumina and silica binders were used, and additional alkaline treatment was conducted to produce hierarchically structured zeolites. Alkaline treatment is the process when the silicon is completely removed from the material. The binder content in the final extruded product was 20% on a dry mass basis. The extrudates were cut into pellets 5 mm in length and additionally were subjected to ion exchange after being dried and calcinated. Zeolites' acidity was enhanced by adding binders, especially silica. The results suggested that the catalysts with less alumina binder content are the most effective catalyst for the production of gasoline from dimethyl ether. The addition of the silica had a negative effect on the deactivation of the catalyst, therefore the alumina binder is more favorable in this case [6].

2.3. Shaping of catalysts and adsorbents from clay materials and their application.

Kaolinite, which belongs to the kaolin group, has a chemical formula of $Al_2Si_2O_5(OH)_4$ and has a wide range of applications in the ceramics, plastic, and rubber industry [7]. According to the latest available data, in 2020 Kazakhstan exported kaolin at a total price equal to $13 600 and placed at the 84th spot among 114 countries exporting kaolin. The main importers of kaolin from Kazakhstan were Kyrgyzstan, China, and Italy [8]. There are 5 kaolin fields in Kazakhstan, located in Aktobe, Akmola, and Almaty regions, with a total amount of 260 million tons [9]. The general price per kg of kaolin in the Kazakhstani market varies from 75 to 340 tenge, which is equivalent to $0.17 to $0.76 respectively [10]. If to purchase kaolin from a chemical company like Merck, its price is $40 per kg [11], while the price of zeolite is $760 per kg [12]. The availability of domestic kaolin in Kazakhstan and its comparatively cheap price make it interesting to investigate the adsorption performance of shaped kaolin compounds.

Kaolin has the potential to be used as a fertilizer, as its adsorption ability is high and its surface can be modified. Kaolin fertilizers can become a good substitution for fertilizers with high nitrogen content. The adsorbents were produced by preparing the paste by adding water to the mixture of 70% kaolin and 30% gibbsite. The paste was granulated into a nearly spherical shape and they were dried and calcinated to enhance mechanical properties and remove the excess water[13]. The prepared kaolin granules were immersed in the commercial urea solution, and about 10 wt% urea was absorbed. The desorption of the urea from the granules was slower compared to the release of the urea from the commercial urea fertilizer, and this led to the gradual consumption of required nutrients by the plant. Additionally, the required amount of urea can be decreased to 50% if the kaolin granules are used as fertilizers [13].

The attractive ability for the adsorption of clays can be utilized in environmental applications, specifically in water treatment. One of the most known water pollutants is dyes, and the removal of methylene blue dye by extruded adsorbents has been investigated. The materials that were used in the experiments were two types of clays, which were labeled red and gray due to their color, zeolite, and the combination of $ZnTiO_3$ and TiO_2 [14]. The dimensions of extruded particles were 2 mm in diameter and 10 mm in length. The materials were combined in different ratios, and individual clays were also extruded. Zeolite and $ZnTiO_3/TiO_2$ were not extruded individually since they could not remain their integrity. The addition of clays as binders plays a significant role in keeping the integrity of the extruded material. In powder form, zeolites demonstrated the best performance in the removal of methylene blue from the solution. The gray clay had the best adsorption capacity among all the options, which was equal to 85.99 mg/g. The addition of $ZnTiO_3/TiO_2$ did not have a significant effect on the adsorption of the methylene blue, but the combination of $ZnTiO_3/TiO_2$ and clay extrudates are effective in the photocatalytic removal of methylene blue [15]. Additionally, extruded materials containing zeolites did not improve the adsorption ability, since the adsorption capacity reduced from 85.45 mg/g to 82.92 mg/g. The reason for this issue could be the decrease in the specific surface area of zeolite being calcinated after the extrusion process. The clays that were used in the study were gathered from Ecuador, so the clay origin is also significant [14].

Bentonite is a type of clay that is mainly produced by the reconstruction of tuff and volcanic ash. The bentonite clays are also used for environmental applications as adsorbents for the removal of undesirable substances. The pollutant that was used in the experiment was Pb^{2+}. Prepared granular composites did not have identical shapes, the approximate dimensions were from 3 to 5 mm and the surface was full of pores. The prepared bentonite extrudates had good resistance to hydraulic damage and were not crushed during the process. About 86% of Pb^{2+} was removed by the bentonite granules in 2.5 h. The equilibrium was achieved after 6 hours, as the adsorption capacity did not change after 6 hours [16].

Extrusion is used for the shaping of the catalysts in all the studies mentioned above, which makes it a promising technique. Kaolin is used as an adsorbent in many applications, including the removal of hydrogen sulfide from biogas [17], treatment of tannery wastewater from heavy metals [12,13], and adsorption of different dyes [20,21]. Kaolin used in all those studies is in a powder form, while there is a lack of studies about the shaped kaolin catalysts.

2.4. Kaolin as an adsorbent for methylene blue.

Dyes are one the most common contaminants that are generated by the processes in the textile industry. Huge amounts of dye and water are consumed by the textile industry and effluents from industrial processes contain a considerable amount of dye [22]. These effluents lead to the coloration of the wastewater, therefore dyes are a possible source of water contamination. Allegre et al. [23] report that more than 80 000 metric tons of reactive dyes are utilized annually, while only 70-80% of the used dyes are fixed to the fabric. Other 20-30% of the dye does not contribute to the process and contaminates and colors the effluent. The addition of colored effluent to the natural water resources, whether the dye concentrations are high or low, can initiate an increase in the chemical oxygen demand, and make wastewater more toxic. Another possible outcome could be the blockage of light penetration, consequently altering the course of the photosynthesis process [24]. Worldwide application and production of dyes create an interest due to potentially harmful effects on the environment, especially on water and its flora and fauna [25]. Methylene blue is one of the most common cationic dyes that is used in the textile industry. Applications of methylene blue include the dyeing materials like silk, cotton, leather, wool, and paper, also methylene blue is useful in the pharmaceutical industry [26]. Dangers that can be caused by methylene blue to human health are vomiting, increase in heartbeat, nausea, tissue necrosis, irritation of skin or eye, etc [27,28].

Removal of dyes from wastewater has become a topic of interest for many researchers, who studied different removal techniques. Chemical coagulation and flocculation [29], membrane separation [30], photocatalysis [31], biological processes [32], advanced oxidation processes [33], chemical oxidation [34], sedimentation, electrochemical techniques, ion exchange [35], and adsorption [36] methods are extensively studied to find the most efficient and economically feasible method of dye removal. Among all of the mentioned techniques, adsorption techniques are proven to be efficient in dye removal, and materials with comparatively high adsorption capacity, such as activated carbon are widely used as an adsorbent [37]. In addition to its high adsorption capacity, high surface area, and ability to be regenerated and reused present activated carbon is the best choice for adsorption. However, the major drawback of using activated carbon is its high operational costs [38]. The pH of the solution, temperature, concentration, structure of the adsorbent, and dispersion’s ionic strength are crucial characteristics that influence the adsorption process. The adsorption kinetics provides information about the change in the concentration of the adsorbate in the solution over time. The basic steps of the adsorption process include the transport of the adsorbate to the adsorbent’s surface surrounded by the film, external diffusion, intra-particle diffusion, and reactions at the surface (chemical or physical) [39].

As the adsorption process is a low-cost treatment method, the next required component is the corresponding low-cost adsorbent material. High expenses associated with activated carbon created a necessity for searching for other alternatives, which appeared to be natural adsorbent materials, like natural clays, biochar, agricultural wastes, and wastes from various industrial processes [40–42]. Among all of these options, clay materials are the most attractive due to several reasons: there are rich sources of clay materials globally and their price is relatively cheap, despite having small particle sizes they owe high specific surface area, and their cation exchange capacity is prominent [43]. Dye adsorption capacities of clay materials have a various range since the experimental conditions and properties of the clay material and the adsorbate dye differ with every experiment. Clay materials can be grouped into several categories, namely kaolin, smectite, illite, attapulgite, chlorite, etc. [44] The considerable feature of clay materials is their structure's net negative charge, which allows the adsorption of positively charged materials [35]. Kaolin is one of the abundant clay materials available at different sites of the world, it has a crystalline structure and can be extracted from rocks. The negative charge at the surface of the kaolin is the result of the isomorphous substitution when silica ions (Si^{4+}) are replaced by alumina ions (Al^{3+}) in the silica layer [45].

Kaolin has a potential in the adsorption of methylene blue, however, Jiang et al. [46] claim that the adsorption capacity of kaolin is lower compared to other adsorbents. They justify this statement by addressing low surface area, as well as the low cationic exchange capacity. Different techniques were approached to increase the adsorption capacity of the kaolin. Modification with acid, base, and $ZnCl_2$ [47], magnetic modification with γ-Fe_2O_3 nanoparticles [48], treatment with sodium salts [49] and modification with cold plasma [42] are the methods studied to improve the adsorption capacity of kaolin. Table 1 demonstrates the performance of kaolin as an adsorbent for methylene blue, and the results differ as each study utilized a particular type of kaolin. Each source has unique numbers since the adsorption capacity is dependent on the experimental conditions and the origin of the kaolin.

Table 1: Adsorption capacities of kaolin from different sources. (* denotes the maximum adsorption capacity estimated by Langmuir isotherm)

Kaolin source	**Modification method**	**Methylene blue concentration (mg/L)**	**Equilibrium time**	**Adsorption capacity (mg/g)**	**Reference**
Tamazert kaolin, Algeria	Heat, acid, acid-base	30-100	5 min for 30 mg/L; 70 min for 80 and 100 mg/L	24-92 (acid-base modified) 111*	[50]
Coal-bearing kaolinite, northern China	Acid	50-600	60 min	78.1 (raw kaolin) 101.5 (acid modified)	[51]
Kaolin, Shanghai First Reagent Co., China	Graphene oxide	5-40	800 min	13.99 (raw kaolin) 7-23 (graphene oxide modified) 28.2*	[41]
Kaolin, west Iraq	No	10-120	Between 5 and 120 min depending on the MB concentration	4-102 240.4*	[40]
Tamazert kaolin, Algeria	No	80-250	20 min	36-44 52.76*	[52]
Tamazert kaolin, Algeria	No	4-37	20 min	7-26 45*	[53]
Kaolin, west Turkey	Plasma	25-100	No data	12.65 (raw kaolin) 22.18 (plasma modified) 51.02*	[42]

2.5. Kaolin treatment techniques.

The favorable economical aspect of kaolin utilization in various applications does not assure its effectiveness, since kaolin has several limitations, which provides a necessity for kaolin treatment. Low acidity, low surface area, impurities and porosity are some of the limitations. To overcome these limitations, many modification methods are studied and reported to enhance the chemical and mechanical stability of the kaolin, as well as the surface area. The kaolin can be modified by alkali, acid and thermal treatments, as well as by mechanochemical ways [54].

Mechanochemical modification methods are executed by industrial grinding or specific micronization processes. The improvement in surface area and pore volume is achieved by the reduction of the particle size. The main drawback of this modification technique is the possible generation of agglomerates as a result of the delamination [55]. Thermal treatment is usually used as a pre-treatment for further modifications and boosts the thermal stability of the kaolin [56]. During the activation of the kaolin by the base, the aluminum and silicon groups tend to lose their protons, and the dealumination and desilication processes proceed at the same time. As a result, the improvement in adsorption capacity, surface area, pore size and acidity can be achieved [57]. Similar improvements are also possible with acid activation. The dissolution of the external layer of the kaolin, as well as the removal of the impurities occurs with the dealumination process. All of these processes change the chemical composition and structure of the material [58]. Different acids have different effects, and inorganic acids are more effective during acid activation compared to organic acids. Despite being less effective, organic acids can maintain the kaolin structure, while the excess usage of inorganic acids can destroy it. It is reported that the increase in the surface area is obtained by the following acids from the most to the least effective ones: nitric acid, perchloric acid, sulfuric acid, hydrochloric acid, phosphoric acid and acetic acid [54,59].

The acid activation of kaolin is reported to be challenging since the kaolin is considered to be inactive in its regular structure, therefore preliminary heat treatment by calcination is necessary before applying any acid treatment [60]. General calcination temperatures of kaolin have a range between 550 °C and 850 °C, which is dependent on the origin and age of the kaolin. The dehydroxylation process usually occurs between those temperatures, and the crystal structure of the kaolin is destroyed and metakaolin is formed [61]. Metakaolin is more reactive compared to kaolin, therefore acid treatment is more effective with metakaolin. Studies that utilize direct acid activation also exist. Gao et al. [51] use H_2SO_4 for acid treatment of kaolin at different conditions and increased the adsorption capacity of kaolin from 78.1 to 101.5 mg/g. The same acid activation was utilized by Zen et al. [62], and they explain the increase in the adsorption capacity with the increased specific surface area or with the clay becoming hydrophobic making it possible to adsorb more dye. Results obtained by Boukhemkhem and Rida [50] demonstrate that the preliminary calcination of the kaolin at 800 °C and further treatment with HCl and NaOH increased the adsorption capacity from 40 mg/g to 110 mg/g. All mentioned adsorption capacity enhancement techniques are planned to be implemented in the current thesis work.

Chapter III - Materials and Methods

3.1. Characterization and preparation of extrudates.

To assess the performance of the extruded catalysts and adsorbents, characterization techniques are important. Mostly used characterization techniques are X-ray diffraction (XRD), physisorption with argon (Ar) and nitrogen (N_2), high resolution-transmission electron microscopy (HR-TEM), and thermogravimetric analysis (TGA), scanning electron microscopy (SEM), BET analysis, etc. [5,13,63]. Useful information that can be extracted from the mentioned techniques is the chemical composition of the reagents and products (by XRD and XRF), the specific surface area of the catalysts (by physisorption and BET analysis), the catalyst surface images (by HR-TEM and SEM) and the thermal stability (by TGA). The mechanical strengths of the prepared pellets are tested by special equipment and several crush strength test and axial compression and tension tests are performed [64,65].

Extrusion experiments are done with Caleva Multi Lab equipment (Caleva Process Solutions Ltd.). Caleva Multi Lab is a universal tool for the preparation of extruded materials and spherical pellets [66]. Numerous studies implemented this equipment in their research, and its availability at Nazarbayev University provides good opportunities for testing new kinds of extruded materials.

3.2. Materials.

The kaolin powder was purchased from Sigma-Aldrich, and the enriched kaolin powder was purchased from Prosco Resources (Ukraine). The methylene blue (pure, certified) from Acros Organics (India) company was used as an adsorbate. The acid treatments were performed by the sulfuric (H_2SO_4) and hydrochloric (HCl, 37%) acids, both are products of the Sigma Aldrich, and the base treatment was performed by the sodium hydroxide (NaOH, >97%), manufactured by Fisher Scientific in the UK. The polyvinyl alcohol (PVA), used as a binder during the extrusion, was acquired from Sigma Aldrich, and it is fully hydrolyzed with a molecular weight ranging from 89 000 to 98 000. The pH was adjusted by hydrochloric acid and potassium hydroxide (KOH) solutions. All solutions were prepared with ultra-pure water, purified by Puris reverse osmosis water system.

3.3. Synthesis of kaolin extrudates (pellets).

3.3.1. Preparation of pellets from kaolin powder.

The catalyst and adsorbent pellets were prepared by extrusion process. Extrusion is conducted by using special extruder equipment called Caleva Multi Lab (Figure 1). This equipment consists of several removable parts for different purposes. In addition to the extrusion part, there is a spheronization part, which could be used to produce nearly spherical products, and a kneading part, where the paste is formed.

In the first step of the pellet preparation process, the required amount of kaolin powder is placed inside the kneading chamber, where two rotary blades rotate and water is added dropwise, ensuring better mixing and dispersion of water throughout the whole kaolin powder. The rotational speed is equal to 100 rpm for both the kneading and extrusion processes. The timer is set for 1 or 2 minutes after all water or binder is added. This time is required to get a fully mixed paste, and it varies depending on the material being prepared. A paste from kaolin and water is produced and extracted for the further extrusion process.

The paste is introduced to the extruder and the paste is extruded through the die with several holes. There are 3 different sizes of dies (1 mm, 2 mm and 3 mm in diameter), which can be useful to study the effect of the pellet size on the adsorption performance. The extruded product has a “noodle” shape, which is subjected to cutting. Cutting is performed by the stationery knife since the extruded product is sensitive to physical contact and the form of the extruded product can be destroyed and special cutting devices cannot be implemented.

After the extruded product is cut into pellets of cylindrical shape, they are put in the oven for drying and removal of the water. The pellets are put into the oven that is already heated to 105 °C for 2 hours. The final step of pellet preparation is calcination, where the volatile substances are removed and pellets become stronger since the pellets should retain their integrity when they are used for water treatment. The calcination temperature is varied from 300 °C to 800 °C. The samples are put into the muffle furnace at room temperature, heated at 10 °C/min rate until the desired temperature and kept at that temperature for 2 hours. Calcinated pellets are withdrawn from the furnace after cooling back to room temperature.

Figure 1: Caleva Multi Lab equipment with interchangeable mixing/kneading, extrusion, and spheronization parts. The last image shows the prepared paste for extrusion.

The appearances of extrudates in their “spaghetti-like” shape and pellets are presented in Figure 2. The recipe for the extrusion was developed by trial and error until the desired paste was obtained. The final amounts required for the extrusion process are 20 g of kaolin powder and 10 ml of water. The cutting of the extrudates into pellets was done by a stationary knife, and pellet sizes were measured by eye. Since kaolin is clay, it becomes soft if contacted with water and it was challenging to use a ruler and cut precisely to the same dimensions. The pellets were able to maintain their shape after being used as adsorbents during experiments. This was achieved by applying calcination, and if this step was missed the pellets would quickly disintegrate.

