Republic of Iraq
Ministry of Higher Education & Scientific Research
University of Kerbala
College of Engineering
Civil Engineering Department

Treatment of Sulfate Produced from wastewater by using adsorption with local Material

Thesis Submitted to the Council of the Faculty of the College of the Engineering/University Of Kerbala in Partial Fulfillment of the Requirements for the Master Degree in Civil Engineering

By:
Ashraf Fakhri Obeid
Supervisors
Prof. Dr. Basim Khalil Nile
Asst Prof. Dr. Maad Farouk

March 2024
Ramadan 1445

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بسم الله الرحمن الرحيم

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا
الْعِلْمَ دَرَجَاتٍ

صدق الله العلي العظيم

(المجادلة: من الآية 11)

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We certify that we have read the thesis entitled " **Treatment of Sulfate Produced from wastewater by using adsorption with local Material**" and as an examining committee, we examined the student "**Ashraf Fakhri Obeid** " in its content and in what is connected with it and that, in our opinion, it is adequate as a thesis for the degree of Master of Science in Civil Engineering.

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Name: Asst. Prof. Dr. Haider Nadhom Azziz
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We certify that the thesis entitled " **Treatment of Sulfate Produced from wastewater by using adsorption with local Material"** was prepared by **Ashraf Fakhri Obeid** under our supervision at the Department of Civil Engineering, Faculty of Engineering, University of Kerbala as a partial of fulfilment of the requirements for the Degree of Master of Science in Civil Engineering.

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Linguistic certificate

I certify that the thesis entitled "**Treatment of Sulfate Produced from wastewater by using adsorption with local Material**" which has been submitted by **Ashraf Fakhri Obeid,** has been proofread, and its language has been amended to meet the English style.

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I certify that research work titled " **Treatment of Sulfate Produced from wastewater by using adsorption with local Material**" is my own work. The work has not been presented elsewhere for assessment. Where material has been used from other sources, it has been properly acknowledged.

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Dedication

I dedicate this work:

To whom I proudly bear his name; my dear Father

To whom did she drink the cup of misery to drink me nectar of happiness; dear mother

To My brothers and sisters

To my friends

For they always being there for me through all of my ups and downs, without even a sigh.

Finally, to those who gave their lives in order for us to live; Martyrs of Iraq.

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In the name of the god compassion and the merciful. Praise be to ALLAH and pray, and peace be on his prophet Mohammed his relatives and companions, and on all those who follow him.

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Abstract

Fouling by sulfate ion contamination constitutes a serious problem in the wastewater treatment. Using a locally produced novel composite adsorbent, the removal of sulfate from a contaminated solution was investigated in this study in batch and continuous mode operations. This adsorbent was made from waste and nearby materials as a low-cost local adsorbent by physical activation of sludge, bentonite, and limestone as (SBL composite) (the sutable dose equal to 0.5 g/50 mL) and was characterized by using FTIR, SEM, EDS, X-ray diffraction analysis (XRD), and BET.

Adsorption studies of the solutions were examined in batch mode through experiments replicated with different values of parameters such as contact time, agitation speed, pH, initial concentrations of contaminant and adsorbent dosages; the best values of these parameters were determined to be (60 min, 250 rpm, 900 mg/L, and 0.5 g/50 mL) respectively based on the higher removal efficiency attained. While the optimal values of these parameters were to be 6 L/hr, 6, 900 mg/L, 20 cm, and 5 multi cycle numbers respectively, for the continuous system, the effect of flow rate, pH, SO4-2 initial concentration, bed height, and multi cycle bed column on the breakthrough curve was studied in column bed continuous systems.

Due to its high determination coefficient (0.9798) in comparison to the other isotherm models, It was found that the Freundlich model provides a superior forecast for the adsorption processes. It was discovered that the sulfate adsorption process adheres to the pseudo-second-order kinetics model after applying both first order and second order kinetic models. These findings support the notion that chemisorption was the adsorption process.

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List of Abbreviations

CFB	Circulated fluidized bed reactor
SBL	sludge bentonite and limestone composite
SB	Sludge and bentonite composite
BL	bentonite and limestone composite
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
XRD	X-Ray Diffraction Analysis
BET	Specific Surface Area
-P	Zeta Potential
ZPC	Zero-point charge
MAE	Mean Absolute Error
MSE	Mean Squared Error
RMSE	Root Mean Squared Error
EDTA	Ethylene diamine tetraacetic acid
DTPA	diethylene triamine pentaacetic acid
BFS,BOS	Blast furnace sludge

List of Symbols

Units	Definition	Symbol
At.wt	Metal atomic weight	g/mole
b	Langmuir constant related to the affinity between the sorbate and adsorbent	L/mg
B	Bed height	cm
C_e	Equilibrium concentration	mg/L
C_e/C_o	Relative concentration or normalized concentration	________ _
Ci	Required metal concentration	mg/L
C_o	Initial concentration of contaminant	mg/L
k_1	Pseudo first order rate constant	1/min
k_2	Pseudo second order rate constant	(g/mg min)
K_F	Freundlich constant related to the maximum adsorption capacity	$(mg/g)(L/mg)^{1/n}$
m	Mass of adsorbent	g
M.wt	Metal salt molecular weight	g/mole
n	Frendlich equilibrium parameter	Kg/m^3
Q	Fluid flow rate	L/h
q_e	Equilibrium uptake capacity, the amount of solute transformed from liquid phase to solid phase	mg/g
q_m	Maximum adsorption capacity	mg/g

q_t	Quantities of sorbate removed from the aqueous solution at time t	mg/g
R	Correlation coefficient	________
R^2	Coefficient of determination	________
t	Time	h
T	Temperature	C
V	Volume of the solution	L
V_1	Required volume of the solution	L
V_2	Dilute solution volume	L
W	Weight of the salt	mg

Chemical symbols.

NO.	Compound	Formula
1	bentonite	Al2O3˙4SiO2˙H2O
2	Limestone	CaCO3
3	potassium sulfate	K2SO4
4	Sodium hydroxide	NaOH
5	Hydrochloric acid	HCl
6	Glycerol	$C_3H_8O_3$
7	Ethanol	C_2H_6O
8	Sodium chloride	NaCl

9	**Barium chloride**	**$BaCl_2.2H_2O$**

Chapter One: Introduction

1.1 General introduction

Freshwater is the primary component of the planet and is necessary for the survival of all living things. As a result of the fast advancement of commercial, industrial, and agricultural activities as well as urbanization, there is a noticeable rise in the amount of wastewater generated by these activities (Shafiq et al. 2018). Many of wastewater will contain a certain concentration of different contaminants such as organics, heavy metals sulfate etc. Due to its toxicity to the environment, sulfate is one of the main industrial pollutants that has drawn a lot of attention in water research (Ntuli et al., 2016; Raper et al., 2018).

Elevated sulfate levels in aquatic environments cause a number of environmental issues, including the mineralization of water, disturbance of the food chain and natural sulfur cycle, and atmospheric discharge of hydrogen sulfide (Marina et al., 2019). Sulfate removal has always been accomplished through the use of traditional wastewater treatment procedures, which have some disadvantages, including high operating and maintenance costs and the need for chemicals to treat the wastewater. Because some of the chemicals employed in the process are also hazardous to the environment, this poses a threat to the ecosystem (Gul, 2013). Regulating bodies are growing more worried about excessive sulfate concentrations in effluents, mostly because of the above-mentioned disadvantages.

The World Health Organization (WHO) established a 250 mg/L sulfate limit for drinking water (Silva, Cadorin et al. 2010), The Iraqi Specification 400 mg/l, while the maximum values of 250 mg/L by Brazil, China and USA and 200 mg/L by Turkey (Duranoğlu, Kadırgan et al. 2012).

Due to the high solubility and stability of sulfate anions in aqueous solutions, the removal of sulfate ions from water is a challenging issue. The biological treatment with sulfate-reducing bacteria is one of the recognized ways for removing sulfate (Rodriguez, Oliveira et al. 2012), membrane, and ion exchange (Haghsheno, Mohebbi et al. 2009) and chemical precipitation (Nurmi, Özkaya et al. 2010).

Additionally, sulfide produced during the biological process can harm methanogens, result in the anaerobic process failing eventually, and even cause issues during the future therapy (Luo, Tsukamoto et al. 2008). In order to avoid fouling and microbiological growth on the surface of the membrane, membrane technologies require both a pre-treatment of the raw drainage by gypsum precipitation and a post-treatment of the concentrated waste streams (usually with high sodium and sulfate contents). These technologies thus cost more and use more energy.

Sulfate can be removed from water and wastewater by chemical precipitation. The significant amount of associated muck, however, is its principal disadvantage. Adsorption is a quick, affordable, and extensively used technique. Additionally, it is ubiquitous in that it can be used to remove both soluble and insoluble materials. Chemical and biological pollutants that are 90-99% effective at being removed. At the industrial level, adsorbent-filled columns and contractors are used to remove contaminants from water. Adsorption may also be utilized for source reduction, potable water reclamation, industrial processes, and other things. As a result, extensive research has been done on adsorption-based water purification (Ali et al.,2005). Large amounts of sludge produced during wastewater and water treatment operations place a heavy burden on the municipality and related industry. (Hii et al., 2014).

1.2 Statement of the problem

Sulfate are the most dangerous among the chemical-intensive sectors due to the emission of significant amounts of wastewater polluted with sulfate. Therefore, before being released into the environment, The wastewater must be treated. One of the most common problems facing environmental engineers is the increase in the concentration of dissolved sulfates in wastewater. Sulfate dissolved in water producing from WWTP is toxic, an increase in its concentration causes health damage to plants as using in irrigation process. The problem lies in the difficulty of separating sulfate from water, due to its high solubility.

1.3 Objectives of the study

1. study the removal of sulfate via adsorption process
2. study of prepare new composite adsorbent, Investigating the ability of bentonite, limestone and sludge as modified composite adsorbent synthesized to remove the sulfate from simulated wastewater was the main objective of this work.
3. Physical activation of bentonite, limestone and sludge as modified component to produce a low-cost local adsorbent.
4. study the effective parameters related to composite adsorbent in batch experiments and continuous systems (column bed). Reducing the concentration of dissolved sulfates in the water producing from WWTP within the range of the Iraqi Specification.