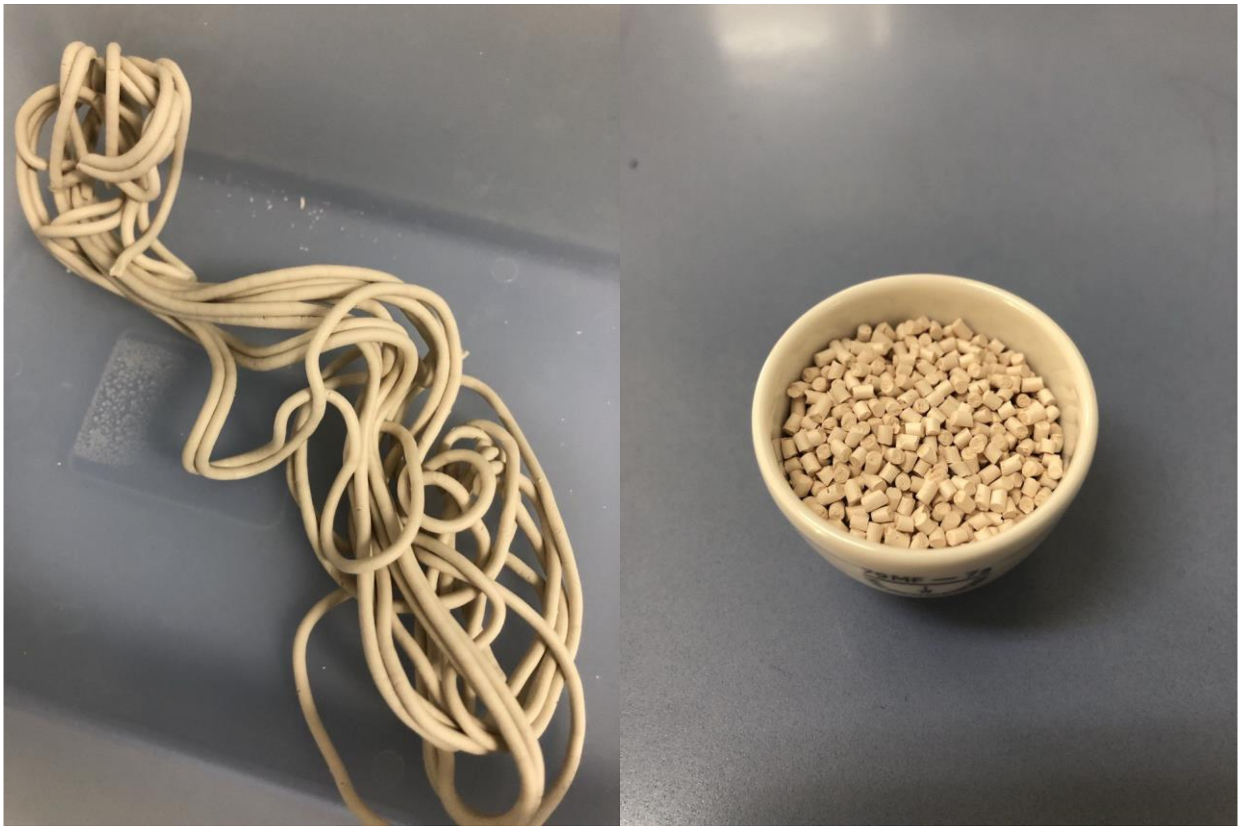


Figure 2: The products of the extrusion process: “spaghetti-like” shape and pellets.

3.3.2. Modification of kaolin powder.

The kaolin powder was modified by applying thermal, acid, and alkali treatments, and several combinations of those treatments were applied to find the most effective one. There are two main treatment methods that were found in the literature:

- Treatment of kaolin clay with 0.1 N H_2SO_4 solution by agitation for 4 hours at room temperature, followed by filtering and washing with water several times. Obtained acid-treated kaolin is dried in an oven at 60 °C for 12 hours. After the drying, the dried filtrate is crushed to get the powdered material;
- The kaolin powder is preliminarily calcinated at 800 °C to get metakaolin. After this step, metakaolin is treated with 2.5 M HCl for 7 hours at 80 °C and filtered after the treatment process. The filtrate was dried for 3 hours at 110 °C. The acid-treated kaolin is treated with 0.5 NaOH solution at the same conditions as the acid.

These treatment methods were implemented and some variations were applied during the period of the study. The preparation of the pellets from activated kaolin differs from the raw kaolin procedure since the activated kaolin demonstrated different behavior during the extrusion process. The procedure is practically the same as presented in Chapter 3.3.1, with some adjustments in the recipe. For the preparation of paste for the extrusion, 12 ml of water is required for 20 g of the activated kaolin powder. Additionally, another batch of pellets was prepared by utilizing PVA solution as a binder to avoid the calcination step. In this case, 7.5 ml of the PVA solution is used for 10 g of the activated kaolin material. The final chosen procedure for the kaolin activation was decided after testing different variations. The steps are:

1. Raw kaolin powder is calcinated for 5 hours in airflow at 600 °C. The kaolin is placed inside the muffle furnace at room temperature and remained there until the temperature reached the value of 600 °C. The rate was 10 °C per min;
2. 25 g of calcinated kaolin is added to 500 ml of 2.5 M HCl solution and stirred by the magnetic stirrer for 7 hours. The temperature of the hot plate is set to 80 °C;
3. The acid-activated powder is filtered by filter paper using a Buchner funnel and flask. Vacuum filtration is applied to speed up the filtration process;
4. Filtered powder is washed with water several times and put into the oven at 110 °C for 3 hours;
5. The dried powder is withdrawn from the filter paper and crushed in mortar to get fine powder;
6. Steps 2 to 5 are repeated with 0.5 NaOH solution;

7. Activated kaolin is ready for further experiments.

3.3.3. Preparation of PVA solution.

The PVA solution was prepared by following the manual developed by Flinn Scientific [67]. The range of the PVA solutions was from 0.05% to 5%. The ultra-pure water was heated up by a hot plate until the water temperature reaches the value between 80 and 85 °C. The required amount of the PVA powder is slowly added to the hot water to ensure that each grain of the PVA is in full contact with the water and that agglomeration is minimized. Continuous stirring is operated during the addition of the PVA to water. After all of the PVA is added, the solution is stirred for 5 minutes, however the PVA is not fully dissolved at this point. The solution is put into the microwave oven for 30 seconds and stirred with a spatula until no PVA is visible in the solution. The number of cycles of putting the solution into the microwave oven differs depending on the concentration of the PVA. The approximate range is between 6 and 10 cycles. Some amount of water can be evaporated, so the solution is filled with water until the initial volume of the solution is reached. Prepared PVA solutions are stored inside the refrigerator.

3.3.4. Preparation of pellets with PVA solution as a binder.

The PVA solution acts as a binder for activated kaolin pellets. The PVA solution is added during the mixing and kneading processes instead of the water. 7.5 ml of PVA solution is necessary for 10 g of the activated kaolin powder. The paste is extruded and cut into pellets, which are put into the oven at 105 °C and dried for 2 hours. Calcination is not required at this point, as the pellets retain their shape during the experiments with the help of the binder.

3.4. Adsorption studies.

3.4.1. Experimental procedure.

The methylene blue concentration was measured by Genesys 150 UV-Visible spectrophotometer at the wavelength of 664 nm, which is the characteristic wavelength for the methylene blue dye. The amount of the taken sample depends on the initial concentration of the solution, as the maximum detectable concentration of the equipment is 10 ppm. A 6-point calibration curve was prepared before the start of the experiments (Figure 3). The obtained equation was used to calculate the concentrations in ppm. Concentrations higher than 10 ppm required a dilution with ultra-pure water, so 50 to 1 500 μL of the sample was taken for each measurement.

Methylene blue dye was used as an adsorbate during the experiments. Methylene blue is in a powder form and methylene blue solutions with different concentrations were prepared based on the requirements. Adsorption experiment steps:

1. Preparation of the methylene blue solution of desired concentrations.
2. Preparation of the adsorbents of required masses.
3. Measurement of the initial concentration of the solution with a UV-Vis spectrometer.
4. Placement of the adsorbents into the methylene blue solution (The pellets were put inside the metal net to ensure the same placement of pellets for all experiments (Figure 4)).
5. Start stirring.
6. Take samples every 30 minutes and measure their concentration with a UV-Vis spectrometer.
7. End the experiment after receiving enough data.

These steps were repeated for every variation of modification of the adsorbent. The adsorption capacity was calculated by the following formula:

$$q_t = \frac{C_0 - C_t}{m} * V \tag{1}$$

Here, C_0 (mg/L) is the initial concentration, C_t (mg/L) is the concentration at time t, m is the mass of the adsorbent in grams, V is the volume of the solution in liters, and q_t is the adsorption capacity in mg of the adsorbed methylene blue per gram of the adsorbent.

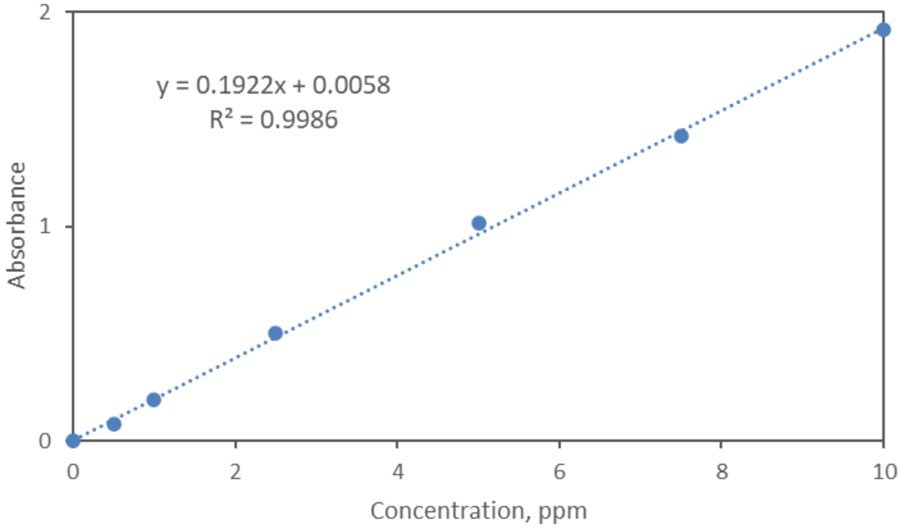


Figure 3: Calibration curve constructed for the concentration calculation of the methylene blue by UV-Vis spectrophotometer.

Figure 4: The experimental setup of the methylene blue adsorption experiments with kaolin pellets.

3.4.2. The pH of the solution and adsorbent dose studies.

The modified kaolin pellets made with 1.5% PVA solution as a binder were chosen for detailed adsorption studies. The first step of the study includes the identification of the effect of the solution pH on the adsorption capacity. The experiments were performed with pH of 4, 6.5

(natural pH of the methylene blue solution), 8 and 10. The pH was adjusted by adding 0.05 M KOH solution to create a basic environment, while 0.1 M HCl solution was added to increase the acidity. The pH with the highest adsorption capacity was chosen and remained the same for all further experiments.

The second stage of the adsorption experiments considered the amount of the adsorbent used. The adsorbent doses that were used: 0.4 g, 0.85, 2 g and 4 g. The adsorbent dose range where no change in the adsorption capacity was achieved was considered a suitable amount for further experiments.

All experiments were done in duplicate. The duration of one experiment is 2 days until the adsorption capacity reaches a plateau. Several samples were taken to ensure no substantial change in the adsorption capacity. Due to a long time of the experiment, the beakers were covered with a parafilm to minimize the loss of the solution by evaporation (Figure 5).

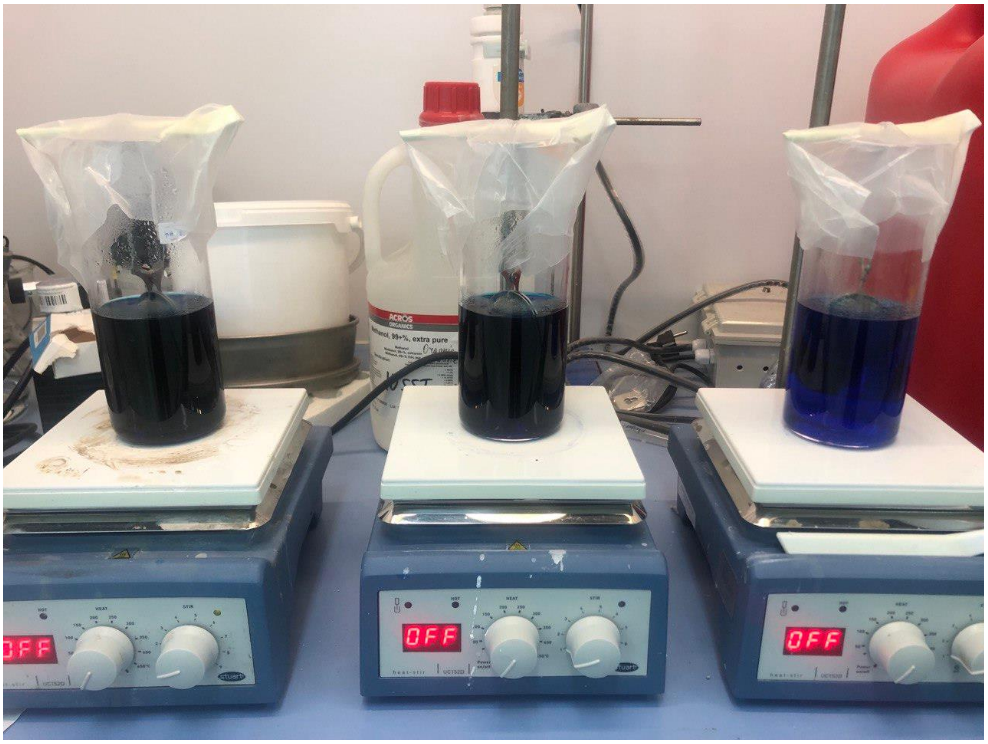


Figure 5: The experimental setup of the adsorption of methylene blue by modified kaolin pellets.

3.4.3. Equilibrium studies.

Adsorption equilibrium studies were performed with the pH and adsorbent dose identified from the previous experiments. Adsorption equilibrium was studied by keeping the same experimental parameters except for the initial concentration of methylene blue. 250 mg of the methylene blue powder was added to 1 L of ultra-pure water to get 250 ppm methylene blue solution. The initial concentrations were varied from 50 to 250 ppm, and the required concentrations were prepared by dissolving the stock solution. The volume of the adsorbed solution was 250 ml and 0.85 g of the kaolin pellets was used as adsorbents. The measurements were taken after 2 days when the equilibrium was achieved. The equilibrium isotherm was plotted by calculating the maximum adsorption capacity:

$$q_{max} = \frac{C_0 - C_e}{m} * V \tag{2}$$

Here, the q_{max} denotes the maximum adsorption capacity in mg/g achieved at the equilibrium. C_0 and C_e are the initial and equilibrium concentrations respectively, measured in mg/L. The mass of the adsorbent is m (g) and the volume of the solution is V (L).

Langmuir and Freundlich isotherm models were used to examine the experimental data and fit the experimental isotherms to these models. Adsorption isotherms are utilized to characterize the equilibrium relationship between the adsorbent and adsorbate, and the appropriate choice of the model is crucial to design further adsorption of methylene blue from the solution. The Langmuir isotherm is represented by the following equation [52]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e};\ R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

q_e and q_{max} are equilibrium and maximum adsorption capacities (mg/g), C_e is the concentration of the methylene blue at the equilibrium (mg/L) and K_L is adsorption free energy constant (L/mg). Langmuir isotherm assumes homogeneous distribution of the adsorbate at the surface of the adsorbent. The R_L value indicates the favorability of the adsorption process.

Freundlich isotherm describes the adsorption on the heterogeneous surface. The Freundlich isotherm is expressed in the form of a non-linear equation [68]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

Here, the q_e and C_e are the adsorption capacity (mg/g) and concentration (mg/L) at the equilibrium and K_F is constant, which has the units of (mg/g)*(L/mg)$^{1/n}$. n represents the Freundlich constant, which describes the favorability of the adsorption.

3.4.4. Kinetic studies.

The kinetic experiments were done to study the kinetics of the adsorption and fit the experimental data to relevant kinetic models. 250 mL of 100 mg/L methylene blue solution was prepared and 850 mg of the kaolin pellets were put into contact with the solution. The samples were taken each 30 minutes and the adsorption capacity was calculated by Equation 1.

The well-known adsorption kinetic models are pseudo-first order and pseudo-second order. The linear equations of those models are [68]:

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

Here, q_e (mg/g) and q_t (mg/g) are adsorption capacities at equilibrium and time t (min) respectively. k_1 (min^{-1}) and k_2 [g/(mg*min)] are pseudo-first-order and pseudo-second-order rate constants respectively. Obtained adsorption data were fitted to these models to find the suitable model.

3.5. Flowchart of the adsorbent preparation.

The final flowchart of the preparation of the final adsorbent is presented in Figure 6. The calcination at a certain temperature for 2 hours can be applied at the final stage if the binder was not utilized. The main purpose of using binder and calcination at the end of the process is to improve the mechanical characteristics of the pellet so it will not disintegrate during the adsorption experiments.