Chapter Two: Literature Review

2.1 Background Review

One of the essential elements for life is water, yet freshwater on Earth is scarce. According to the research, half of the world's population would reside in water-stressed areas by 2025 (WHO et al., 2019). Water is necessary for human consumption as well as for business and agriculture. It appears that agricultural and industrial processes can contaminate water (MDWP et al., 2018).

The literature lists a wide range of pollutants, including heavy metals, that can be found in surface water, groundwater, and industrial wastewaters (Joseph et al.,2019) dyes (Yagub et al.,2014) pesticides (Souza et al.,2020) pharmaceuticals (Carmalin et al.,2018) personal care products (Yang et al.,2017) hormones (Lee et al,.2007) virus (Springthorpe et al.,2007) radioactive elements (Zhang et al.,2019) phenol derived compounds (Ahmaruzzaman et al.,2008), sulfate and other emerging contaminants (Rodriguez-Narvaez et al.,2017). These substances are hazardous and poisonous to the environment and general public's health when found in waterways and wastewaters, as the literature has abundantly shown (Taheran et al.,2018; Wilkinson et al.,2017).

As scientists working in the field of environmental chemical engineering, it is actually our responsibility to create and synthesize materials, procedures, and technologies that enable the reuse, management, and decontamination of water. Water treatment can be achieved by a variety of technologies, each with disadvantages and advantages (Cheremisinoff et al., 2002). But here, adsorption is the main topic. Adsorption is a unit operation in which a solid phase (the adsorbent) and a fluid (in this case, water) are involved. One or more dissolved pollutants (the adsorbate) are present in the fluid phase. Water is purified as a result of the dissolved pollutants being moved from the liquid phase to the adsorbent surface (Bonilla-Petriciolet et al., 2019).

The following benefits of adsorption make it a popular choice for treating water: it is highly effective, simple to use, can be applied to a variety of solids, and allows for the recovery of both the adsorbent and the adsorbate (Bonilla-Petriciolet et al.,2017; Ali et al., 2002). It is crucial to emphasize that adsorption is a competitive and effective cleaning process when the pollutants' concentration in the water ranges from ng L^{-1} to mg L^{-1} (Cooney et al.,1999).

2.2 Adsorbent materials

The design of an adsorption process for the treatment of water and wastewater depends critically on the selection, development, and characterization of the adsorbent material. The following qualities are necessary for an appropriate adsorbent for treating wastewater:

1- Reasonably priced and easily accessible: Since 70% of operational costs are related to the adsorbent, a sizable quantity of the material needs to be produced or acquired promptly and delivered to the treatment plants.

2- Chemical stability: The adsorbent may be affected by the differences in the chemical properties of various water matrices, such as conductivity, ionic strength, and pH. The substance must therefore be chemically stable.

3- Mechanical stability: Because continuous wastewater treatment is carried out in columns, the adsorbent also needs to be stable in order to prevent high-pressure drops and preferential routes.

4- Good physicochemical and textural properties: The adsorbent should have a large surface area and pore volume as well as functional groups that can interact with pollutants on the surface. These qualities are significant and have an impact on the following criteria.

5- High adsorption capacity: Adsorbents must have a high contaminant absorption rate per gram of material. This reduces the amount of adsorbent needed for the treatment, facilitates phase separation after adsorption, and reduces the amount of physical space needed.

6- large efficiency: To guarantee the intended standard quality is met and the requirements are followed, a large percentage of contaminants should be removed from the water and delivered to the adsorbent.

7- Fast kinetics: The adsorbent's characteristics should enable rapid achievement of high adsorption efficiency and capacity. Because of this, the entire treatment period is short, which affects the treatment facility's size and, in turn, its capital cost.

8- Potential for regeneration and reuse: To reduce operating expenses, the adsorbent should, if at all feasible, be readily regenerated and utilized more than once.

2.3 Adsorption Process

Adsorption (using wood sawdust, carbon nanotubes, and activated carbon as adsorbents), Ion exchange, Chemical precipitation, and Electro-chemical treatments (electro-deposition, electro-flotation, and electro-coagulation) are some of the most recent methods used to remove sulfate from wastewater (Azimi et al. 2017). In order to comply with environmental regulations and to protect people's health and safety, sulphate must be removed from aqueous solutions (Ahmed et al. 2012; Sadon et al. 2014).

As a result, there has been a surge in demand for technologies like adsorption that are sustainable in terms of economy, efficiency, energy, and the environment. Long used for the treatment of water, the capacity of certain solid materials to remove dissolved substances (considered a promising technique due to the feasibility, durability, and efficiency) or the adsorption technology principle. This method has been used for the treatment of wastewater in a variety of settings for about 100 years, and it has maintained its significance throughout this time (Saha T.K. 2010). A mass transfer technique is used to move a small number of substances from the liquid phase to a solid surface, where they are subsequently bound by chemical and/or physical interactions. This separation process is typically known as adsorption (Hasbullah et al. 2014). Adsorption technique can be applied in a batch, semi-batch, or continuous manner (Leinroth and Sherwood 1964; Souza et al. 2012).

The mass transfer resistance to the adsorption process, which is a mass transport phenomenon, is provided by the solute and the adsorbent, respectively, and will always be present in the process. Figure 2.1 shows the sequence of resistance to mass transfer quite clearly (Abdul-Hameed 2009).

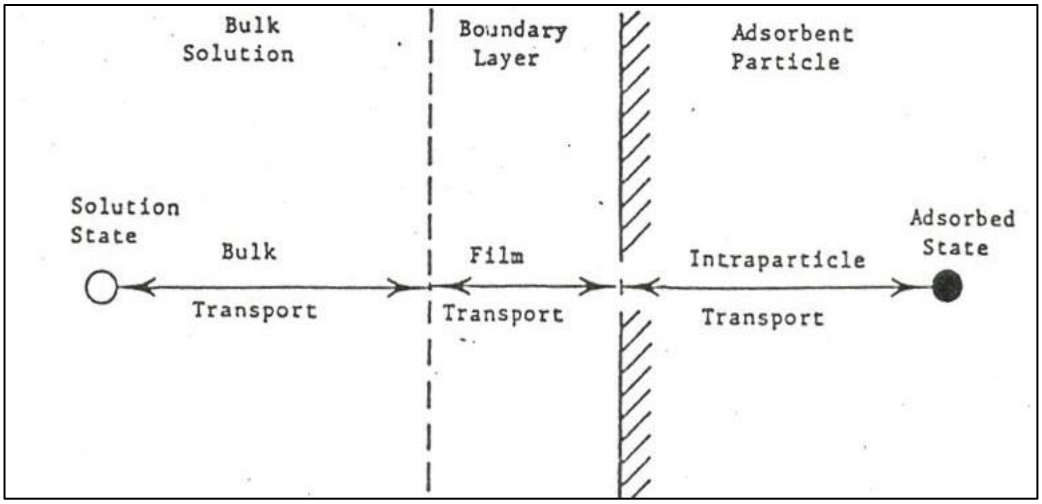


Figure 2.1The series of the resistance to the mass transfer in the adsorption process (Nazeeh 2016).

As shown in Figure 2.1 and Table 2.1, there are actually four stages in the adsorption process that allow contaminants to move from the bulk state to the adsorbed state on the adsorbent surface. One or more of these stages may be used to regulate the amount of solute adsorbed on the adsorbent at the time that adsorption occurs. External diffusion (the first two phases) is typically quick as long as there is enough agitation to prevent the concentration gradient in contaminated water from rising (Mckay and Oyrwsurn 1980).

Table 2.1The stages of adsorption process (Mckay and Oyrwsurn 1980).

№	Description of the stage
1	The solute molecules are moved to the adsorbent outer surface from the majority of the solution.
2	the solute molecules' migration across the interface and their adsorption on sites on external surfaces.
3	molecules of the solute moving through the adsorbent's pores.
4	binding of the pore and capillary spaces of the adsorbent through interaction of solute molecules with accessible spots on the internal surface.

According to Ansari and Mohammad-Khah (2009), the solid surface that the contamination adsorbed on is known as the adsorbent and the contamination is known as the adsorbate. Adsorbents include things like silica gel, resins, activated carbon, and porous clays. Compost, fly ash, waste shell material, iron ochre, and a combination of BFS and BOS were the five inexpensive materials that demonstrated strong adsorption process capabilities.

Numerous fields, including pharmacology, medicine, biological and soil science, chromatographic analysis, catalysis, industry, and pollution, make use of the phenomenon of substances binding to the solid surface of the adsorbent (Sun 1994; Qiu et al. 2009). Due to the presence of numerous different heavy metals in industrial wastewater, different metals competed for adsorption sites on the adsorbents (Zhang, X. et al. 2016). The interaction effects brought on by the diverse components of wastewaters are influenced by a number of parameters, including the quantity and nature of the adsorbent, pH, and initial metal content (Jain et al. 2016). Several factors (Table 2.2) have an impact on the adsorption processes (Abdul-Hameed 2009; Zaker et al. 2013).

Table 2.2 Factors controlling the process of the adsorption (Abdul-Hameed 2009; Zaker et al. 2013).

№	Description of the factor
1	the adsorbent's physical and chemical characteristics (surface area, pore size, particle sizes, chemical make-up, etc.).
2	The adsorbate's physical and chemical characteristics (such as its molecular weight, polarity, and size).
3	pH and temperature of the liquid phase that is the influent.
4	both the initial concentration of the contaminants and the influent flow velocity.

Researchers are paying close attention to studying and employing the adsorption process as a method for eliminating inorganic and organic contaminants from wastewater in accordance with the benefits and drawbacks of the process, It has a simple design, can remove both organic and inorganic material even at low concentrations, is a unit operation that is (quite straightforward, safe, and suitable), allows for regeneration of the adsorbents, and is a low-cost process. But recovery of the product could necessitate an expensive, specialized distillation or extraction, and used adsorbent might be regarded as hazardous waste (Rashed 2013).

2.4 Adsorption Process Types

2.4.1 Physical Adsorption

Physical adsorption is the process by which the molecules of the solution are drawn to and held to the solid surface. Particles on the surface of pore walls are drawn there by van der Waals forces. The physical adsorption can take place by applying an adequate and reasonable amount of energy to break the attraction forces when the adsorptive is under pressure and the temperature is similar to or below the boiling point (Figure 2.2) (Berger and Bhown 2011). When the temperature rises, the required energy on the adsorption site tends to escape, which speeds up desorption (Benco et al. 2003; Moor et al. 2009). This reversible process occurs at low energy of adsorption, resulting in the adsobate not strongly attached to the adsorbent.