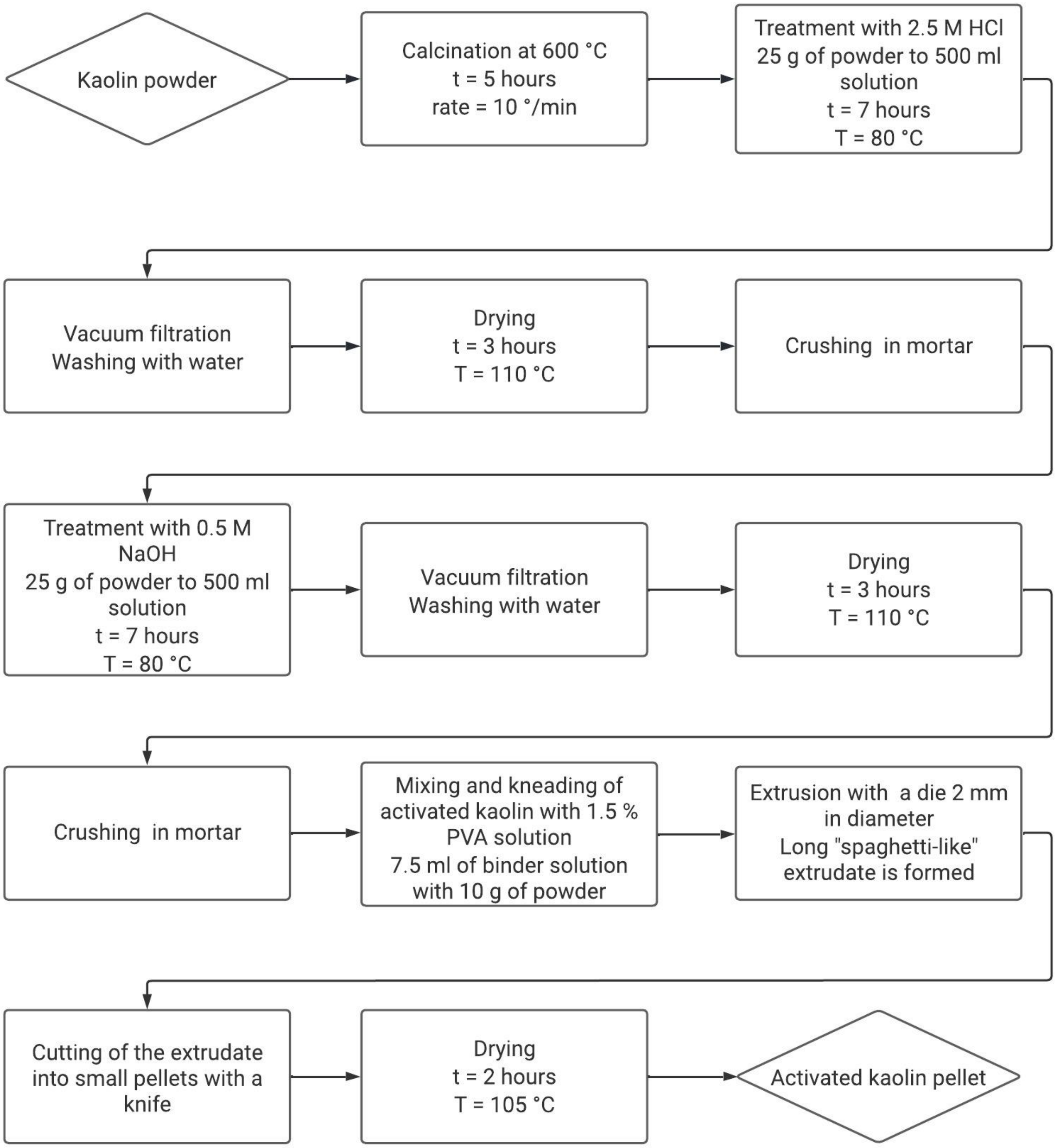


Figure 6: The flowchart of the process of making adsorbent pellets from kaolin by extrusion.

Chapter IV - Results and Discussion

4.1. Material characterization.

4.1.1. Thermogravimetric analysis (TGA).

The thermal analysis was performed by Simultaneous Thermal Analyzer 6000. The sample was heated at a 10 °C/min rate from 30 °C to 800 °C in a nitrogen atmosphere. The thermal analysis of the parent kaolin is presented in Figure 7. The single-stage decomposition is observed between 400 °C and 600 °C, where about 12 wt.% loss takes place. This corresponds to the dehydroxylation of kaolin, when water and hydroxyl groups are withdrawn from the material. A similar pattern was achieved by Boukhemkhem and Rida [50], where 12.5 wt.% weight loss occurred at 450 °C. It is stated that the weight loss during the dihydroxylation of kaolin is equal to 13.76% according to the following reaction:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$$

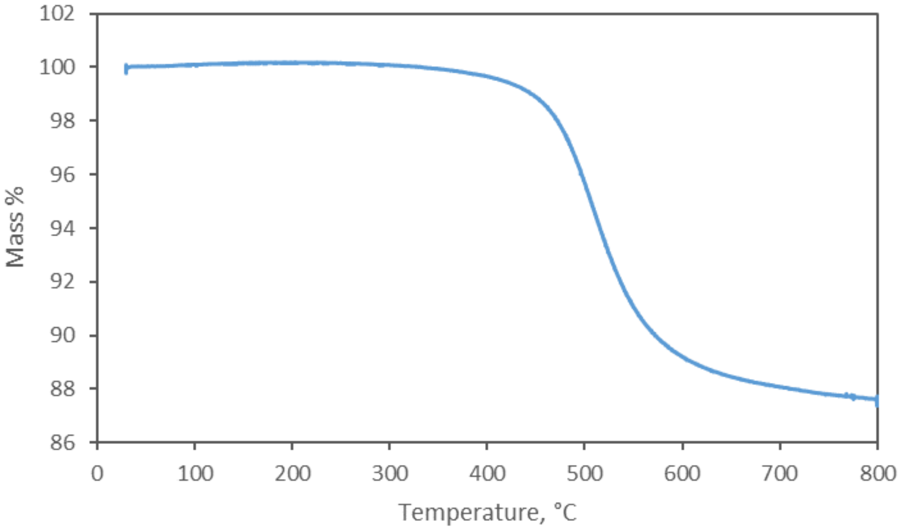
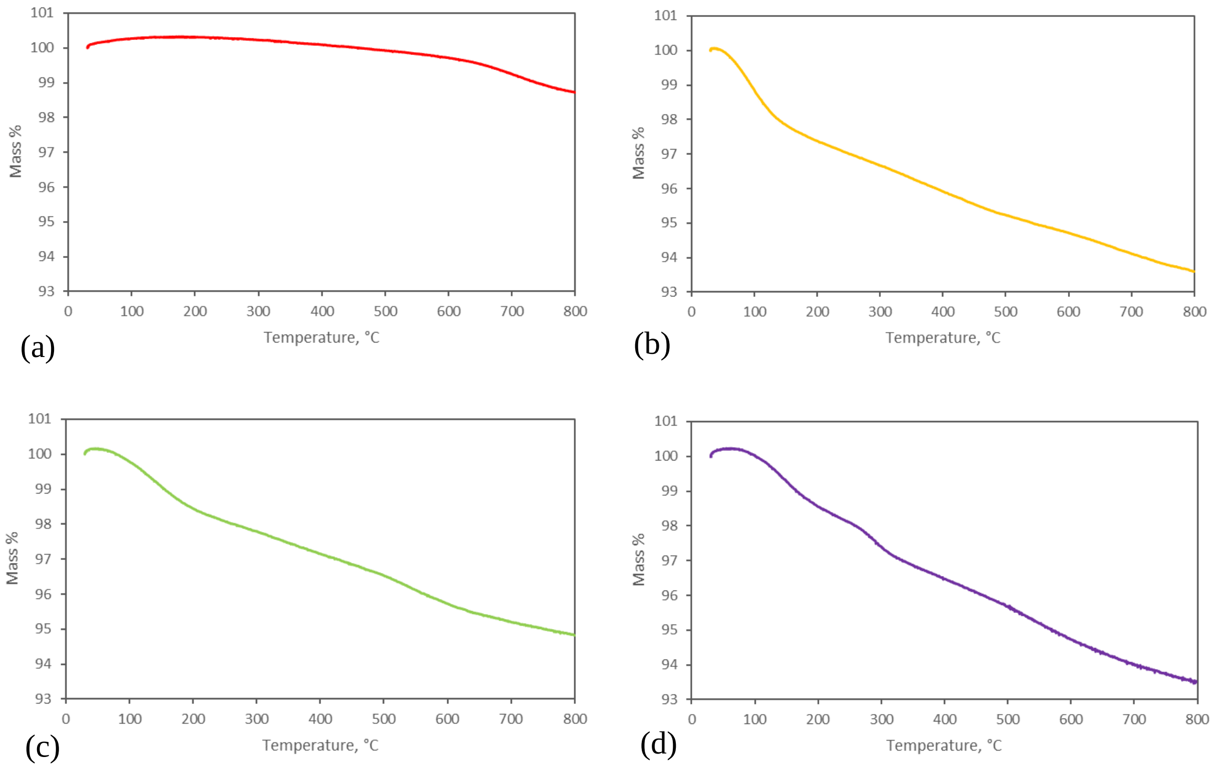


Figure 7: Thermal analysis of the parent kaolin powder.

At the stage of dehydroxylation, between 450 °C and 650 °C, the kaolin changes to metakaolin [13]. Figure 8 demonstrates the thermal analyses of the modified kaolin at each stage of its preparation. The calcinated kaolin shows a small change in the mass due to being already dehydroxylated. Little weight loss could be the result of the presence of some impurities. Acid and acid-base treated kaolin powders show a maximum 6.5 wt.% loss, which could be the physisorbed water that was left on the particles during the contact with acid and base solutions. No decomposition and similar weight loss are also observed in the case of the pellets.



(a) (b) (c) (d)

Figure 8: TGA graphs of (a) calcinated kaolin at 600 °C; (b) acid-treated kaolin; (c) acid-base-treated kaolin and (d) kaolin pellets made from modified kaolin with 1.5% PVA solution as a binder.

4.1.2. X-ray diffraction (XRD).

Rigaku Smartlab X-ray diffraction system was used to scan the XRD patterns of the kaolin and its modifications. The samples were scanned at 0.05° step from 5° to 90°. The voltage and current supplied were equal to 40 kV and 50 mA respectively. The XRD patterns were presented in Figure 9 from until 50° for better representation, as no more peaks were detected after this angle. The XRD pattern of the parent kaolin provided peaks at 8.9°, 12.3°, 17.7°, 19.8°, 20.4°, 21.4°, 24.9°, 26.7°, 27.5°, 34.9°, 36°, 37.7°, 38.4°, 39.3°, 45.4°. The XRD pattern of kaolinite clay studied by Klosek-Wawrzyn et. al. [69] was similar to the present results. Peaks corresponded to 3 different groups of clay materials: illite, kaolinite and quartz. The peaks of kaolinite disappeared after the calcination. This could be the result of the change in the crystal structure of the kaolin to metakaolin. The quartz and illite were detected from each sample. A little trace of kaolinite was noticed in acid and acid-base treated kaolin powders.

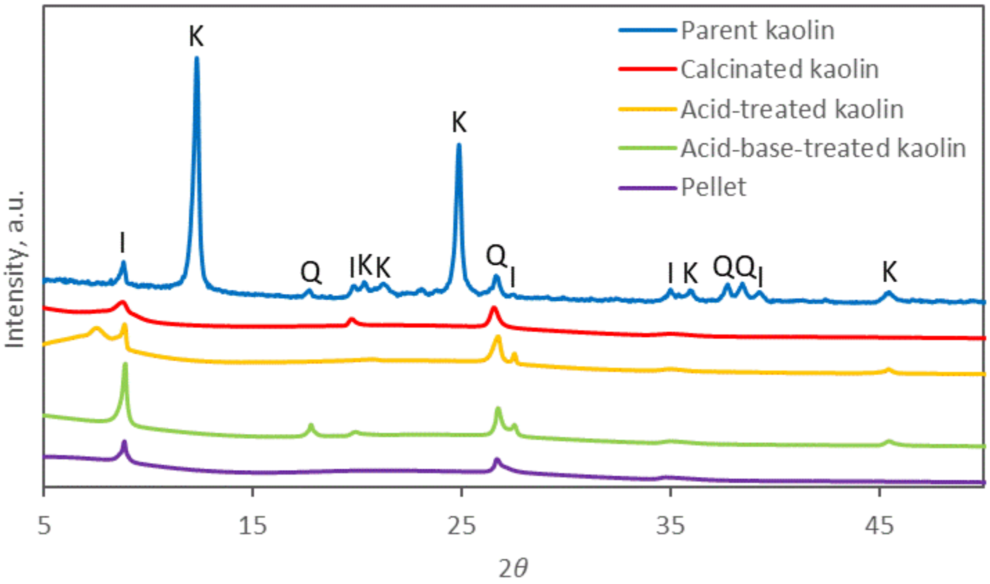
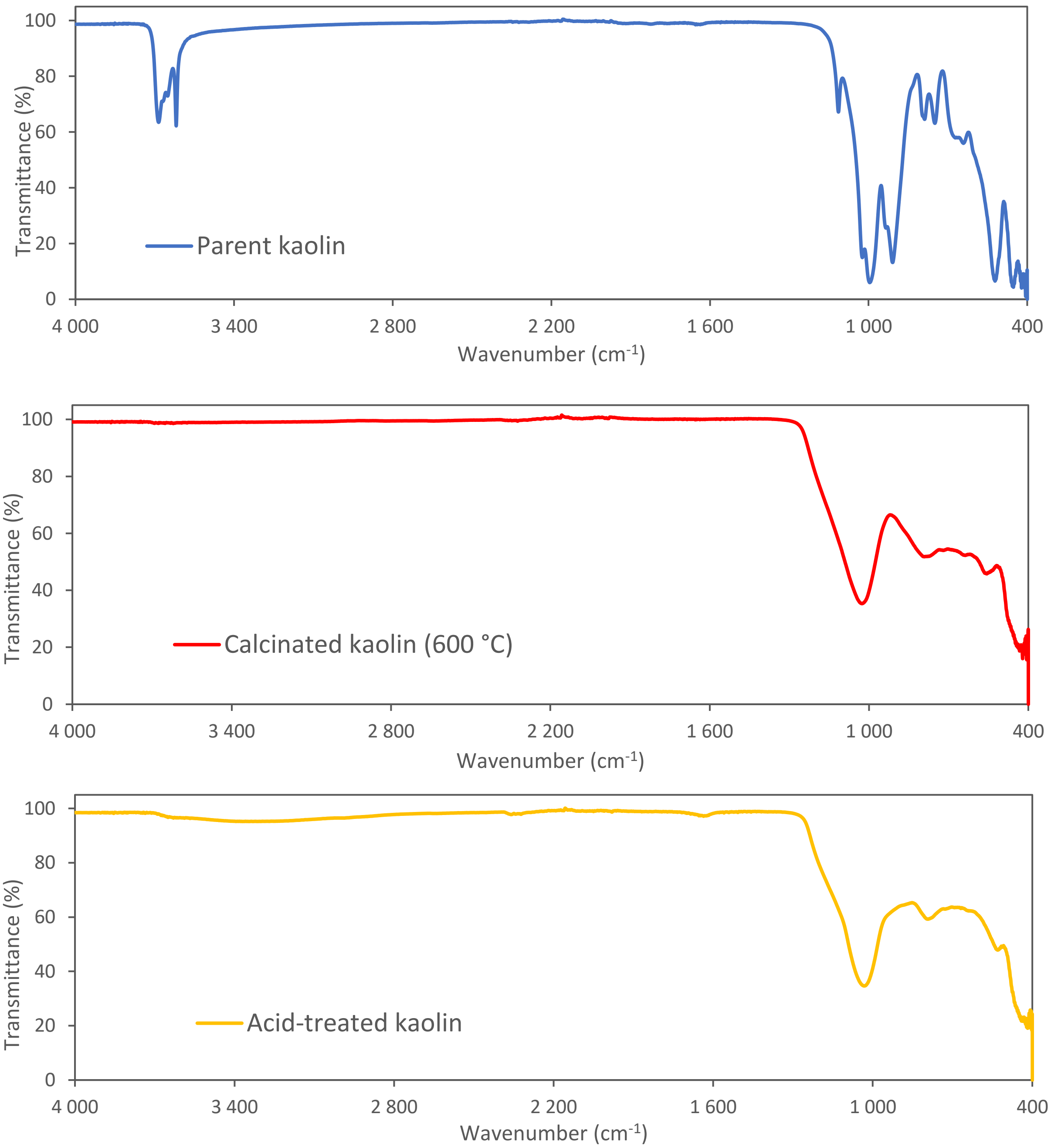


Figure 9: The XRD pattern of the parent kaolin and its modifications. I – illite, K – kaolinite, Q – quartz.

4.1.3. Fourier Transform Infrared (FTIR).

The FTIR spectra were recorded by Nicolet iS10 spectrometer. The spectra of the parent kaolin and its modifications at each stage are shown in Figure 10. The FT-IR spectra of the parent kaolin changed after being calcinated at 600 °C. No further significant changes were noticeable after treatment with acid and base, as well as with the addition of the PVA solution used to make the pellets. The sharp peak uptake of 3686 cm^{-1} and 3619 cm^{-1} at the spectra of the parent kaolin corresponded to the vibration of the -OH stretch, which described the presence of hydroxyl groups. Vibrations of Si-O functional groups were obtained at 996 cm^{-1} and 910 cm^{-1}, indicating the presence of quartz (SiO_2). The deformation of the -OH group linked to $2Al^{3-}$ was also characterized by those wavelengths. The peaks at 522 cm^{-1} and 453 cm^{-1} were obtained due to Si-O-Si bending. The FT-IR spectrum of the parent kaolin is similar to the spectra of kaolin materials studied by Saikia and Parthasarathy [70]. The peaks corresponding to hydroxyl groups disappeared after the calcination and further treatments, as all hydroxyl groups were removed after the thermal treatment. The only significant peak that is noticeable at the remaining FT-IR spectra is around 1 000 cm^{-1}, which shows the Si-O stretching of clay materials.