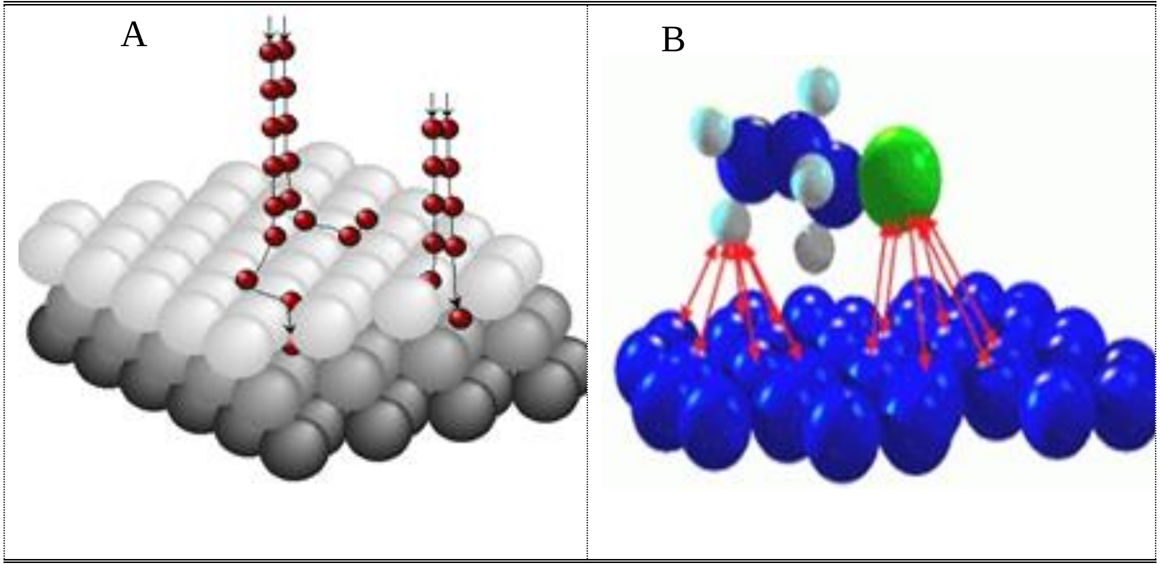


Figure 2.2 Physisorption weakly binding sites and (B) chemisorption strongly binding sites (Jarullah 2013).

2.4.2 Chemical Adsorption

At chemical adsorption, there is a real chemical bonding. In order to interact the adsorbed molecules with the adsorbent surface and form a chemical compound (Figure 2.2) (Hayeeye et al. 2018; Mindhe et al. 2017), strong electronic interactions are formed. Chemical adsorption typically requires a large amount of energy to break the chemical complex because of the chemical changes that took place, making the opposite of this sort of adsorption challenging (Králik 2014). Chemical adsorption can typically occur to produce the necessary energy at temperatures greater than the boiling point (Moor et al. 2009). Table 2.4 (Kadhim 2010; Karbalaee 2010) lists the distinctions between the various forms of adsorption.

Table 2.3 The physical adsorption and chemical adsorption difference (Kadhim. 2010).

№	*Physical adsorption*	*Chemical adsorption*
1	The weak van der Waals forces are what cause physisorption.	Chemical bond that involves the sharing of electron pairs between atoms.
2	Low heat of adsorption	High heat of adsorption
3	As the temperature rises, it gets smaller.	It grows as the temperature rises.
4	Not firmly adhering to the surface are adsorbates.	Strong surface attachments of the adsorbate.
5	It can be reversed.	It is permanent.
6	It happens at a cool temperature.	Any temperature can cause it to happen.
7	It lacks specificity	It is quite particular.

2.5 Adsorbents Types

Commercial adsorption has been dominated by generic forms of adsorbents, including silica gel, activated carbon, polymeric adsorbents, and molecular sieves of carbon and zeolites. Certain adsorbents, like zeolites, are found naturally, whereas the majority are produced. The characteristics of each adsorbent include the porosity, pore structure, and type of the adsorbing surfaces (Kadhim 2010; Karbalaee 2010).

Depending on the porosity, adsorbents can be classified into porous and non-porous. In the first type, the components being accessible to remove from the wastewater as the internal surface area of this type is high. But relatively the external surface area of the another adsorptive type is very small (Abdul-Hameed 2009). For choosing an adsorbent, the decision must be take according to several factors are listed below (Knaebel 2011);

1) Adsorbent availability.

2) Adsorbent cost.

3) Effectiveness degree, generally high selectivity must join with high adsorption capacity.

2.5.1 Activated Carbon

Activated carbon (AC), which is made from carbonaceous plant and animal materials such lignite, wood peat, nutshells, petroleum coke, coals, and bones, is the adsorbent substance that is used the most frequently and is regarded as the most well-known (Kammerer et al. 2014). According to the availability of raw materials, more research is currently being directed toward less expensive, recyclable, effective, and sustainable adsorbents. Since the AC is a very versatile product, it can be made from a variety of raw materials (El-Shafey et al. 2017).

Activated carbon has great physical qualities, but its price is just expensive (Dias et al. 2007). Therefore, alternative adsorbents have been created in developing nations using low-cost materials (found in industrial waste or in nature) in an effort to reduce costs (Kaur et al. 2013). Byproducts and agricultural waste, such as orange peel, sawdust, rice husks, wheat straws, coffee grounds, cotton balls, banana peels, pine cones, wood, peat, and tobacco stems, are some of these that were mentioned above.

These resources can be utilized to create inexpensive activated carbon, which can then be used to treat wastewater by acting as an adsorbent to remove heavy metals. Accordingly, this production method is used to minimize agricultural waste disposal and pollution, is eco-friendly, and is also reasonably priced (Amin et al. 2017; Leimkuehler 2010). As stated in Table 2.5 (Ahmida et al. 2015), there are two major techniques used in the synthesis of AC from raw natural materials: chemical activation and physical activation.

Table 2.4Description of physical and chemical activation (Amor et al.2015; Verla et al. 2012).

№	Physical activation	Chemical activation
1	Typically, heat reactions are involved.	requires two main processes that are often performed in sequence: heating and chemical treatment.
2	At temperatures below 700^{o} C, physical activation takes place.	Typically, the heating process uses less heat than physical activation.
3	After pyrolysis, oxidizing gases like air, CO_2, and steam of water are used during physical treatment.	Chemical agents such alkaline chemicals (KOH, NaOH, Na2CO3, and NaHCO3), acid chemicals (HCl, H2SO4, and C2H4O2), and other chemicals (ZnCl2, etc.) are introduced during chemical treatment.
4	This procedure is used to expand the porous structure's surface area or size, which boosts the ability of activated carbon materials to absorb substances.	Activated carbon materials can have their surface area or size of their porous structures improved using this technique, as well as their surface functional groups.

After a raw material has been activated, its physical characteristics must be assessed in order to distinguish it from a large number of other possible materials. When selecting the raw material, there are a number of crucial considerations that must be made, including the chemical character and structure of the carbon surface, the size and composition of the granules, the pore volume and distribution, and the specific surface area of the pores (Ahmad et al. 2012).

2.5.2 Low-cost adsorbent

The substances that are employed as adsorbents are explained, along with their adsorption characteristics. Dehydroxylating aluminum hydroxide yields activated alumina, a highly porous substance. It is employed as a desiccant and drinking water filter to remove fluoride, arsenic, and selenium. Fluoride levels can drop from 0.5 ppm to less than 0.1 ppm as a result of it. A metric ton of activated alumina costs between $700 and $800 USD.

According to recent research, modified alumina might make an effective adsorbent for cleaning wastewater of different contaminants. (Ghosh, Gupta, and others, 2012). Because of their strong affinity for several metal ions and huge surface area, zeolites are the best inorganic ion-exchange adsorbents. It is advised that modification be done at low temperatures because modified zeolites have superior adsorption qualities than untreated ones. (Motsi et al.2009) used natural zeolite to compare the adsorption of component mixtures with synthetic AMD. Fitting adsorption data for different isotherm models, including Freundlich, Langmuir, and Langmuir–Freundlich, was done by Stanic et al. (2009). In batch systems, natural zeolite shown exceptionally high adsorption capabilities for the removal of Pb (II) from water.

A common ingredient for making adsorbents, which are used to remediate wastewater, is chitosan. It has demonstrated good adsorption characteristics for the adsorption of 60 elements from river and seawaters and is employed in many different ways in modified form (Oshita et al. 2009) have altered the cross-linked chitosan using serine, phenylarsonic acid, iminodiacetic acid, catechol, and iminodimetyl phosphonic acid. The characteristics of metal adsorption by chitosan from several actual coal mining wastewaters (Fe (II), Al (III), and Cu (II) were noted. Arsenic (V) is simpler to adsorb from wastewater than arsenic (III), and this issue can be resolved by converting As (III) to As(V) by preserving pH. Approximately 96% of the arsenic was able to be adsorbed at a pH of 4, and the utilization of crab shell chitin and chitin complex produced some intriguing results. Double column and microcosm test were examined to AMD treatment, and the microcosm test was more effective with the use of crab-shell chitin. Ethylene diamine tetraacetic acid (EDTA)-modified chitosan was found more effective for Co (II) and Ni (II) removal from liquids than diethylene triamine pentaacetic acid (DTPA)-modified chitosan. Combined adsorbents made of EDTA-modified chitin and DTPA modified silica gel revealed good adsorption properties for Co removal.

Since over a century ago, silica gels have been utilized as adsorbents; however, because of their superior adsorption properties, scientists have recently become interested in using them as adsorbents from aqueous systems. Numerous scientific studies carried out in this field over the past few years have proven this. Nonetheless, a significant drawback of silica gels from an environmental perspective is their inability to biodegrade in soil or water (Repo et al., 2011). investigated Co (II) and Ni (II) removal from model liquids with silica gel materials functionalized with both EDTA and DTPA (Taha et al.2012). used silica gels as composite nanofibrous material for membranes preparation. (Mahmoud et al.2011) studied silica dioxide nano powder and Aspergillus ustus combination as adsorbent material for Cd (II) removal from real aqueous samples. Due to the high carbon concentration in biochemical sludge, municipal sewage sludge has drawn more attention as a potential material for adsorbents used in wastewater treatment.