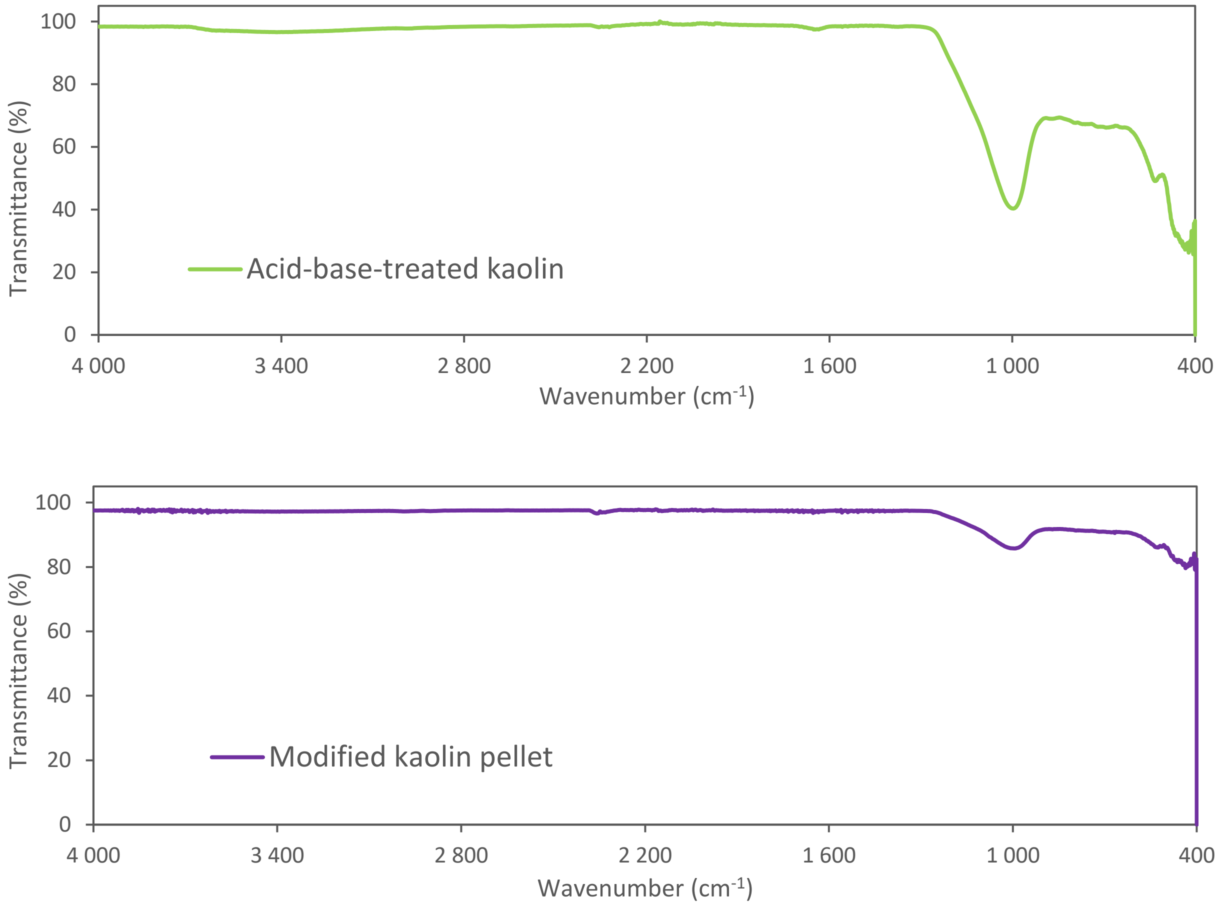


Figure 10: The FT-IR spectra of the parent kaolin and its modifications.

4.1.4. Scanning Electron Microscopy (SEM).

Scanning electron microscope ZEISS Crossbeam 540 was operated to get the images of the samples and study the morphological and surface characteristics of the kaolin and its modifications. Obtained SEM images are demonstrated in Figure 11. The kaolin powder has an irregular shape, and the crystal shape is visible. Many pores and crevices are present, and the particles are not layered, but some small parts appear at the surface of the larger parts. After the application of the calcination, pores are blocked. No considerable change on the surface can be detected from the images of acid and acid-base-treated kaolin powders. More sharp edges were formed after acid-base treatment. The surface of the extruded pellet is smooth, without major holes or cracks, showing a good connection between the particles. A close look at the surface of the pellet showcases a tight disposition of the layers with many pores where the absorbate can be stored.

The elemental analysis was made with EDS analysis for kaolin powder, and the top 3 elements were oxygen (40.5%), silica (27.6%) and aluminum (25.2%). The higher percentage of oxygen is due to the appearance of silica and aluminum in oxide forms (Appendix B).

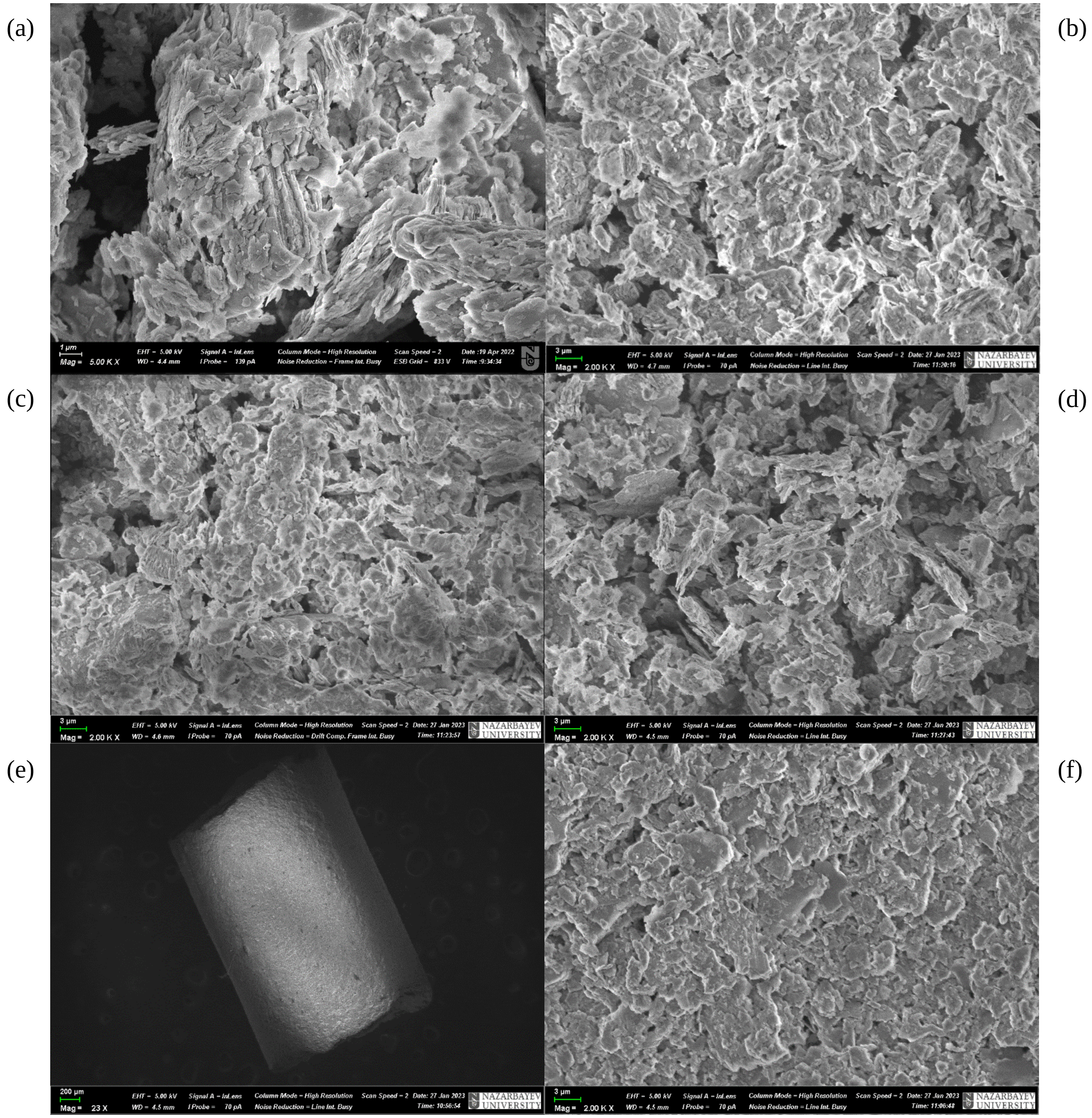


Figure 11: SEM images of (a) parent kaolin; (b) calcinated kaolin at 600 °C; (c) acid-treated kaolin; (d) acid-base-treated kaolin and (e) kaolin pellets made from modified kaolin with 1.5% PVA solution as a binder; (f) the surface of the pellet.

4.1.5. Specific surface area.

The specific surface area is an important characterization of catalysts and adsorbents. It demonstrates the potential of the material for adsorption. The specific surface area of the adsorbents was measured with different devices due to the unavailability of the porosimeter device at Nazarbayev University during the period of characterization, therefore part of the adsorbents was analyzed in labs in Greece. The specific surface areas of activated kaolin pellets prepared with PVA solutions were measured by Nitrogen Porosimeter (automated gas sorption analyzer) equipment manufactured by Quantachrome Instruments (results from this equipment are labeled with a * in Table 2). The Brunauer, Emmett and Teller (BET) theory was used for the calculation of the specific surface areas. All BET results are tabulated in Table 2. The specific surface area of the initial kaolin was 55.6 m^2/g. The surface area increased to 72.58 and 87.49 after the implementation of the calcination and acid treatment. The application of base treatment decreased the surface area of calcinated and acid treatment kaolin, and the same effect was noticed on only calcinated kaolin. In the study of Boukhemhem and Rida [50], the same trend in the change of the surface area was noted. The initial specific surface area of their kaolin powder was equal to 14 m^2/g. The value changed to 16 m^2/g, 191 m^2/g and 45 m^2/g after consecutive application of calcination, acid and base treatments respectively. The calcination of tested kaolin may cause the aggregation of particles after dehydroxylation, which generated grains with more pores and increased surface area [71]. The acid treatment causes Al^{3+} extraction from the surface of the kaolin, which creates new openings on platelet edges [58,60]. The decrease after the base treatment occurred due to the potential blockage of pores by Na^+ ions [50].

Table 2: Specific surface areas of kaolin powder and its modifications.

Sample	Surface area (m^2/g)
Pellets with no calcination	41.35
Pellets calcinated at 600 °C	35.09
Pellets calcinated at 400 °C	41.08
Raw kaolin	55.60
Calcinated kaolin, 600 °C	72.58
Kaolin, HCl treated	87.49
Kaolin, NaOH treated	39.82
Kaolin, HCl and NaOH treated	53.18
Pellets with 1.5% PVA*	21.83
Pellets with 5% PVA*	14.08

4.1.6. X-ray fluorescence (XRF).

The elemental analysis of the parent kaolin was performed by Niton XL3t GOLDD$^+$ portable XRF analyzer. The sample was subjected to X-rays to identify the composition of existing metals in the structure of the kaolin, and the results in percentages were presented in Table 3. The major portion of kaolin consists of silicon and aluminum. Small traces of potassium, iron, magnesium and titanium were present. 56.49% of the kaolin was not identified, and the reason for this was the presence of the mentioned metals in the form of oxides.

Table 3: The elemental analysis of the kaolin obtained from XRF analysis.

Element	**% Percentage**
Si	23.14
Al	16.69
K	1.67
Fe	0.758
Mg	0.587
Ti	0.404
P	0.114
Ca	0.061
V	0.013
Rb	0.014
Zr	0.012
Cr	0.010
Nb	0.006
Pb	0.006
Bi	0.005
Sr	0.005
Zn	0.004
Other	56.49

4.2. Adsorption experiments with different kaolin forms and modifications.

4.2.1. Pellets made from the parent kaolin.

The adsorption experiments involving the kaolin pellets were performed for a long time until the equilibrium was achieved. The methylene blue concentration was measured every 1 hour and results are presented in Figure 12. The gap between the measurements corresponds to the nighttime when no measurements were taken. Figure 12 shows the effect of the calcination temperature on the adsorption capacity of the kaolin pellets. It can be observed that the highest value is demonstrated by 2 mm (in diameter) pellets calcinated at 600 °C, and the adsorption capacity is equal to 1.43 mg/g. Additionally, the duration of the experiment was too long, taking more than a day to complete the experiment. The results show that the adsorption capacity increases from 500 °C to 600 °C calcination temperature and decreases at 700 °C and 800 °C calcination temperatures. One batch of pellets with a diameter of 3 mm was prepared and calcinated at 500 °C. Its adsorption capacity is lower in comparison with the 2 mm pellets calcinated at the same temperature, so larger sizes decreased the adsorption capacity. The adsorption ability of the kaolin powder was investigated since the adsorption capacity of the pellets was too small.

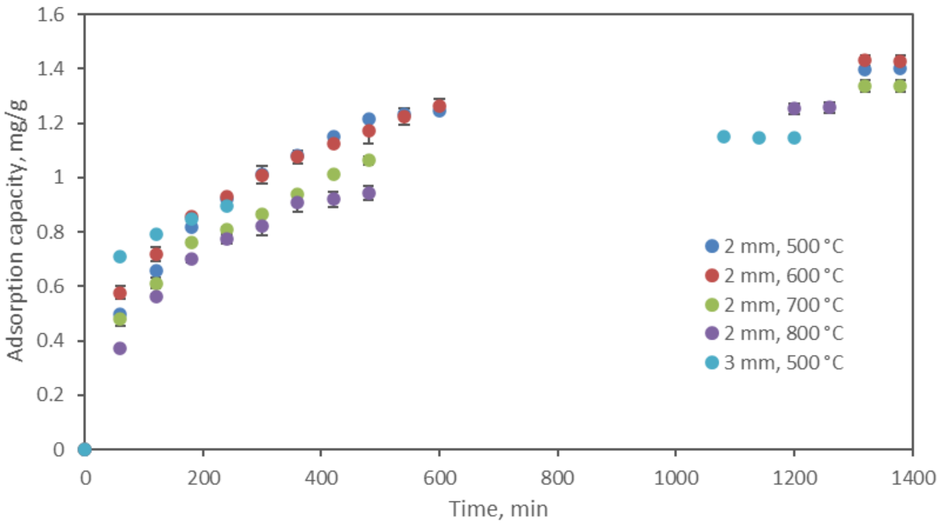


Figure 12: Adsorption capacities of the kaolin pellets calcinated at different temperatures, and with different sizes for 500 °C. Experimental conditions: C_0 = 30 mg/L, m_c = 4 g, V = 200 ml.

4.2.2. Adsorption experiments with kaolin powder.

The adsorption capacity of the kaolin powder shows a value of around 9.25 mg/g, with some errors. Taking into account the current value, the adsorption capacity of the enriched kaolin is higher than the kaolin and equal to 11.67 mg/g. This demonstrates that the origin of the kaolin is an important characteristic, since different kaolin perform differently. The values of the adsorption capacities are not impressive, therefore the low adsorption capacities of the pellets were expected. Some modifications found from the literature review were implemented to improve the performance of the kaolin powder.

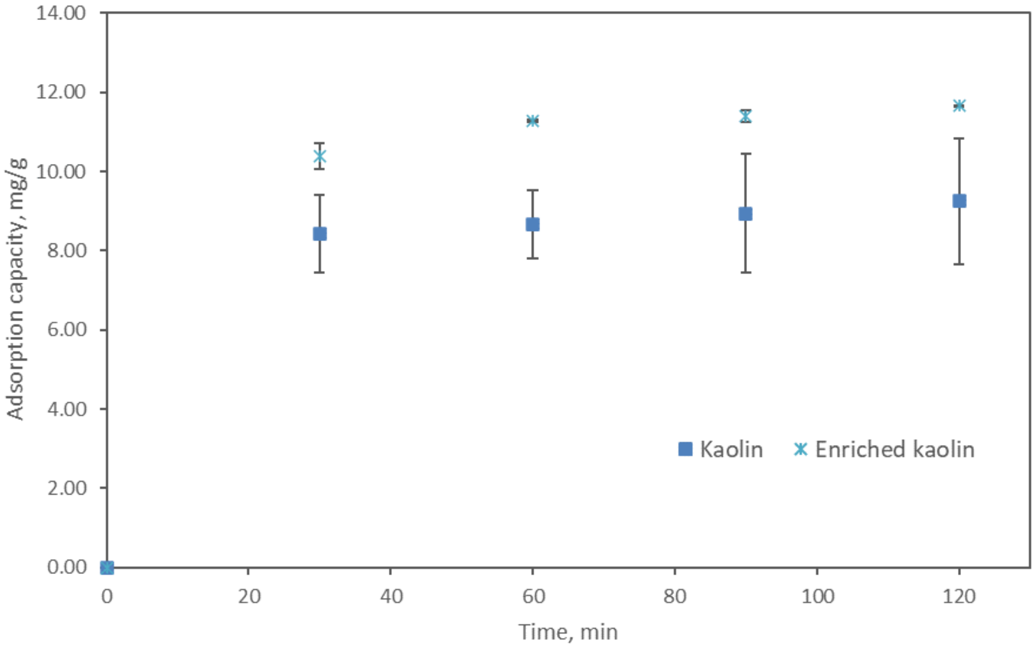


Figure 13: Adsorption capacities of kaolin and enriched kaolin powder. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

4.2.3. Acid pre-treatment of the kaolin powder.

The first attempt in improving the adsorption capacity of kaolin powder was acid pretreatment with 0.1 N H_2SO_4. Both parent kaolin and enriched kaolin powders were treated. The results of the acid treatment are presented in Figure 14.