Various techniques, including carbonization, physical and chemical activation, and combinations, have been observed for the activation of sewage sludge-based adsorbents. Creating high surface area adsorbents from sewage sludge wastes is most effectively achieved through chemical activation using alkali metal hydroxides. Adsorbents of this kind will be very useful in mining wastewater treatment if less expensive methods of pre-treating municipal sewage sludge are discovered. (Gómez-Pacheco et al.2012).

2.6 Sludge

For towns and businesses, sludge management and disposal are a major issue. Heavy metals, bacteria, and other pollutants are present in the sludge. Accordingly, effective sludge management is required. Improper sludge treatment and disposal lead to secondary environmental issues as greenhouse gas emissions, pollution of the groundwater table, and contamination of the soil (Samolada and Zabaniotou, 2014). According to Ding et al. (2012) and Devi and Saroha (2016), the primary disposal methods are landfills, road paving, incineration, forestry and land reclamation, compression into construction blocks, marine dumping, and carbonization.

The conventional techniques of disposing of sludge, like field application and landfill, are severely strained due to the lack of available landfill sites and the significant danger of contaminating farmland (Smith et al., 2009). The solid waste can also be incinerated, which produces a high energy output and significantly reduces the volume needed for final disposal. The production of dioxins and other harmful combustion byproducts, however, is a significant drawback of this method (Gomez-Pacheco et al., 2012).

The enormous amounts of sludge created during wastewater treatment operations put the town and the impacted enterprises under a great deal of stress. As per Hii et al. (2014), the expenses incurred in treating and disposing of the sludge account for 25–65% of the total operational cost of secondary wastewater treatment. Therefore, it is important to identify a sludge disposal option that is both affordable and environmentally friendly.

2. Definition and components of sludge

Sludge is a solid or semi-solid waste product that is often considered hazardous and is produced during the wastewater treatment process. Depending on its origin, the sludge can be divided into two categories: primary sludge and secondary sludge. Sedimentation, filtration, coagulation, and flotation are the main processes used to clean wastewater.

The result is primary sludge, which is mostly inorganic. Secondary sludge is produced during the secondary wastewater treatment process and is biological in nature, much like activated sludge treatment. During secondary wastewater treatment, the microorganisms reduced the wastewater's BOD by breaking down the organic content. This led to the development of microbial biomass, which gathered as secondary sludge.

The secondary sludge is difficult to dewater due to its biological composition, so in order to increase its dewatering capacity, it is blended with the primary sludge prior to disposal. The composition of the sludge is influenced by the amount of pollutants present, the kind of initial wastewater treated, and the type of treatment employed. There are two different kinds of sludge: industrial and municipal wastewater. Sewage sludge is the complex, heterogeneous mixture of undigested organic and inorganic components that is produced during the treatment of municipal wastewater. Undigested peptides, lipids, and carbohydrates were present in the wastewater, whereas soil and artificially produced polymers were the sources of inorganic matter.

Sewage sludge is rich in nitrogenous compounds because the microorganisms used to cleanse wastewater have a high protein content (Samolada and Zabaniotou, 2014).

2.7 Composite adsorbents

One of the best and least expensive methods for wastewater cleaning is adsorption. Various substances, including metal oxide, clay minerals, agricultural and industrial wastes, carbons, polymers, and others, have been employed as adsorbents over the past ten years. Although adsorption has grown to be one of the most popular methods for treating sewage, it has some drawbacks, including poor selectivity, efficiency, and reusability of the adsorbents. A novel adsorbent with a promising adsorption capacity needs to be created. One method entails creating composites by adding waste elements to the generated matrix as reinforcement.

Typically, the dispersed phase is made up of the reinforcing component and the pro-adsorbent material forms the continuous phase. Such reinforced modified composites have increased mechanical and specific strength as well as excellent chemical, corrosion, and oxidation resistance. These composites can be used in a variety of working environments and have a large surface area (Khaskheli, et al. 2016; Kumar et al. 2013b). Concerns about the sustainable growth of humanity are driving research toward low-cost materials for adsorption applications. The utilization of low-cost adsorbent materials, such as industrial waste and byproducts, shows the potential for the removal of metallic ions. Ahmaruzzaman (2011), Devi and Saroha (2016), and Siddiqui et al. (2016).

claim that it is possible to achieve the twin objectives of cleaning up contaminated wastewater and recovering discarded resources by employing waste-derived adsorbent to recover or remove metal ions from the environment. The possibility of using industrial waste as a cheap supply of adsorbents has been investigated. Byproducts or materials that are thrown from numerous industrial operations make up industrial waste.

These industrial waste products have several advantages, such as low cost, easy accessibility, and few processing needs. Industrial leftovers or waste include things like blast furnace slag (BFS), eggshells (EG), fly ash (FA), vineyard pruning debris, lignin, red mud (RM), and other items (Ahmad et al. 2016; Ahmaruzzaman 2011; Devi and Saroha 2016). Ahmed and Ahmaruzzaman (2016) provided a concise summary of the adsorption properties of the many kinds of industrial waste/by-products used as an adsorbent for the purification of wastewater, as well as Ahmaruzzaman (2011).

2.8 Parameters Affecting Adsorption in Batch Mode

Generally, the removal efficiency of treating the contaminated solution could be affected by different factors. These factors that effect on the sulfate adsorption capacity could be exhibited as below.

2.8.1 Contact Time

Contact time is a significant component that affects the effectiveness of metal ion adsorption. The adsorption process, which is divided into two steps based on the lengthening of the contact time, started with a strong and abrupt increase in removal because there were so many free surface sites and pores that could be used for sorption in the early stages (Al-Hares 2014).

However, the impact of these parameters gradually decreased in the second step, and it took a long time to reach the steady state condition. As a result, it was difficult to occupy these sites and pores because they were already full of ions and had run out of room (Karthikeyan et al 2005).

2.8.2 The pH Value

The type of adsorbate or adsorbent for the adsorption process is chosen based on the ideal hydrogen ion concentration (pH) value. One of the key factors affecting the effectiveness of ions being removed from wastewater is this variable. For various pollutants' chemical forms, a change in pH value will have an impact on the adsorption capacity.

The phenomena of the adsorption capacity of heavy load ions from aqueous solutions increasing with increasing pH values has been explained by a number of mechanisms. According to numerous studies (Aldor et al. 1995; Nabizadeh et al. 2005), Reduced pH levels lead to an accumulation of H^+ ions on the adsorbent surface, hence intensifying the struggle between H^+ and metal ions there. Numerous characteristics of acids, bases, suitable buffers, or contaminants must be chosen in order to control the pH value. When the pH reaches a certain level, metal complexes precipitate because the metal's solubility may be reduced. Therefore, every metal precipitation must have a lower pH value than the pH solution that is chosen (Lopez et al. 2000).

2.8.3 Contaminant Initial Concentration

One of the elements that the adsorption method heavily depends on is the initial concentration of the pollutant. According to Vijayaraghavan and

Yun (2008), the capacity of the adsorbate to transfer to and absorb on adsorbent surface from the solute largely determines the physical and chemical properties of the contaminated material.

For a particular dose of the adsorbent, the amount of the adsorbate increases along with the initial concentration. The adsorption process won't be improved by this increase since the adsorption sites will quickly get saturated, which will reduce the adsorption yield (El-Sayed et al. 2010; Bouras et al. 2017). Additionally, because there will be more surface area available for adsorption at low ion concentrations, the removal capacity will be concentration independent (Ahmad et al. 2018).

2.8.4 Adsorbent Dose

The parameter of adsorbent dosage has a significant impact on the extent of the adsorption process. As the adsorbent dose is increased, the surface area as the amount of the adsorbent rises, more binding sites are created, which in turn increases the amount of solute adsorbed.

According to Vijayaraghavan and Yun (2008), this implies that an increase in adsorbent dosage is directly inversely related to an increase in removal efficiency. When the adsorbent dose is further increased above the ideal amount, the adsorption sites will overlap as a result of the adsorbent particles being too crowded (Palaniswamy R. Veluchamy 2017), yet there is no discernible change in the adsorption process.

2.8.5 Agitation Speed

Variations in the value of the agitation speed parameter, which is regarded as a crucial element for the adsorption process, have an impact on the effectiveness of pollutants being removed from polluted solutions. When the agitation speed is increased, the removal efficiency also increases. Because the boundary layers narrow out at high agitation speeds, the agitation speed influences the adsorbate's dispersion speed in these layers (Anwar et al. 2010).

When the speed is low, the adsorbent will accumulate as an upper and lower layer, burying various active sites at the bottom rather than spreading throughout the solution. Because it is a surface phenomenon, the adsorption process is active in the adsorbent's upper layer but not in its lower layer. Because the removal of pollution is minimized at higher speeds because the time to adsorb is insufficient, the speed value should be appropriate to contain all the binding sites available for adsorbate to adsorb. This happens as a result of the production of vortex phenomena, which causes the adsorption to be non-homogeneous (Vijayaraghavan and Yun 2008; Parvathi et al. 2007).

2.9 Adsorption Isotherm

An equilibrium relationship describes the concentrations of the adsorbate in both the liquid phase and the adsorbent particles. The adsorption isotherm, which is typically employed to explain the sorption/bio-sorption process at a given temperature, serves as a representation of this relationship. The adsorption isotherm can be used to assess whether adopting a specific adsorbent material for a given application is feasible (Banat et al. 2000).

A plot between the amounts of adsorbate per unit weight of adsorbent/bio-sorbent (qe) and the concentration of the adsorbate in solution (Ce) demonstrated this relationship. The amount described by the mass of the adsorbent is always standardized to enable comparisons between various materials (Sulaymon and Abdul-Hameed 2010).

The amount of adsorbate per unit weight of sorbent/bio-sorbent typically increases when the concentration is raised. Figure 2.3 (Abdul-Hameed 2009) depicts several ideal isotherm shapes as an arithmetic scheme.

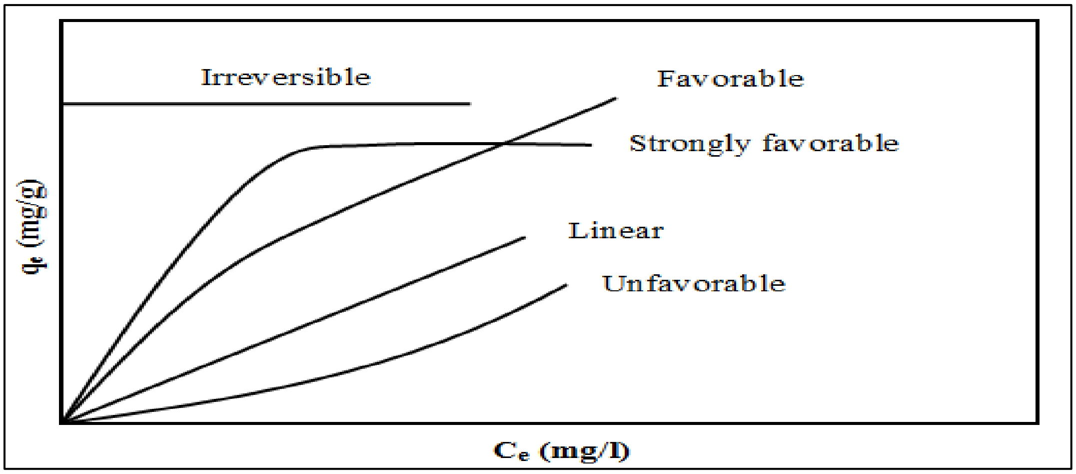


Figure 2.3 Adsorption equilibrium isotherm kinds (Abdul-Hameed 2009).

The resulting linear isotherm, at which the amount of adsorbed solute is proportionate to the remaining equilibrium concentration of the sorbate in solution, has disappeared through the origin. Unfavorable isotherms are those that cause the bed's mass transfer zone to be broadly lengthy and the solid loading they produce to be comparatively low (Figure 2.3).

A favorable isotherm that is convex upward results when the resulting solid loading is relatively high at low concentration in the solution. These isotherms allow us to infer that the specific feature, which depends on the make-up of the adsorbate-adsorbent system, is an adsorption. The irreversible adsorption is a limiting example of a strongly favorable isotherm where the amount of adsorbed solute is independent of concentration falls to minimal values (Najim 2016).

2.10 Isotherm Models

From many types of an isotherm models that used to describe the adsorption process, the following type was selected for contaminant adsorption in single component system (Table 2.5).

Table 2.5 Equations, Parameters and Fundamental characteristics of the Langmuir, Freundlich, Sips and Radke–Praunsitz isotherm models for single system.

Isotherm model	Equation	Isotherm model parameters	Fundamental characteristics	Reference
Langmuir model (2.2)	$q_e = \frac{q_m b C_e}{1+bC_e}$	q_m: Theoretical maximum adsorption capacity (mg g−1). b:Langmuir adsorption constant (L mg−1).	The model's presumptions were that adsorption only occurs at specific, localized sites, that one molecule always occupies an adsorbent site, and that all adsorbate molecules exert the same amount of energy, regardless of the presence of additional molecules. Additionally, there is no communication between nearby adsorbed molecules.	*(Allen, et al., 2004)*
Freundlich model (2.3)	$q_e = K_F C_e^{1/n}$	Heterogeneity factor *1/n*, K_F is Freundlich constant indicates	It takes into account multilayer adsorption and imperfect sorption on heterogeneous surfaces.	*(Tapan Kumar*

		the capacity (mg/g)(L/mg)$^{1/n}$		*Saha 2010)*
Sips Model (2.4)	$q_e = \frac{K_s C_e^{\beta_s}}{a_s C_e^{\beta_s}+1}$	*Ks* (L/mg) and a_s *(kJ/mol)* are the Sips constants. β_s is a Sips model exponent equal to (1/*m*) and *m*= parameter that shows the system's heterogeneity.	It anticipates displaying diverse surfaces in the best light possible. If the adsorbate concentration is low, the Freundlich isotherm is reached; if the adsorbate concentration is large, the Langmuir isotherm is reached.	*(Hubbe et al. 2011).*
Radke–Praunsitz Model (2.5)	$q_e = \frac{K_{RP}C_e}{1+\left(\frac{K_{RP}}{F_{RP}}\right)C_e^{1-N_{RP}}}$	K_{RP} and F_{RP} are Radke–Prausnitz model constants. N_{RP} the Radke–Prausnitz model exponent.	Three paramours are used in simple expression and empirically.	*(Foo and Hameed 2010)*

To evaluate the visibility of Langmuir model in the adsorption process, dimensionless parameter (***Rs***) termed of separation factor as in following expression is used:

$$\boldsymbol{R_s} = \frac{\mathbf{1}}{\mathbf{1}+\boldsymbol{bC_o}} \tag{2.6}$$

The ***Rs*** can be used for specifying whether an adsorption is favorable or unfavorable according to limits described in Table (2.6).

Table 2.6Limits of separation factor.

R_s	Type of isotherm
R_s>1	Unfavorable
R_s=1	Linear
R_s=0	Irreversible
0< R_s<1	Favorable

2.11 Adsorption Kinetics

The sorption kinetics, process design and the operation control for any applicable applications are very significant. In order to design a suitable adsorption treatment process, it is very important to estimate the rate at which the dissolved contaminant is adsorbed from solution. So, the good estimation of the mechanism of the reaction pathways and the adsorption reaction can be obtained from the sorption kinetics that is important in treatment of wastewater ***(Puranik, et al., 1999).***

From many types of the kinetics models that used to describe the mechanism of adsorption process, the following type were selected (Table 2.8).

Table 2.7 Equations, Parameters and Fundamental characteristics for the Pseudo First Order and Pseudo second Order kinetic models.

Kinetic model	Equation	Isotherm model parameters	Fundamental characteristics	Reference
Pseudo First Order (2.9)	$\boldsymbol{q_t = q_e(1 - e^{-k_1 t})}$	k_1 (1/min) is the constant of Pseudo first order rate constant (q_e *and* q_t) are the amount of contaminant adsorbed from the aqueous solution by (mg/g) at equilibrium and at time *t* respectively.	This kinetic model presupposes that the ratio of vacant sites to the rate of sorption site occupation is linear.	*(Faisal and Naji 2019)*
Pseudo second Order (2.10)	$\boldsymbol{q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right)}}$	k_2 (g/mg min) is the constant of Pseudo second order rate.	Each ion's sorption energy is constant and unaffected by the amount of surface contact. There are no interactions	***(Ho and McKay 1999)***

			between sorbed ions during the sorption, which solely takes place at discrete places. In comparison to the initial rate of sorption, the sorption rate is essentially nil. This equation predicts performance across the whole adsorption process range and appears to be governed by the chemical sorption mechanism as a rate-regulating step.	

2.12 Continuous System

The system bed reactors (column bed) have been more utilized in the food industry, chemical industry, wastewater treatment and pharmaceutical industry ***(Najim 2016)***. The contact time can be increased when using previous beds in series and the capacity of the adsorbent can be increased when using those in parallel ***(Abdul-Hameed 2009)***.

The bed dynamic should be understood to successfully operate and design the adsorption process of bed. This, at specified operating condition, leads to design the breakthrough curves ***(Sulaymon and Ebrahim 2008)***.

The adsorption process effectiveness may be increased in the presence of the magnetic field for the mixture of sulfate but this effectiveness decreases when the concentration increases ***(Rajczykowski and Loska 2018)***.

2.12.1 Column Bed

Because of its excellent mass transfer rate between the particles and the fluid as well as between the bed's walls and the particles, column beds are frequently utilized in engineering. The advantages of these chemical reactors are that the ability to handle a high amount of materials and many kinds of particles, constant bed temperature, good heat transfer, the problem of fixed bed high-pressure drop is avoided, the contact efficiency of fluid-particle is high and the interface surface areas between the particles and the fluid (liquid) is large ***(Al-Hares 2014)***.

A friction process is created between the granular particles because of upward fluid motion that is passed through a packed column of adsorbent, and then the lifting force of particles is created because of friction process. The expansion of the bed occurs and the particles are separated from others when the liquid velocity increased, also the behaviour of the particles in the bed is to be like a fluid. At this time, the fluidization phenomenon is started.

Then, a bubbling fluidized bed is created at an additional increase in the velocity where it is generated an excessive liquid bubble through the bed. A turbulent fluidized condition is created when the velocity is furthermore increased where the solids are captured in the fluid and ran away.

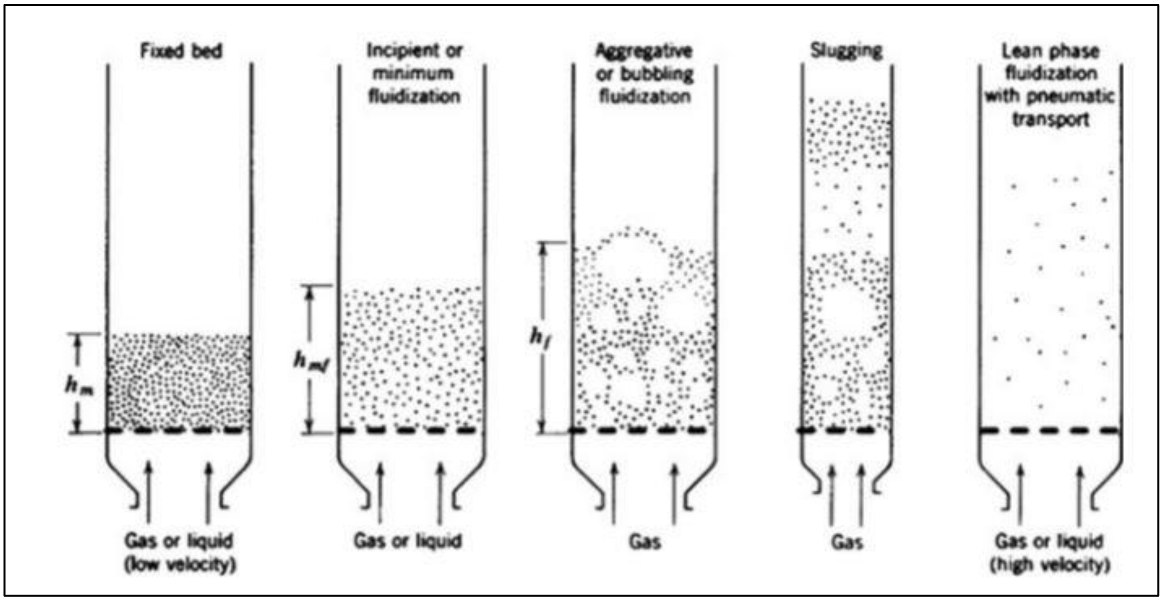


Figure 2.4 the fluidization states (Ilamathi et al. 2014).