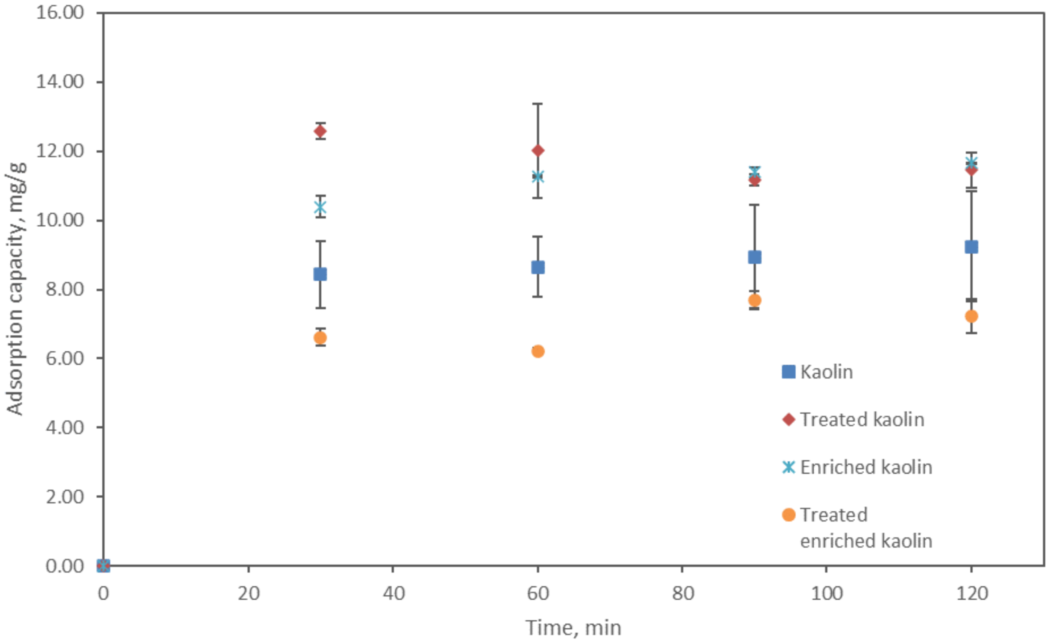


Figure 14: Adsorption capacities of the kaolin and enriched kaolin powder and their acid-treated modifications. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

The adsorption capacity of the kaolin powder increased from 9.25 mg/g to 11.45 mg/g, which could not be considered satisfactory. The opposite trend was noticed with the enriched kaolin powder, as the adsorption capacity decreased from 11.67 mg/g to 7.22 mg/g. Due to this observation, further experiments were decided to be done with the kaolin powder, and after finding a successful method of adsorption capacity improvement, enriched kaolin could be tested further. Gao et al. [51] applied a similar treatment with H_2SO_4, but the treatment procedure had some differences. In that research, the 3 g of powder was placed inside the three-neck flask with a condenser, and 15 mL of concentrated H_2SO_4 was added and heated to a particular temperature. The powder treated at 200 °C for 30 minutes demonstrated the best result among other options, and the adsorbed amount of methylene blue increased from 72% to 90%. In the present experiment, the parent kaolin removed 33% of methylene blue, while the enriched kaolin removed 41%. After the treatment, the percentage rose to 38% and fell to 25% respectively. Acid treatment with H_2SO_4 positively affected the parent kaolin and negatively affected the enriched kaolin.

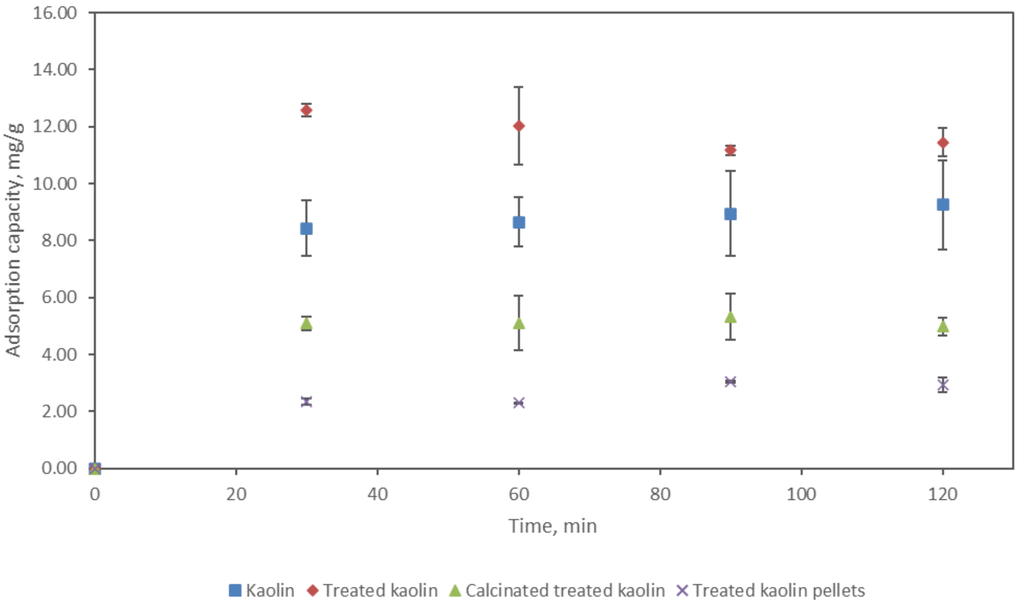


Figure 15: Adsorption capacities of the kaolin powder and its treated modifications. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

The calcination after the acid treatment was applied to observe how the material would react to the calcination, since the pellets required a calcination step at the end of their preparation. Calcination at 600 °C after the acid treatment decreased the adsorption capacity from 11.45 mg/g to 4.98 mg/g, while the extruded pellets made from the acid-treated kaolin showed 2.95 mg/g adsorption capacity. This observation demonstrated the negative effect of calcination on the adsorption properties of kaolin after the acid treatment. The pores and the acid active sites could be blocked as a result of high temperatures. The acid-treated kaolin pellets had higher adsorption capacity than the kaolin pellets without any treatment, as the values are 2.95 mg/g and 1.43 mg/g respectively. The negative effect of the calcination on the adsorption capacity led to the new treatment method, where the calcination was done before the acid treatment, and followed by the treatment with NaOH [50].

4.2.4. Calcination of the kaolin powder and subsequent acid and base treatment.

Preliminary calcination of the kaolin is necessary to convert the kaolin to metakaolin, which is more reactive with the acid [61]. Studies where the calcination was used before the acid treatment report increased adsorption capacity and specific surface area of the kaolin material [48,50,72].

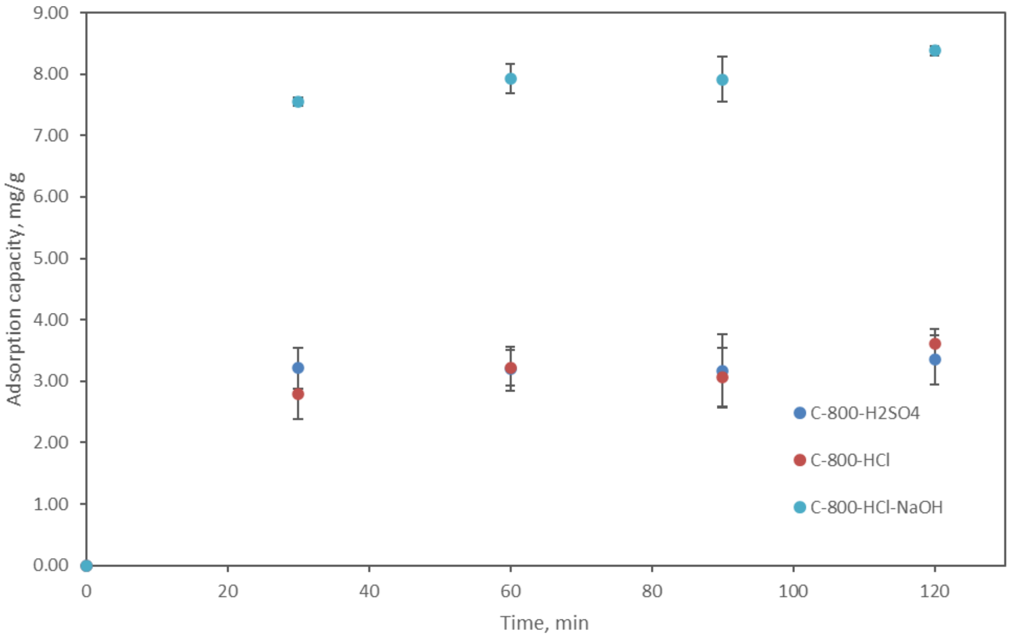


Figure 16: Adsorption capacities of the kaolin powder, initially calcinated at 800 °C and post-treated with acid and base. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

Figure 16 demonstrates how the preliminary calcination affected the adsorption capacity. The treatments with HCl and H_2SO_4 showed similar results, 3.62 mg/g and 3.35 mg/g, respectively. 800 °C calcination was applied by Zen et al. [62]and Gao et al. [48], and both studies obtained increased adsorption capacity after applying calcination and acid treatment. Comparing Figures 13 and 16, the adsorption capacity of the parent kaolin is larger than the activated adsorbents. The highest value was achieved by implementing base treatment right after the acid treatment, which was 8.38 mg/g, which is close to the values got by the parent kaolin. Since the adsorption capacity values after implementing preliminary calcination and further acid and base treatments demonstrated promising results, calcination at different temperatures was applied to find the most efficient calcination temperature, which could result in higher adsorption capacities. The first attempts were done with 400 °C and 600 °C calcination temperatures.

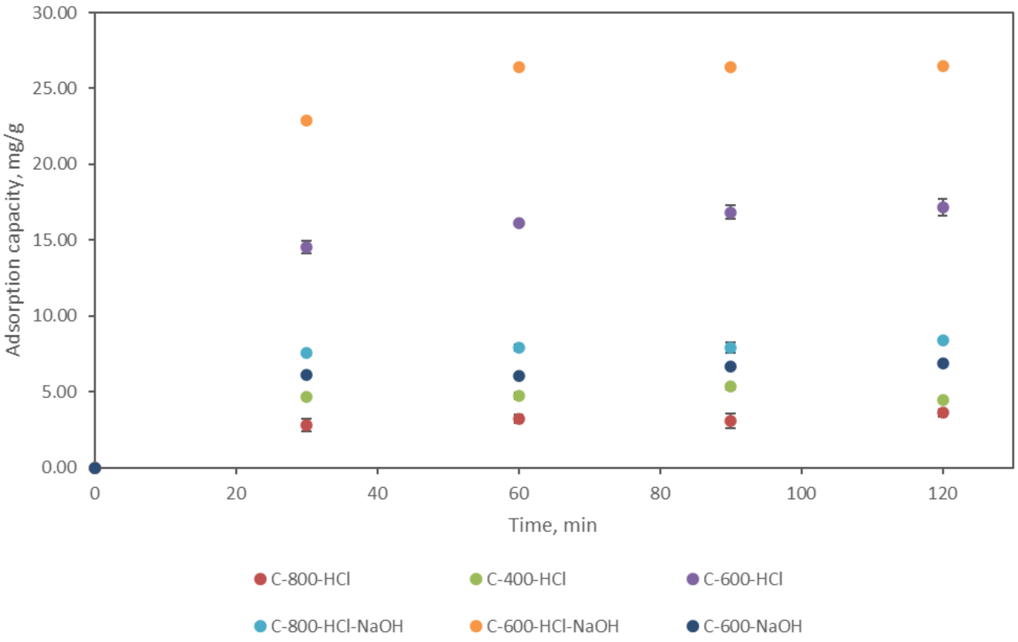


Figure 17: Adsorption capacities of the kaolin powder initially calcinated at different temperatures and post-treated with acid and base. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

The adsorption capacities of the acid-treated powders calcinated at 400 °C and 600 °C were higher than 800 °C (Figure 17). However, the adsorption capacity value for 400 °C calcinated and acid-treated powder was 4.49 mg/g, compared to 17.16 mg/g achieved by the 600 °C calcinated acid-treated powder. So, 400 °C calcination temperature was not studied further. The highest value of adsorption capacity was shown by the kaolin powder, which was calcinated at 600 °C and treated with the acid and base respectively. The final value is 26.47 mg/g. Direct implementation of the base treatment was not effective, achieving only 6.89 mg/g adsorption capacity.

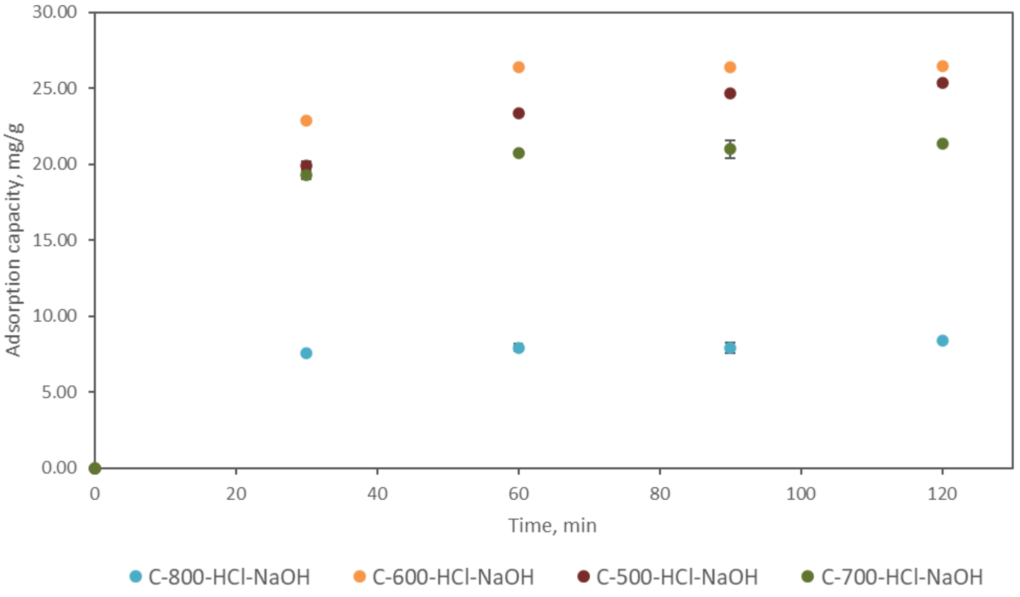


Figure 18: Adsorption capacities of the kaolin powder initially calcinated at different temperatures and post-treated with acid and base. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

The final values of the adsorption capacities for the powders calcinated at different temperatures are illustrated in Figure 18. The highest value still belongs to the kaolin calcinated at 600 °C, followed by the 500, 700, and 800 °C, respectively. Taking into account the adsorption capacity of the untreated original kaolin was 9.25 mg/g, 26.47 mg/g was achieved by applying calcination, acid, and base treatment. This is the final point of the experiments with the kaolin powder. Further experiments are aimed to prepare pellets from the treated powder and assess their adsorption performance.

4.2.5. Adsorbent pellets made from modified kaolin by extrusion.

Pellets prepared from the activated kaolin were prepared and tested for methylene blue absorbance. The calcination was applied after the formation of the pellets, and the temperature varied from 200 °C to 600 °C (Figure 19). Additionally, pellets prepared without the calcination step were examined. Such pellets demonstrated superior adsorption capacity compared to other alternatives, with 13.65 mg/g adsorption capacity. Calcination at 200 °C resulted in 6.94 mg/g adsorption capacity, while pellets calcinated at higher temperatures had significantly less capacity with a maximum value of 3.04 mg/g. The main reason for this behavior was the pellet's ability for keeping its shape throughout the experiment. Pellets that were not calcinated and calcinated at 200 °C were crushed and disintegrated after the experiment, which led to the conclusion that the higher values of the adsorption capacity correspond to the activated kaolin powder that was formed after the destruction of the pellets. The minimum calcination temperature required to keep the shape of the pellets is 300 °C. Despite keeping the shape, higher calcination temperatures produce pellets with low adsorption capacities. The active adsorption sites can be blocked after the calcination. Wang et al. [61] characterized kaolin after being calcinated at different temperatures, and concluded that the specific surface area decreases with increasing calcination temperature.

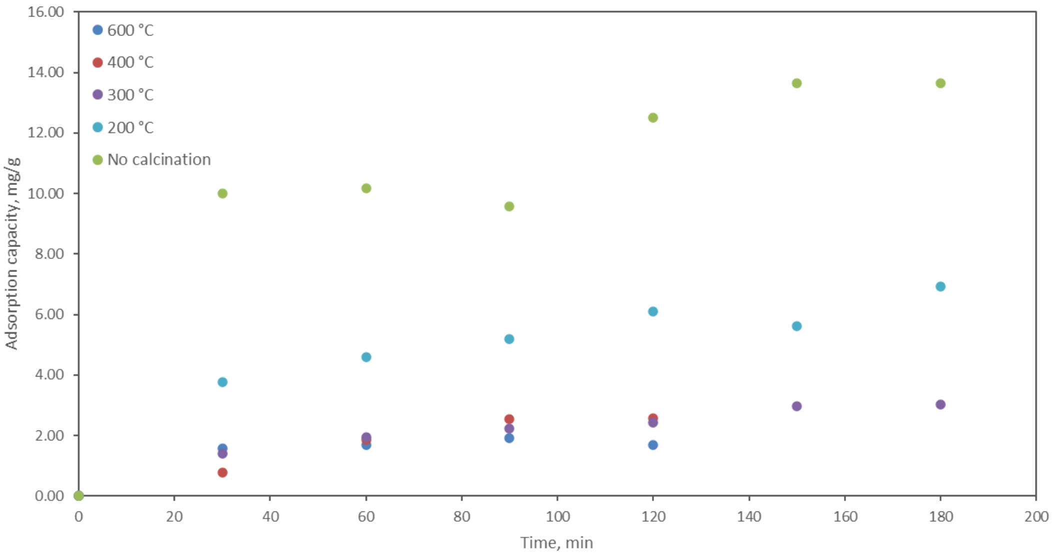


Figure 19: Adsorption capacities of pellets made from modified kaolin by extrusion calcinated at different temperatures. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

Application of the binder instead of the calcination was the next step in the development of the kaolin adsorbent that can retain its shape and demonstrate higher adsorption capacities.