The bed of the adsorbent particles is suspended in liquid medium of the two-phase fluidization (liquid and solid), and these phases are contacted between them in an intimate, and as a result the mass transfer becomes good ***(Al-Hares 2014)***.

The process of fluidization depends on the surface characteristics of the particle, size distribution of the particle, particle size and density of the particle. At the unique value of the flowing velocity, the particles is begin to fluidize where the force of fluid frictional drag balances the particle gravity force in the fluid ***(Sulaymon et al. 2013)***.

2.12.2 Factors Affecting Continuous System

By plotting the ratio of (C_e/C_o) versus the time (concentration in different contact time relative to initial concentration of adsorbate), it can be obtained the breakthrough curves for metal adsorption, which are obtainable at various operation conditions ***(Yahayaa et al. 2011)***.

The point on the curve at which the bed is in equilibrium with the contaminated solution during operation and followed by low additional adsorption of contaminants from the contaminated solution is called the breakpoint (Figure 2.5). This point is often taken at the range (0.05 to 0.1) of the ratio of (C_e/C_o) and it is advisable to replace or reactivate the adsorbent at this point ***(Abdul-Hameed 2009***).

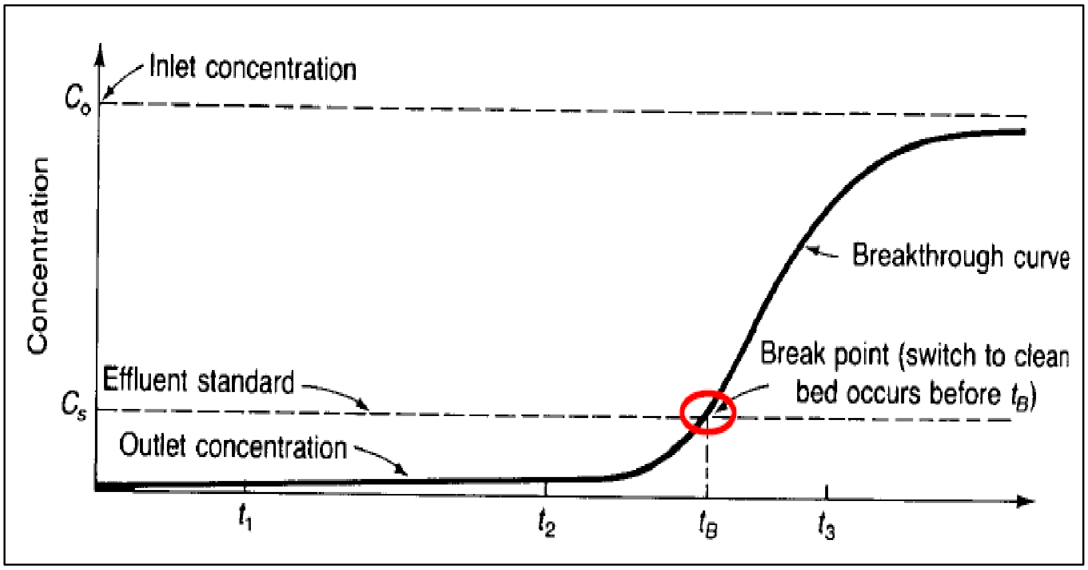


Figure 2.5 A breakthrough curve typical profile (Hussein 2012).

Some important factors that affect the adsorption process in the continuous column system are the length of the contaminant path line exposure to a magnetic field, flow rate, initial metal concentration, pH and bed depth.

1) Circulation bed.

Circulated fluidized bed reactor (CFB): The riser or circulating fluidized bed (CFB) reactor is a development of the traditional fluidized bed reactor. Given the high velocity, back mixing is significantly reduced, and co-current up flow nature of the CFB reactor (Grace, 1990). The efficiency of the contact between the carrying fluid(s) and the particles is also increased because of the increasing slip between the phases.

The improvement of CFB would benefit some biochemical processes where continuous solids recirculation, independent control of phase holdups is required, and intensified mass transfer. The CFB is comparatively new type of reactor in which solid particles are circulated between the riser and the downer. While the desorption process takes place in the lower column, the adsorption process takes place in the riser. Because of advancements in genetic engineering, concerns about resource conservation and environmental safety, and the desire to recover contaminants from large volumes of wastewater stream discharge from industrial and biological broths, there has been a surge in interest in this field in recent years (Mazumder et al., 2009).

The CFB embodies the concept of particle recirculation between the two beds, where two distinct environments are maintained simultaneously and they are linked by the liquid–solids recirculation (Chowdhury et al., 2008). CFB are probably going to locate an enormous number of uses in the biological and biochemical, where the significantly improved interfacial contact efficiency can lead to much more effective processing means. Moreover, the nature of the CFB with adsorption-desorption units under one system makes the bioprocesses continuous, leading to a further increase of efficiency and reduced processor size.

2) Effect of Flow Rate:

When the flow rate is higher, the breakthrough usually is quicker occur because of the mass transfer rate is increased that leads to an increase of a quantity of contaminant adsorbed on the adsorbent ***(Bayramoğlu et al. 2006)***.

The pollutant is left the bed before occurring equilibrium because the time of solute diffusion becomes low and the residence time of the solute in the bed becomes insufficient that leads to reduce the adsorption capacity ***(Han et al. 2006)***.

3) Effect of Inlet contaminant Concentration:

The breakthrough curve is affected significantly by the initial ion's concentration changing because when this concentration is increased, the more adsorption sites can be occupied. The slope of the breakthrough curve is steeper at larger influent concentration with the lower time ***(Goel et al. 2005)***.

4) Effect of pH:

The adsorption capacity of adsorbent is influenced by the parameter pH because of it has to control the ionization degree of basic and acidic compounds. In addition, the adsorption process of solute is clearly effected by this an important parameter of the aqueous solution ***(Esmail 2016)***.

5) Effect of Bed Height (Weight):

A rise in the height of the bed of the column leads to an increase in the adsorption capacity because the adsorbent loaded mass is largely effect on the solute accumulation in an adsorption column ***(Meshko et al. 2001)***.

The reason of an increase in the solute uptake according to an increase in the bed height was due to that the amount of adsorption sites is increased as an increase in adsorbent doses related to an increase of bed height in the adsorption column ***(Malkoc and Nuhoglu 2006)***.

2.13 Literature Survey

Nirmala and Muruganandam, 2013 focused on liquid- solid circulating fluidized bed (LSCFB) hydrodynamics and biosorption of cadmium using immobilized micro-organism in a LSCFB. Work is carried out to estimate the solids circulation rate, solids holdup using sodium alginate beads of 4mm diameter and density of 1010 kg/m3. Cadmium concentration at regular intervals was determined by EDTA titration with xylenol orange as indicator and hexamine as buffer. The cadmium biosorption efficiency in batch and in LSCFB, respectively, are found to be depending on the strain of microorganism used, time, quantity of micro-organism used and initial cadmium concentration.

Pei-lun SANG and Yun-yan WANG, 2012 Sulfate adsorption by poly(*m*-phenylenediamine)s (PmPDs) with various oxidation states synthesized through chemically oxidative polymerization was investigated. Series of sorption experiments were conducted, and the adsorption mechanism and the relationship between oxidation state and adsorption performance were studied with the characterization of Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), pH tracking and energy calculation. The results show that the adsorption performance in acidic solution is improved with the decrease of oxidation state of poly(*m*-phenylenediamine) (PmPD). The rate constant is as high as 425.5mg/(g·min) in the short equilibrium time of 30 min. The estimated highest adsorptivity of sulfate ions is 95.1%. According to the Langmuir equation, the adsorbance is 108.5 mg/g. The sulfate desorption efficiency is about 95% and the accumulative adsorbance is up to 487.95 mg/g in 5 cycles.

This study focused on adsorption of sulfate from wastewater by using low-cost material as an adsorbent that activated by physical method and the parameters effected on adsorption process was studied in batch and continues system (contact time, PH, initial con. Of ion, adsorbent dose, and agitation speed) (flow rate, pH, adsorbate initial concentration, bed height and cycle bed number) respectively.

Chapter Three: Experimental Work

3.1 Introduction

Batch and continuous trials were used in the experimental activity. For the batch and continuous systems, respectively, there were around 32 and 24 tests in the first section. Batch experiments were used to prepare and assess the composite adsorbent and to determine the ideal conditions in order to extract sulfate from simulated wastewater. The effects of contact time, pH, adsorbent dose, adsorbate initial concentration, and agitation speed were investigated in these experiments.

In the continuous systems, 360 experiments each were carried out for the column bed system. The impacts of flow rate, pH, adsorbate initial concentration, bed height and cycle bed number as shown in figure (3.1)

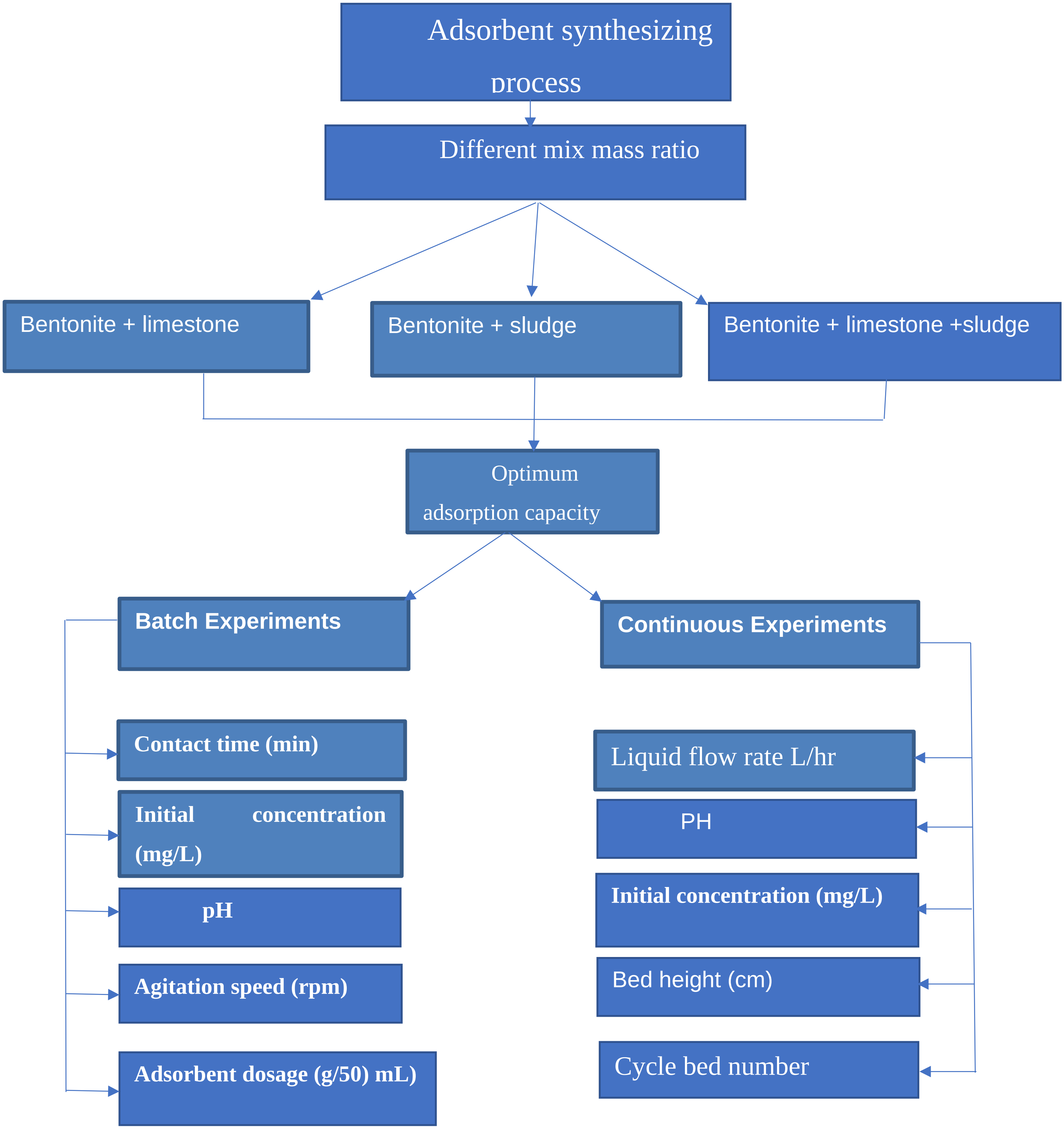


Figure 3.1 The Procedure of the Experimental Work

3.2 Equipment

The needed equipment used in the research was tabled in the Table (3.1)

Table 3.1Equipment description used in the experimental work.

№	Type equipment	Usage
1	Grinder	for Petiole grinding.
2	Sieve	to sieve the grinding Petiole.
3	Furnace	for preparation the local adsorbent from petiole by activation.
4	Electrical balance	for weighting the materials used in this work.
5	pH meter	for measuring the pH of the water samples.
6	Electric Shaker	for the batch sorption tests.
7	Glass ware,	for the batch sorption tests.
8	spectrophotometer	for measuring the concentration of dissolved SO_4 ions under consideration.
9	Laboratory Thermal Oven,	used to drying the adsorpent after modification.
10	Filter paper	to filter the samples solution
11	Flowmeter, (100-500) ml/min	to adjust the amount of water.
12	Water Pump	to pump the solution
13	Glass Column	for the continues system

3.3 Materials

3.3.1 Chemical materials

The chemical material used in present study

Table 32. shows the Chemical materials used in this study.

NO.	Compound	Formula	Phase	Source
1	bentonite	Al2O3˙4SiO2˙H2O	solid	commercial markets.
2	Limestone	CaCO3	solid	commercial markets
3	Sludge	………..	solid	WWTP Karbala
4	potassium sulfate	K2SO4	Solid	Limited fine-chem. SD
5	Sodium hydroxide	NaOH	solid	Alpha Chemical
6	Hydrochloric acid	HCl	liquid	GCC
7	Glycerol	$C_3H_8O_3$	liquid	commercial markets
8	*Ethanol*	C_2H_6O	liquid	commercial markets
9	Sodium chloride	NaCl	solid	commercial markets
10	Barium chloride	$BaCl_2.2H_2O$	solid	commercial markets

3.3.2 Adsorbent preparing.

- The city of Karbala's wastewater treatment plant provided the dewatered sludge. The limestone and bentonite samples were gathered from retail marketplaces.

- Three composites were prepared from this material with different mix mass ratio as follow; sludge bentonite and limestone (SBL) composite, sludge and bentonite (SB) composite and bentonite and limestone (BL) composite in different mass ratio as will come.

- These materials were cleaned with distilled water to get rid of the dirt, and they were then dried in a laboratory thermal oven at 105 degrees Celsius for 24 hours before being crushed. The materials were sieved using the sieves with mesh sizes ranging from 1.18 to 0.600 mm, as seen in Figure (3.2).

- The physical activation approach was used to activate the sludge bentonite and limestone (SBL) composite. The steps involved mixing the material in an electric shaker set at 25 °C for 30 minutes while adding bentonite gradually to the water, adding sludge with water, and adding limestone gradually to the water.

- The solution is then filtered. The filter is burned in the oven for two hours at (800) °C using filter sheets.

- The resulting is grinding by grinder and sieved. the mixture of sludge, bentonite and limestone at mass ratios of 4:1:1, 3:1:1, 2:1:1, 1:4:1, 1:3:1, 1:2:1, 1:1:4, 1:1:3, 1:1:2, and 1:1:1. The SB and BL composite was prepares by same procedure of SBL composite with different mass ratio it be from two material ; 4:1, 3:1 , 2:1 , 1:1 , 1:2 , 1:3 , 1:4.

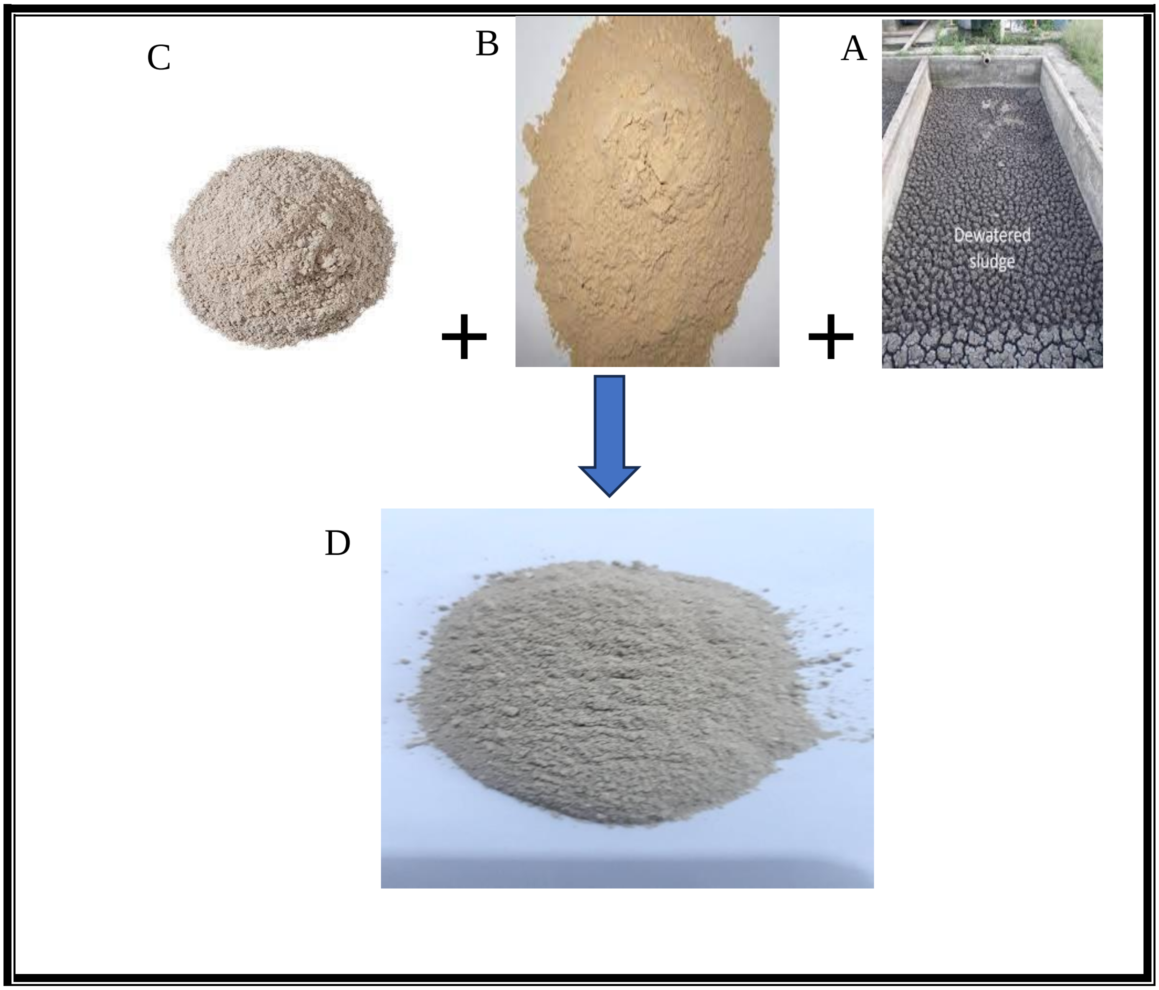


Figure 3.2 Process of Low-cost local adsorbent preparation (A) sludge, (B) bentonite, (C) limestone, (D) SBL composite.

- the preparation of sludge as an adsorbent by same process of three composite (pei-lun et al. 2012).