4.2.6. Kaolin pellets with PVA solution as a binder.

The results of the experiments with new pellets are showcased in Figure 20. Pellets made with 0.05% PVA solution were the most efficient in removing methylene blue dye from the solution, having an adsorption capacity of 18.2 mg/g. The adsorption capacity decreases with the increasing concentration of the PVA. Since PVA is now integrated into the structure of the pellet, some of its parts could be occupied by PVA, decreasing the surface area. BET results demonstrated that pellets made with 5% PVA solution possess less specific surface area compared to the pellets made with 1.5% PVA solution.

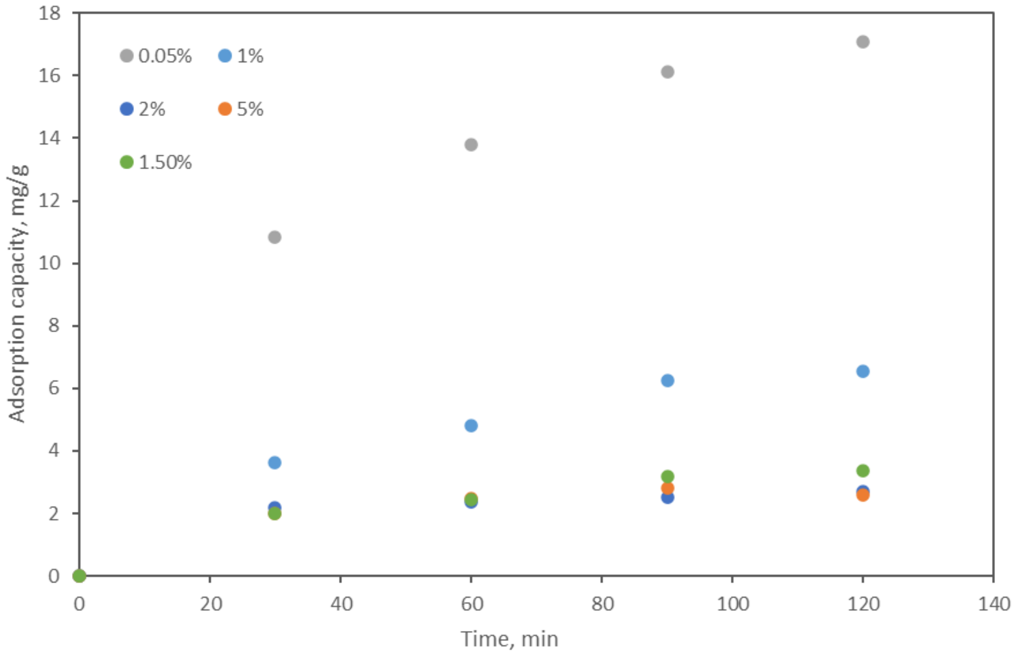


Figure 20: The adsorption capacity of pellets made from activated kaolin and PVA binder of different concentrations. Experimental conditions: C_0 = 100 mg/L, m_c = 1.7 g, V = 500 ml.

However, the same trend noticed with the calcination temperature can be observed with the PVA concentration. The highest adsorption capacities were achieved with 0.05% and 1% PVA solutions, but the shape of the pellets was destroyed and became powder. Pellets made with 1.5% and higher PVA solutions were strong and endured adsorption experiments that lasted for 2 days. 1.5%, 2% and 5% PVA solutions had similar results after 2 hours of the experiment, but the highest result was 3.37 mg/g, which corresponds to the 1.5% PVA solution. Additionally, pellets showed a slow but continuous increase in the adsorption capacity, therefore experiments for longer hours were performed to reach the equilibrium. All further experiments were done with the pellets made from activated kaolin and 1.5% PVA solution, as it was chosen as the most promising option among all tested adsorbents. Kinetic, equilibrium, effects of the solution pH and the adsorbent dose studies are presented in the next section.

4.3. Detailed methylene blue adsorption studies on activated kaolin pellets.

4.3.1. Effect of pH of the methylene blue solution.

The impact of the solution pH on the adsorption capacity was analyzed by adjusting the pH of the solution to 4, 6.5, 8 and 10. The natural pH of the solution was equal to 6.5. All experiments were done in duplicate with a maximum standard error of 0.38. Other experimental parameters, except for the pH, remained constant: initial methylene blue concentration = 100 mg/L; adsorbent mass = 850 mg; solution volume = 250 mL. The maximum value of the adsorption was recorded after 2 days of the experiment’s duration. Obtained results are demonstrated in Figure 21.

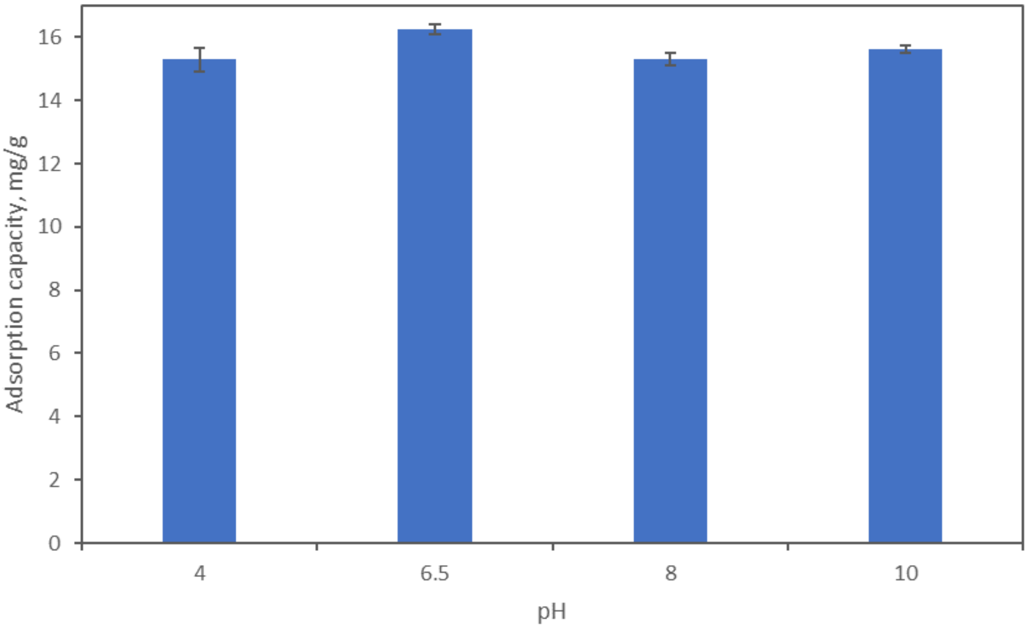


Figure 21: Effect of solution pH on the methylene blue adsorption by activated kaolin pellets.

The maximum adsorption capacity was noticed for the solution with natural pH of 6.5. The value was 16.26 mg/g, and the minimum value was 15.29 mg/g. Since the difference in the adsorption capacity is not significant at different pH values, 6.5 pH can be considered to be the optimum choice. Similar results were reported by Jawad and Abdulhameed [40], when they tested the adsorption capacity of the Iraqi red kaolin. Their tested range of pH was from 2 to 10, with an increment of 1. The natural pH of the methylene blue solution was 7. The acidic pH values, from 2 to 6, had 79.2 mg/g capacity, while the basic values, from 7 to 10, had 88.3 mg/g adsorption capacity. The difference is not significant, and the change in the adsorption capacity was only observed from the transition from pH of 6 to 7, and after this point no change in the capacity was found. pH value of 6 was considered the optimum pH for the adsorption of methylene blue by Iraqi kaolin in another study [73]. The efficiency of the basic pH values is the result of the formation of the positive charge inside the solution, while the surface of the kaolin is negatively charged, so the adsorption is more favorable. Figure 22 presents the final pH values after the completion of adsorption experiments. All solutions became basic, reaching pH values from 8.61 to 8.77.

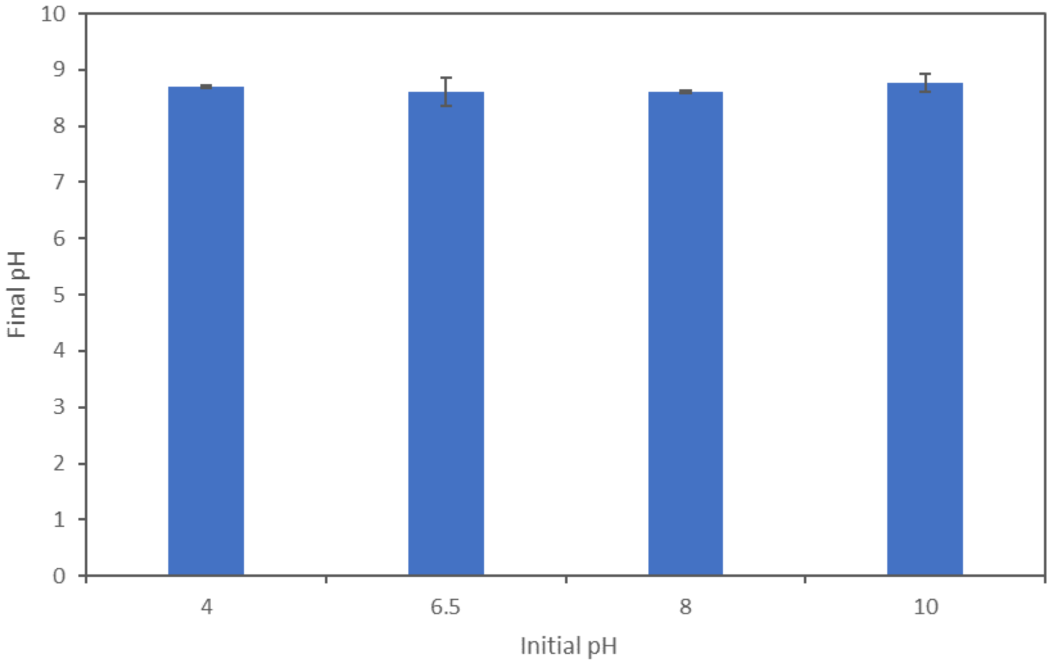


Figure 22: The pH evolution of methylene blue solutions after adsorption experiments.

4.3.2. Effect of the adsorbent.

Identification of the optimum amount of the adsorbent is essential for rational usage of adsorbent per experiment. The adsorbent was added to 100 mg/L methylene blue solutions at different amounts: 0.4 g, 0.85 g, 2 g and 4 g. The volume of the solution remained to be 250 ml and no pH adjustment was done. Maximum adsorption capacities were obtained after 2 days and documented in Figure 23.

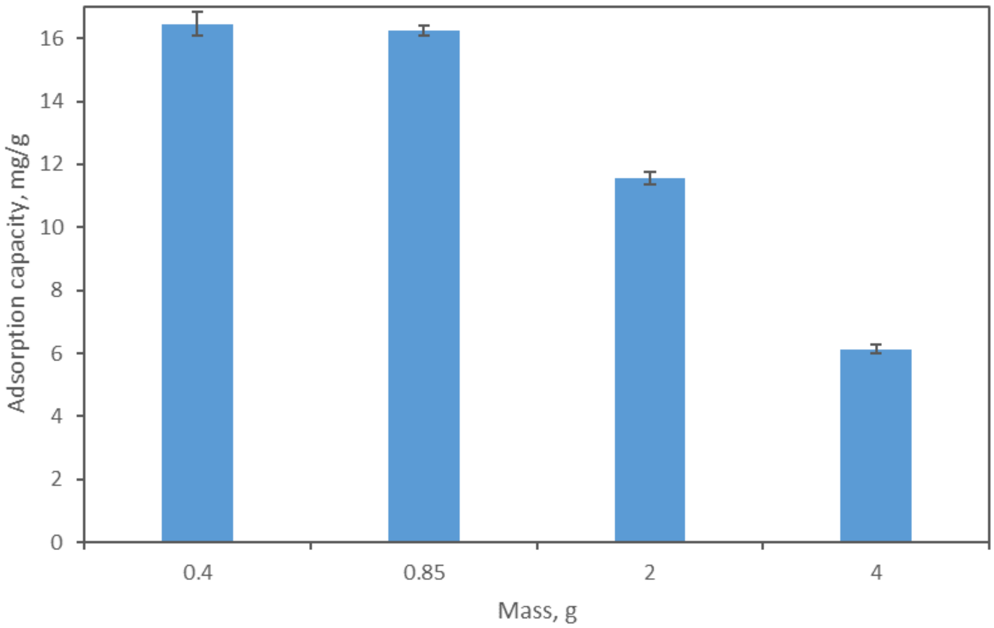


Figure 23: Effect of adsorbent dose on the methylene blue adsorption by activated kaolin pellets.

The adsorption capacity decreased with the increased amount of the adsorbent used. There is a small change in the adsorption capacity between 0.85 g and 0.4 g, therefore the adsorbents used at that range will produce the highest adsorption capacities, nearly reaching 16 mg/g. Usage of less amount of adsorbent is convenient, however 2 days are required to achieve 16 mg/g adsorption capacity. Figure 24 presents the maximum adsorbed amount of methylene blue, where the dominance of a higher adsorbent dose is evident. For 100 mg/L initial concentration of methylene blue, 4 g of adsorbent removed 92% of the methylene blue, while 0.4 g and 0.85 g of adsorbent removed only 20% and 40% after 1 day (Figure 25). Despite the fact of having less adsorption capacity with 4 g of the adsorbent, more methylene blue removal was achieved. Additionally, kaolin’s market provides opportunities for using more materials with low prices due to the existence of domestic fields and affordable prices. The same conclusion was stated by Mouni et al. [52], as no increase in the adsorption was achieved by using more than 1 g of the adsorbent. Utilization of more amount of the adsorbent creates more adsorption sites and increases the surface area, however at some point all adsorption sites became occupied leading to no significant rise in methylene blue removal.

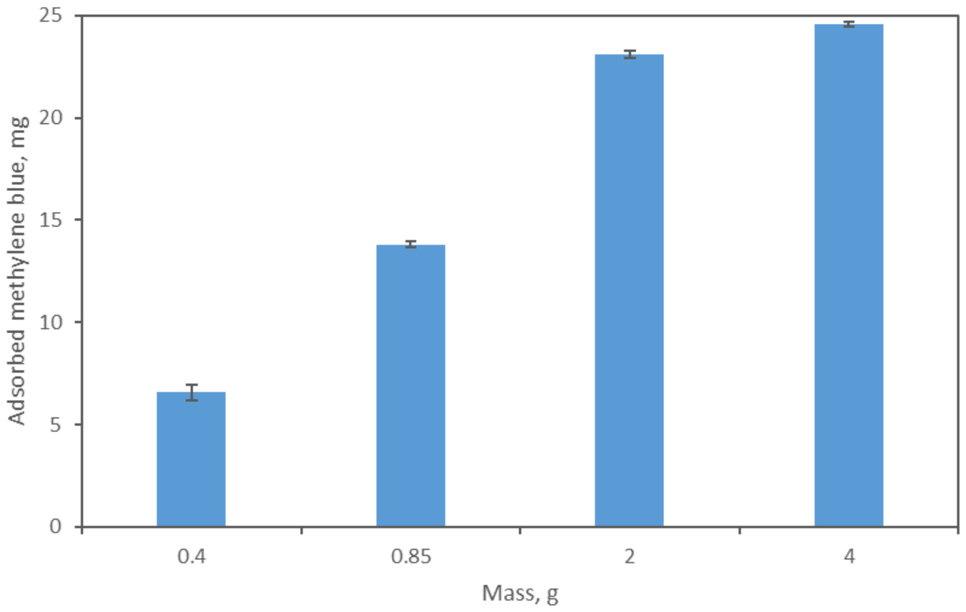


Figure 24: The maximum adsorbed amount of methylene blue by different adsorbent doses.

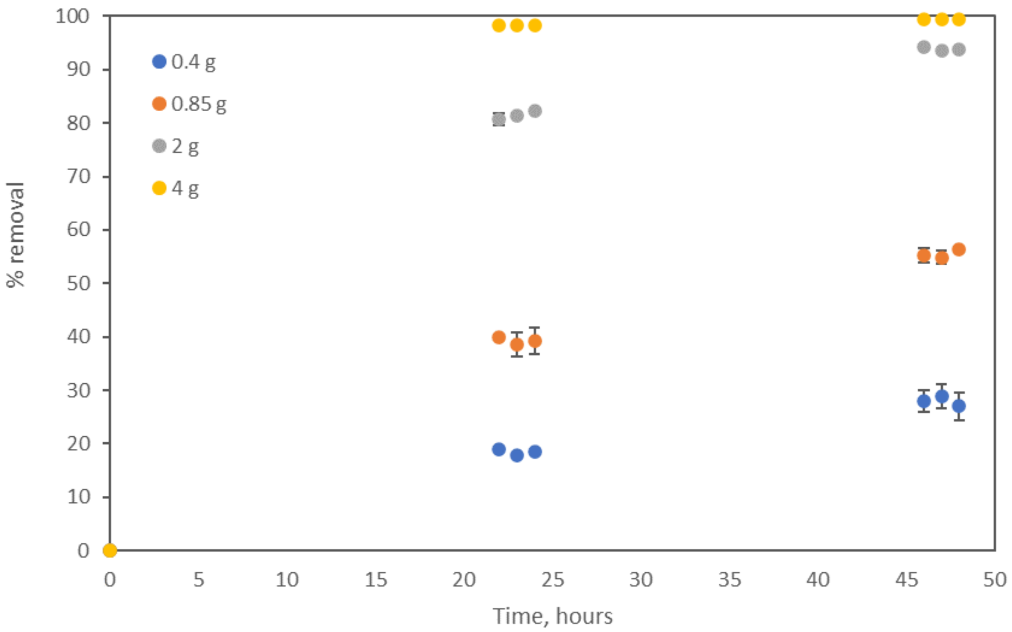


Figure 25: Removal percentage of methylene blue by different adsorbent doses.

4.3.3. Equilibrium studies.

The equilibrium studies were conducted at different initial methylene blue concentrations, in the range of 50 mg/L to 250 mg/L, and the maximum adsorption capacities were recorded. The highest adsorption capacity, 20.04 mg/g, was achieved by treating 250 mg/L methylene blue solution (Figure 26). 19.95 mg/g adsorption capacity was demonstrated by the treatment of 200 mg/L methylene blue solution, so the change in adsorption capacity after 200 mg/L initial concentration was insignificant and reached a plateau.

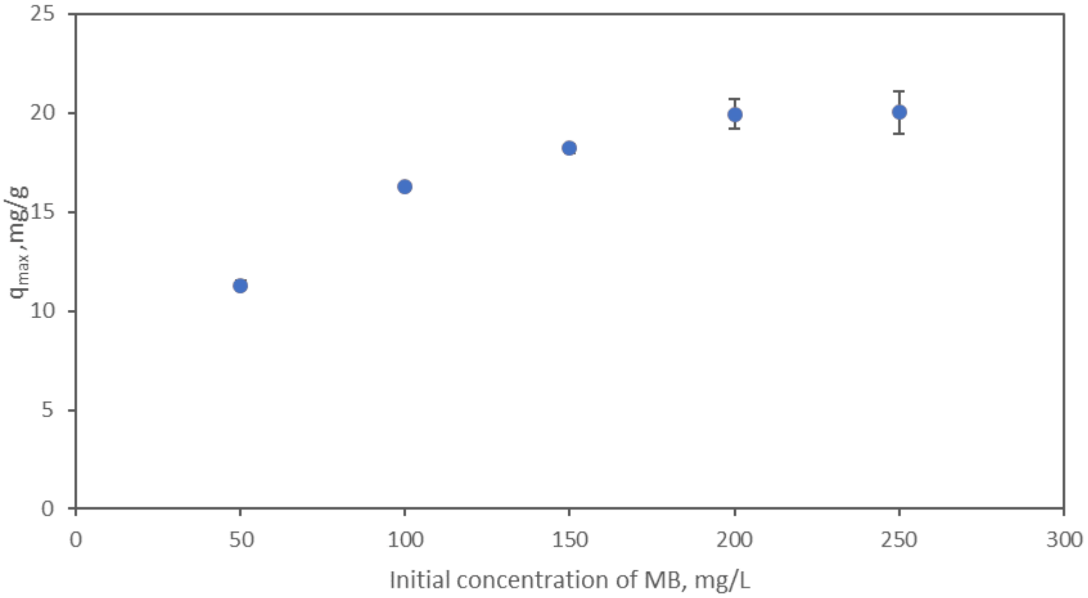


Figure 26: Maximum adsorption capacities of the activated kaolin pellets at different initial methylene blue concentrations.

The experimental data were fitted to Langmuir and Freundlich models, and the linear form of those models was plotted and shown in Figure 27. The R^2 value is 0.9991 for the Langmuir model and 0.9663 for the Freundlich model. The adsorption of methylene blue by activated kaolin pellets fits better with the Langmuir model, which indicates the monolayer adsorption on the surface of the adsorbent. The R_L value of Langmuir isotherm is equal to 0.208, meaning that the adsorption was favorable. The maximum adsorption capacity calculated by Langmuir isotherm was 21.6 mg/g, while the experimental value is 20 mg/g. This also shows the validity of the Langmuir model for this adsorption process. The value of n in the Freundlich model was 4.47, which is greater than 1, meaning the good adsorption ability of the adsorbent. All values found after fitting to Langmuir and Freundlich models are listed in Table 4, and the comparison plot is given in Figure 28.

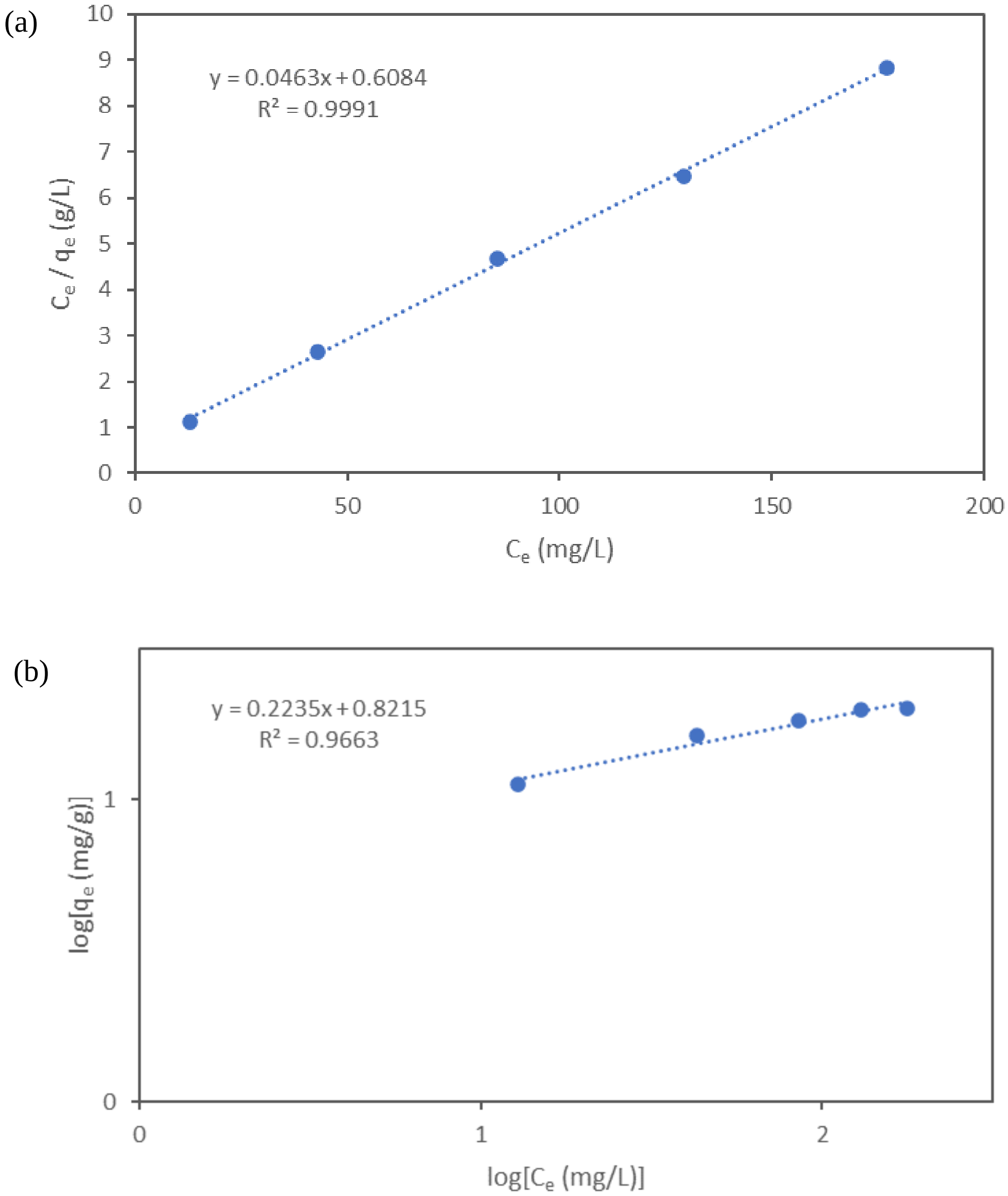


Figure 27: Linear plots of (a) Langmuir and (b) Freundlich models.

Table 4: Parameters of Langmuir and Freundlich isotherm models fitted to experimental results.

Model	Experimental	Langmuir				Freundlich		
Parameter	q_{max}	q_{max}	K_L	R_L	R^2	n	K_F	R^2
Value	20.04 mg/g	21.58 mg/g	0.076 L/mg	0.208	0.9991	4.474	6.63	0.9663

Boukhemhem and Rida [50] studied the adsorption equilibrium of methylene blue adsorption by modified Tamazert kaolin. The modification included thermal, acid and base treatments, which were also used in this thesis work. According to their results, the Langmuir model had better fitting than the Freundlich model. The R^2 values were 0.94 and 0.9 respectively, and the experimental q_{max} and calculated q_{max} by the Langmuir model were 110 mg/g and 104.16 mg/g. Gao et al. [51] fit the experimental equilibrium data of untreated kaolin and acid-treated modification of the kaolin to Langmuir and Freundlich isotherms. The maximum adsorption capacity of acid treated kaolin was 101.5 mg/g, while the parent kaolin had 78.1 mg/g. Both equilibrium models showed good linearity, however the R^2 value was higher when the Langmuir model was fit to the adsorption with the parent kaolin, while the Freundlich kaolin was more suitable for acid-activated kaolin. In both mentioned works the material was in a powder form.

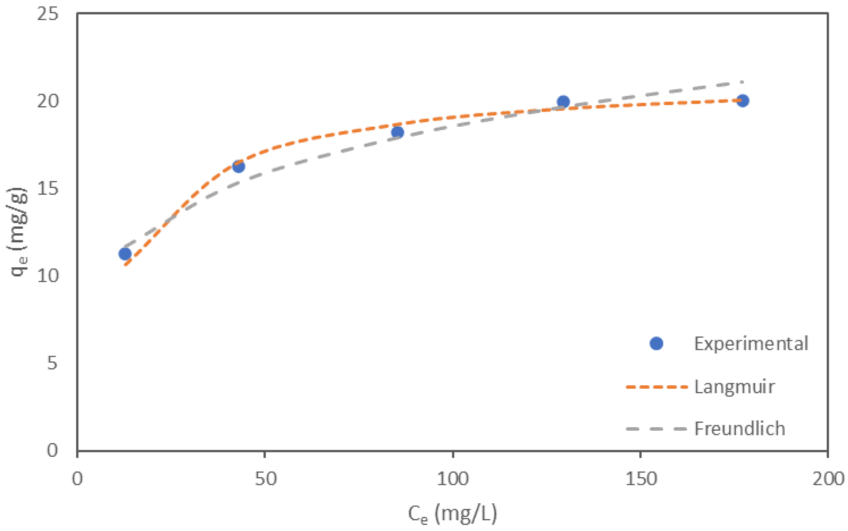


Figure 28: Comparison of experimental results obtained from equilibrium adsorption of methylene blue.

The compliance between the experimental values and the Langmuir isotherm model is well represented by Figure 29. The experimental and theoretical adsorption capacities were plotted against each other and the dashed lines are the regions of 10% error. Only the first point is located near the error line, while the remaining 4 points lay on the linear straight line showing good linearity between the values.

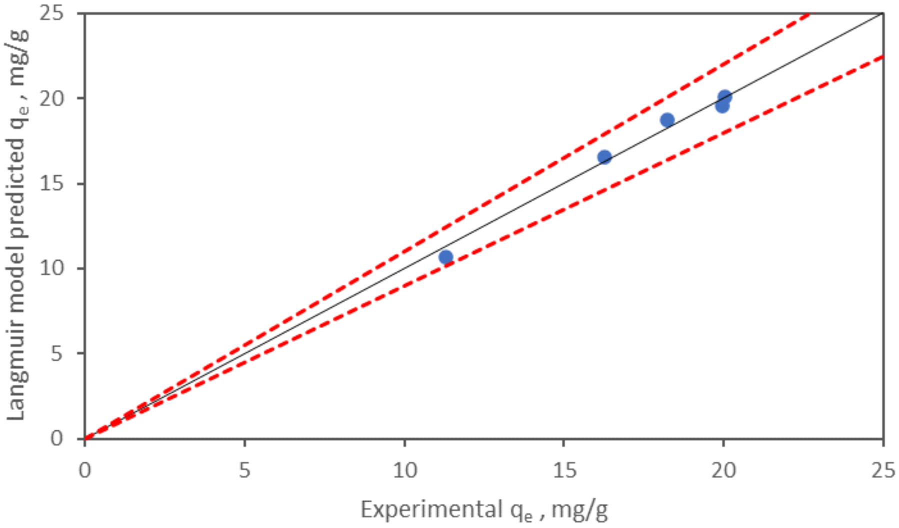


Figure 29: Adsorption capacities predicted by Langmuir isotherm vs experimental adsorption capacities. Dashed lines indicate a 10% error region.

4.3.4. Kinetic studies.

The kinetic experiment was performed by activated kaolin pellets to adsorb the methylene blue from 100 mg/L methylene blue solution. The duration of the experiment was 10 hours, and samples were taken each 30 minutes for concentration measurements. The experiment was done in duplicate and errors were displayed. The evolution of the adsorption capacity over time is shown in Figure 30. After 10 hours, the 8 mg/g adsorption capacity was achieved, and 28% of methylene blue was removed.

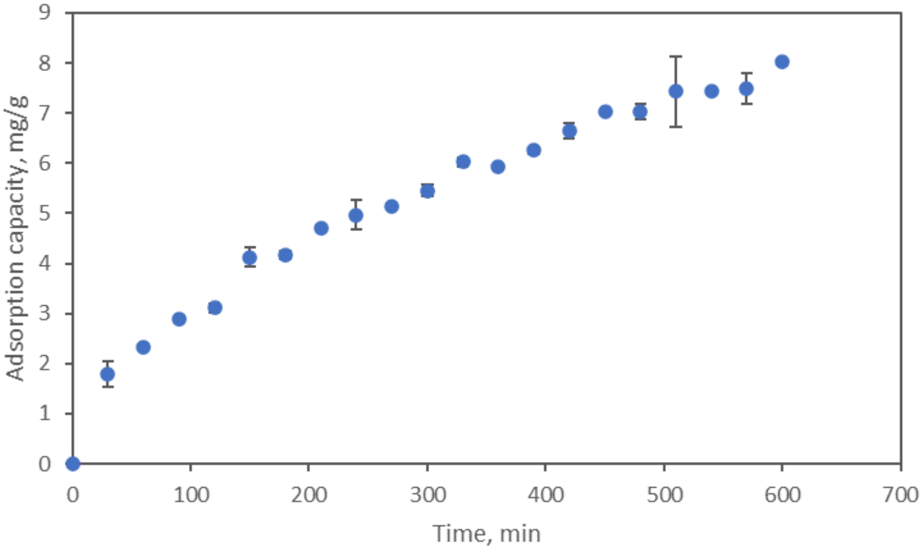


Figure 30: The evolution of the adsorption capacity of activated kaolin pellet over time. Experimental conditions: C_0 = 100 mg/L, m_c = 0.85 g, V = 250 ml.

The experimental values of adsorption capacities over time were analyzed by pseudo-first-order and pseudo-second-order kinetic models. R^2 values of pseudo-first-order and pseudo-second-order kinetic models were equal to 0.9722 and 0.9606, respectively. The adsorption kinetic mechanism of the activated kaolin pellets follows a pseudo-first-order kinetic model more accurately compared to a pseudo-second-order. All model parameters can be found in Table 5. The equilibrium adsorption capacity calculated by the pseudo-first-order kinetic model was closer to the experimental value, and the relative error was 9.4%. The equilibrium adsorption capacity calculated by the pseudo-second-order kinetic model deviated from the experimental value by 34.3%. The kinetic studies of the methylene blue adsorption made by the application of the acid-base activated kaolin powder [50], raw Algerian kaolin powder [52,53] and kaolin powder with graphene oxide modification [68] concluded that the adsorption kinetics follows the pseudo-second-order kinetic model. Rida et al. [53] and He et al. [68] explain this behavior with chemisorption being the rate-limiting step of the adsorption process. The better fit of the pseudo-first-order kinetics to the adsorption by activated kaolin pellets suggests that the adsorption process mainly proceeds by physisorption [74].

Table 5: Kinetic model parameters of methylene blue adsorption by activated kaolin pellets.

Model	Experimental	Pseudo-first-order			Pseudo-second-order		
Parameter	q_e	q_e	k_1	R^2	q_e	k_2	R^2
Value	16.26 mg/g	14.73 mg/g	$9.94*10^{-4}$ min^{-1}	0.9722	10.69 mg/g	$3.74*10^{-4}$ g/(mg min)	0.9606

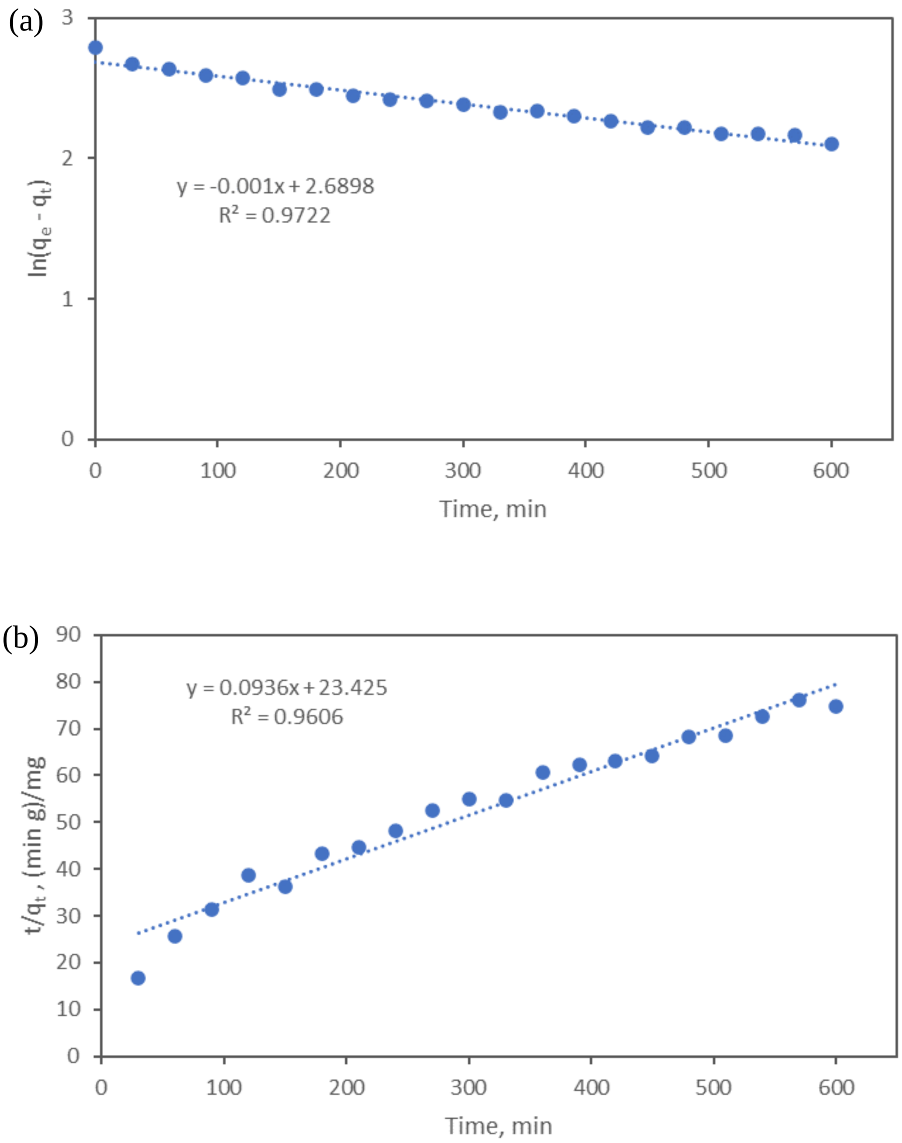


Figure 31: Linear fittings of the experimental data to (a) pseudo-first-order and (b) pseudo-second-order kinetic models.

Chapter V - Conclusion

This thesis work explored the potential of kaolin pellets made by extrusion as an adsorbent for methylene blue dye. Different modifications of kaolin were experimented with to find the most efficient modification. Thermal, acid and base treatments were applied to kaolin powder to increase its adsorption capacity. The pellets were prepared by an extrusion device, and their mechanical strength was improved by calcination and the application of PVA as a binder material. Comprehensive adsorption studies were implemented for kaolin pellets made from activated kaolin by the way of extrusion and the addition of 1.5% PVA binder solution. Activation of the kaolin powder was done via thermal pre-treatment by calcination, treatment with HCl and treatment of NaOH. The combination and subsequent use of these treatments increased the adsorption capacity of the parent kaolin. The effects of solution pH, adsorbent dose, initial methylene blue concentration, equilibrium and kinetic studies were reported and analyzed. The Langmuir and Freundlich models were used for equilibrium studies, and pseudo-first and pseudo-second kinetic models were applied for kinetic studies. The results of all experiments led to the following conclusions:

- The adsorption capacity of the parent kaolin powder was 9.25 mg/g.
- The most efficient treatment process included 3 steps: calcination at 600 °C, treatment with 2.5 M HCl, treatment with 0.5 M NaOH. The adsorption capacity of the activated kaolin powder increased to 26.47 mg/g.
- The extruded pellets can be successfully prepared by following 3 recipes: (a) 20 g of untreated kaolin powder + 10 ml of water followed by drying and calcination; (b) 20 g of the activated kaolin + 12.5 ml of water followed by drying and calcination; (c) 10 g of the activated kaolin powder + 7.5 ml 1.5% PVA solution followed by drying.
- To maintain the shape of the adsorbents after the experiments, the calcination temperature should be higher than 300 °C or the percentage of the PVA solution should be no less than 1.5%.

- The activated kaolin pellets made with 1.5% PVA solution are the most promising adsorbent for methylene blue, and had reached 16.26 mg/g adsorption capacity.
- The pH of methylene blue solution had no significant effect on the adsorption capacity. All solutions were in a basic environment after the experiments.
- The 0.85 g adsorbent dose was the optimal adsorbent dosage (V_{sol} = 250 mL; C_0 = 100 mg/L), however 4 g of adsorbent removed 99% of kaolin compared to 56% removed by 0.85 g after 2 days.
- The equilibrium concentration was reached after 2 days of the experiments. The Langmuir model was more suitable than the Freundlich model to describe the adsorption behavior of activated kaolin pellets.
- The adsorption kinetics followed the pseudo-first-order kinetic model, indicating that the adsorption was done by physisorption.

The recipe of the adsorbent from kaolin by extrusion, which had both satisfactory mechanical and adsorption characteristics was developed as a result of this work. The future potential work could be the exploration of treatments with other acid and base solutions, the study of the potential of kaolin extrudates in the adsorption of heavy metals like mercury, cadmium, etc., and the application of doping on pellets with metals.

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Appendices

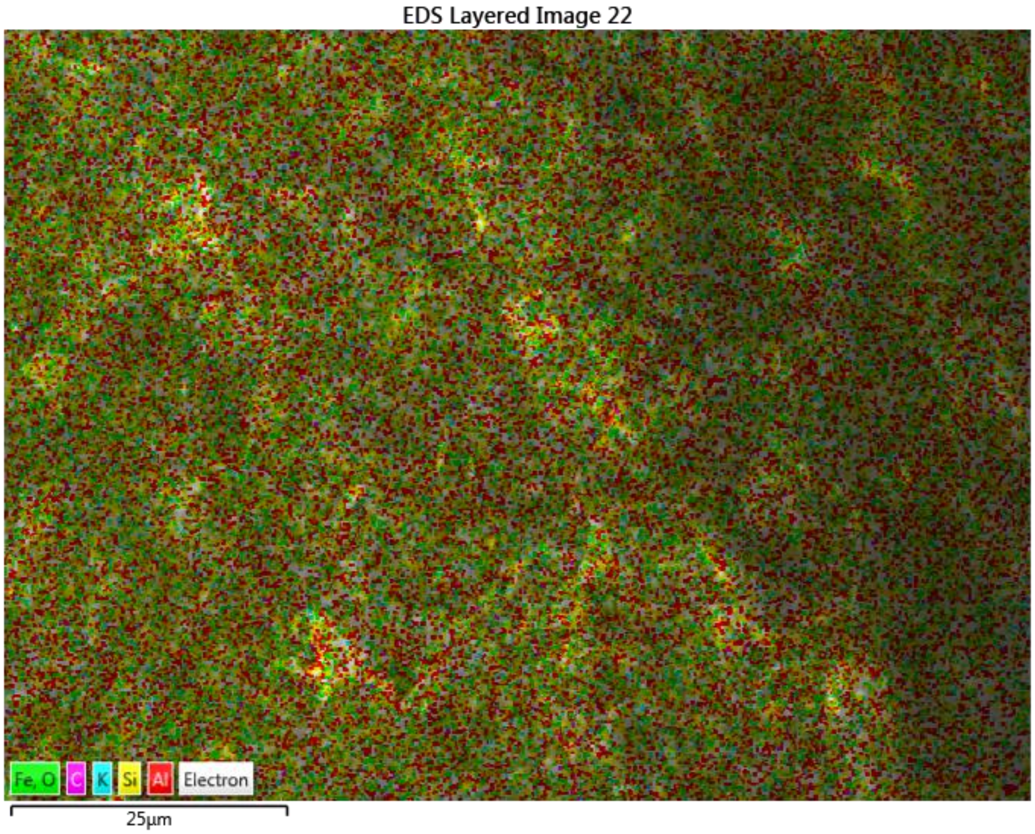
Appendix A.

Table 6. Summary of adsorption capacities of all materials used in experiments.

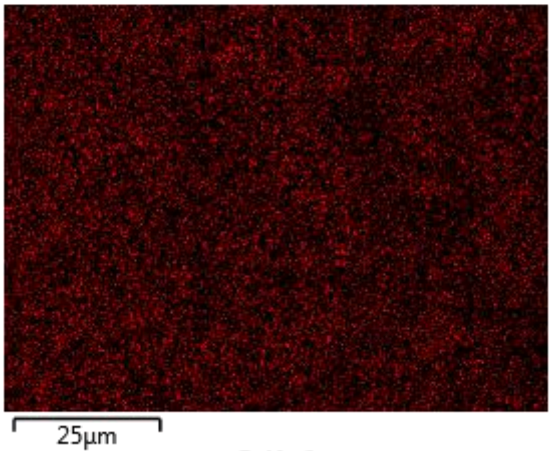
Material	Adsorption capacity (mg/g)
Kaolin powder	9.25
Kaolin pellet, 500 °C (no treatment)	1.4
Kaolin pellet, 600 °C (no treatment)	1.43
Kaolin pellet, 700 °C (no treatment)	1.34
Kaolin pellet, 800 °C (no treatment)	1.26
Enriched kaolin	11.67
Kaolin, treated with H_2SO_4 (no calcination)	11.45
Enriched kaolin, treated with H_2SO_4 (no calcination)	7.22
Kaolin, treated with H_2SO_4, calcination at 600 °C	4.98
Kaolin pellet prepared from H_2SO_4 treated kaolin powder, calcination at 600 °C	2.95
800 °C calcinated kaolin, treated with H_2SO_4	3.35
800 °C calcinated kaolin, treated with HCl	3.62
400 °C calcinated kaolin, treated with HCl	4.49
600 °C calcinated kaolin, treated with HCl	17.16
600 °C calcinated kaolin, treated with NaOH	6.89
800 °C calcinated kaolin, treated with HCl and NaOH	8.38
700 °C calcinated kaolin, treated with HCl and NaOH	21.4
600 °C calcinated kaolin, treated with HCl and NaOH	26.47

500 °C calcinated kaolin, treated with HCl and NaOH	25.34
Treated kaolin pellets, 600 °C	1.69
Treated kaolin pellets, 400 °C	2.57
Treated kaolin pellets, 300 °C	3.04
Treated kaolin pellets, 200 °C (lost form)	6.94
Treated kaolin pellets with no calcination (lost form)	13.65
Treated kaolin pellets, 0.05% PVA (lost form)	17.09
Treated kaolin pellets, 1% PVA (lost form)	6.56
Treated kaolin pellets, 1.5% PVA	16.26
Treated kaolin pellets, 2% PVA	2.69
Treated kaolin pellets, 5% PVA	2.60

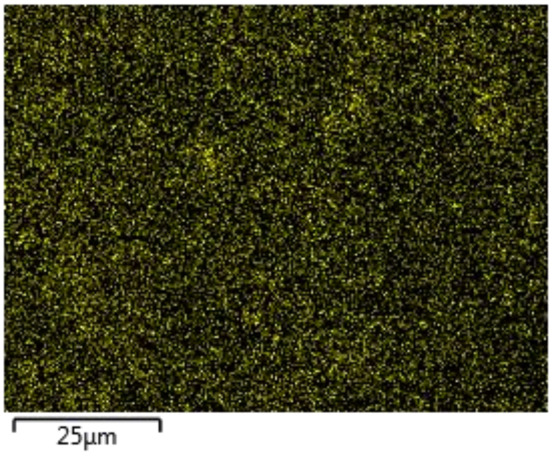
Appendix B.



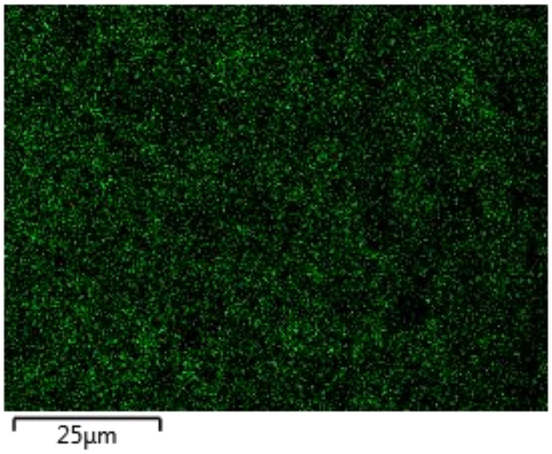
Al Kα1



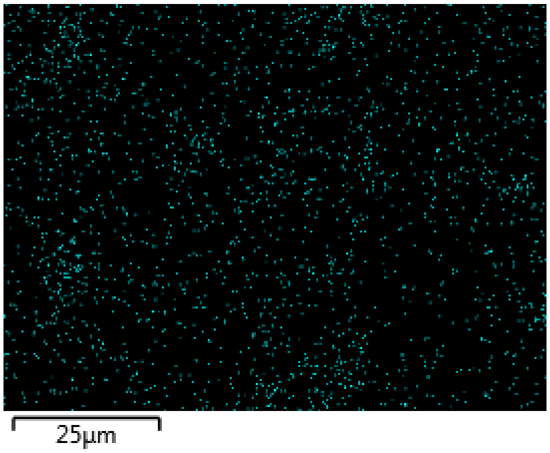
Si Kα1



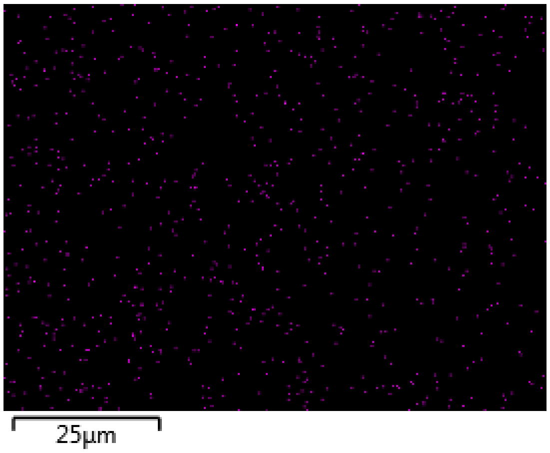
O Kα1



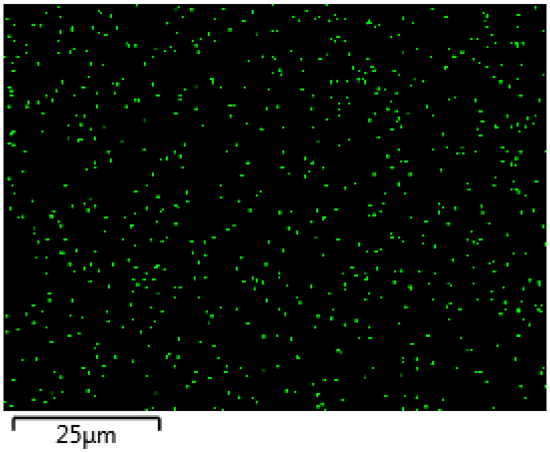
K Kα1

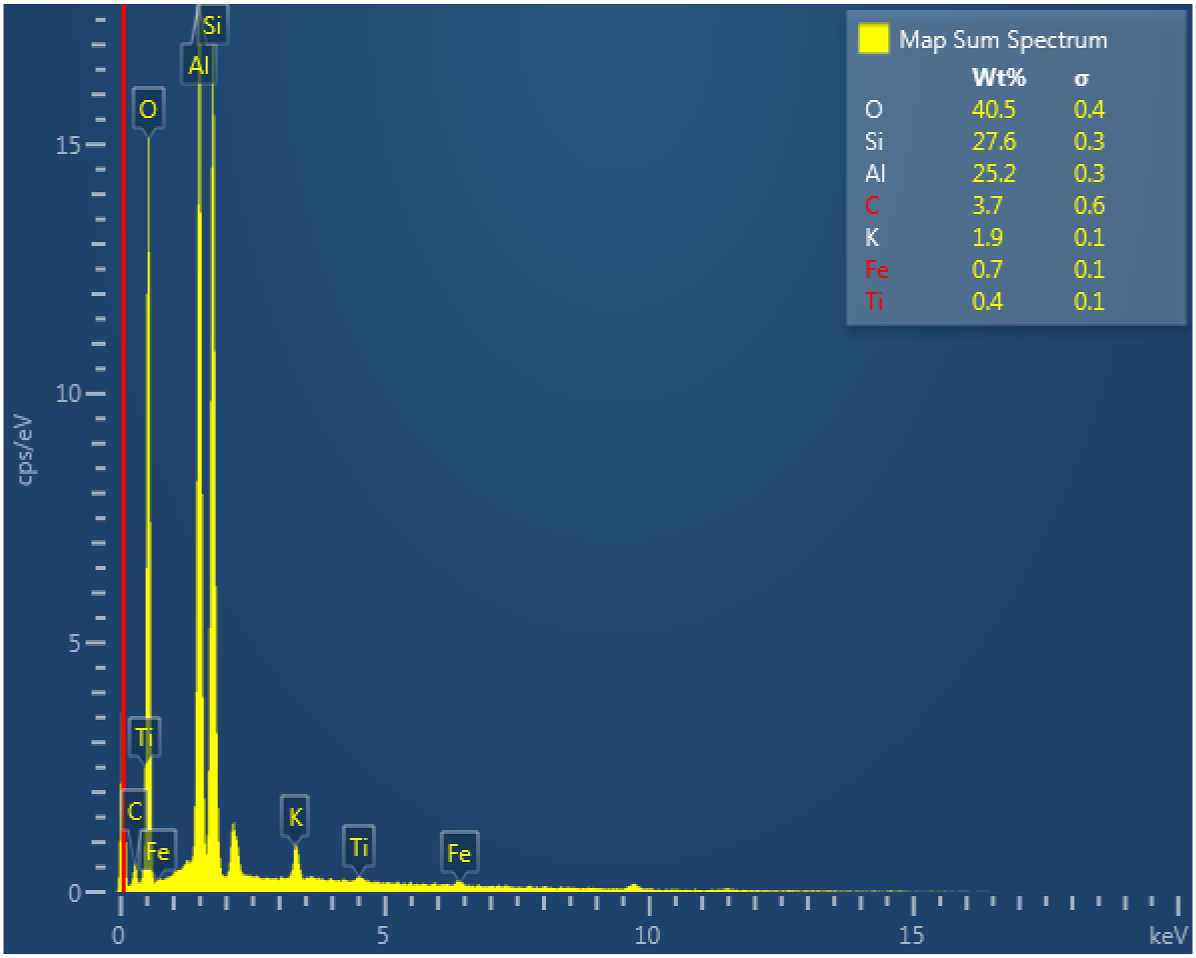


C Kα1_2



Fe Kα1





Map Sum Spectrum

	Wt%	σ
O	40.5	0.4
Si	27.6	0.3
Al	25.2	0.3
C	3.7	0.6
K	1.9	0.1
Fe	0.7	0.1
Ti	0.4	0.1

Figure 32. EDS analysis of kaolin powder.