3.3.3 Adsorbate preparing.

Using Eq. 3.1 and assuming total dissolution, the necessary sulfate concentration was obtained (Nazeeh, 2016):

$$\boldsymbol{W}\mathbf{=}\ \boldsymbol{C_i} \times \boldsymbol{V}\,\frac{\boldsymbol{M.wt}}{\boldsymbol{At.wt}} \tag{3.1}$$

Where: **W**= the weight of the salt (SO_4) (mg), **V**= volume of the solution (L), **Ci**= the required (K_2SO_4) concentration (mg/L), **M.wt**= the salt molecular weight (g/mole) = 174.259 **,At.wt**= the SO_4 atomic weight (g/mole) [16+(4*8)]=48.

sulfate solution with the concentration of 900 mg/L was prepared by dissolvingK_2SO_4 (3.267 g) in distilled water. After preparation the sulfate solution with a 900 mg/L concentration, It was maintained at 25 ºC, the laboratory temperature. 0.1 M HCl or 0.1 M NaOH was used to alter the pH of the prepared solution as needed, and the stock solution was utilized to obtain any necessary concentration of SO4. For obtaining the concentrations (100, 200, 300, 400, 500, 700, and 900 mg/L) of sulfate that were required for experiments. Initially, each stock solution was made using Eq. 3.1 to achieve a concentration of 900 ppm. It was then diluted using Eq. 3.2 to achieve the desired concentration. The pH of each solution was additionally adjusted as needed using 0.1 moles of HCl or 0.1 moles of NaOH. ***(Facui et al., 2016)***.

$$\boldsymbol{C_1} \times \boldsymbol{V_1} = \boldsymbol{C_2} \times \boldsymbol{V_2} \tag{3.2}$$

Where:

$\boldsymbol{C_1}$= concentration of solution (1000) mg/L.

$\boldsymbol{V}_1$= volume of the solution (L).

$\boldsymbol{C_2}$= solution's diluted concentration (mg/L).

V_2= diluted volume of the solution (L).

3.4 The Characterization of the Adsorbent

The adsorbent has been characterized using a variety of techniques, including Zeta Potential (-P),Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscope (SEM),Specific Surface Area (BET),Fourier Transform Infrared Spectroscopy (FTIR) ,andX-Ray Diffraction Analysis (XRD).

The FTIR of the adsorption was used to verify the presence of functional groups. The morphology of the sample was depicted in the SEM photos of the adsorbent, and the material's chemical composition was given by EDS. SEM and EDS were performed at 15 kV using the S-4800 SEM. The phase and content of the material were described using XRD. The Cu Ka radiation (k = 1.5406) was measured using the Rigaku D/max 2500 diffractometer at a voltage of 40 kV and an energy level of 200 mA. The Brunauer-Emmett-Teller (BET) theory, which analyzes the physical adsorption of molecules of gases on solid surfaces, can be used to calculate the specific surface area of materials. (Thommes et al., 2015). The BET was measured using the automated adsorption analyzer gas (autosorb-iQ, Quantachrome Instrument). By employing Zetasizer (Nano-ZS), -P demonstrated the value of the adsorbent isoelectric point in order to comprehend the adsorbent behavior at various pH levels.

3.5 The Parameters of the Experimental Work

The experiments were investigated in two types: 1) Batch experiments, which including kinetic and equilibrium isotherm; 2) Continuous experiments, which including column bed. Table (3.3) shows batch and continuous major parameters that investigated in the experimental work.

Table 3.3 Batch and continuous major parameters that study in experimental work.

Mode of operation	Parameter with units	Ranges	Purpose
Batch	Contact time (min)	5, 10, 20, 30, 60, 120, and 180	to find the best contact time of removal
	pH	2, 4, and 6	to find the best pH of removal
	Initial con. of contaminant (mg/L)	100, 200, 300, 400, 500, 700, and 900	to find the best Initial con. of removal
	Amount of adsorbent dosage (g/50 mL)	0.05, 0.1, 0.2, 0.3, 0.3, 0.4, 0.5, and 0.6	to find the best adsorbent dosage of removal
	Agitation speed (rpm)	50, 100, 150, 200 and 250.	to find the optimum agitated speed of removal.
Continuous	Liquid flow rate, (L/h)	6, 9, 12 and 15	to study the variation of breakthrough curves at different flow rate.
	pH	3,4,5 and 6	to study the variation of breakthrough curves at different pH.
	Initial concentration, (mg/L)	100, 200, 300, 400, 500, 700, and 900	to study the variation of breakthrough curves at different

			initial concentration.
	Bed height (cm)	5,10, 15 and 20	to study the variation of breakthrough curves at different bed height.
	Cycle bed number	1,2,3,4, and5	to study the variation of breakthrough curves at different cycle.

3.5.1 Batch experiments

To establish the ideal circumstances and equilibrium data for the treatment process, batch experiments were conducted. Adsorbent dosage, initial contaminant concentration, pH, contact time, and agitation speed were some of these factors. A 50 cm^3 of an aqueous solution containing sulfate was placed in each of ten conical flasks, each measuring 250 cm^3. For each experiment, the pH of the prepared solution was changed as necessary, and 0.1 M HCl was added to attain the desired pH. In order to achieve equilibrium, mixtures were shaken, and the solution and adsorbent were then separated using a filter. AAS (atomic absorption spectrophotometer flame) was used to measure the residual sulfate concentration in the filtrate.

The solutions' kinetic studies were investigated throughout a range of times (5, 10, 20, 30, 60, 120, and 180 min) ***(Sharifnia et al. 2016)***, pH (2, 4, 6, 9 and 11) ***(Larous et al. 2005)***, different initial concentrations of contaminant (100, 200, 300, 400, 500, 700, and 900 mg/L) ***(Benzaoui et al. 2018)***, different adsorbent dosages (0.05, 0.1, 0.2, 0.3, 0.3, 0.4, 0.5, and 0.6 g/50 mL) ***(Benzaoui et al. 2018)***, and different agitation speed (50, 100, 150, 200 and 250 rpm) ***(Benzaoui et al. 2018)***.

Equation below was used to determine the amount of pollutant adsorbed on the adsorbent based on experimental data (***Wang and Chen, 2009***).

$$q_e = (C_o - C_e)\frac{V}{m} \tag{3.3}$$

Where: C_o and C_e represent the initial and equilibrium concentrations of contaminant in the solution (mg/L), V is the volume of solution in the flask (L) and m is the mass of adsorbent in the flask (g).

3.5.2 Colum Experiment

The breakthrough curves were studied by the column experiments using column bed system. The bed is loaded by the low-cost adsorbent synthesized from SBL. The solution was taken from a cylindrical plastic container (80 L), and then it flows through the bed with selected flow rate measured by the flow meter (Figures 3.3 and 3.4).

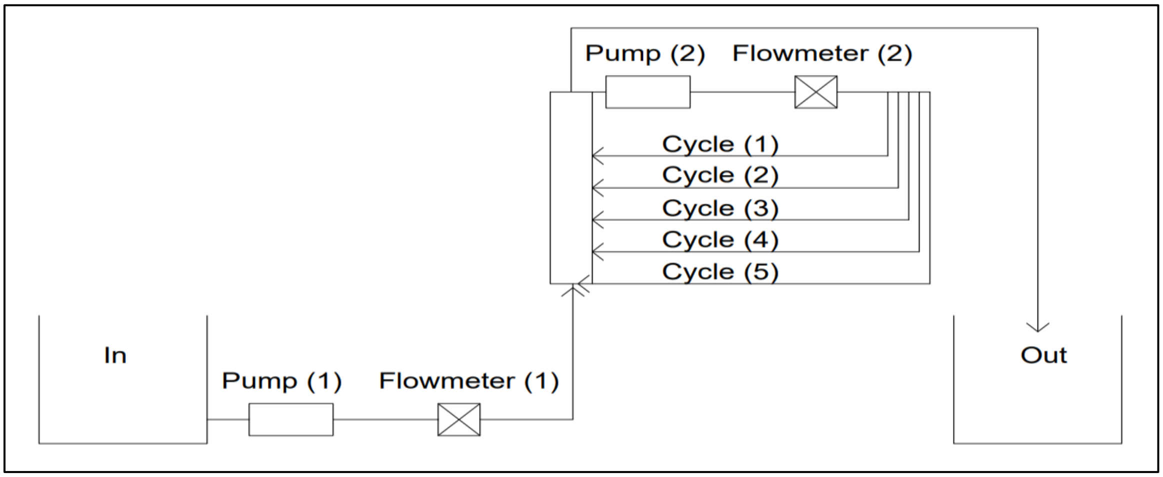


Figure 3.3 Schematic diagram of column experiment system

***** Column bed system; (1: Feed container. 2: Valve. 3: Pump. 4: Solution flow meter. 5: Meshes. 6: SBL composite. 7: Cycle, 8: Collecting container.).

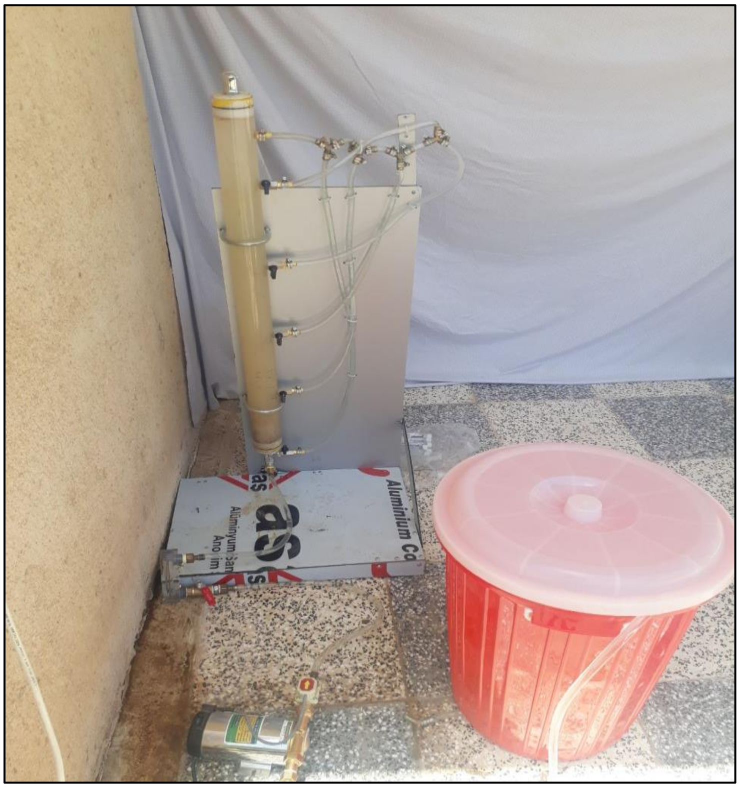


Figure 3.4 Column experiment system

Before each experiment, the deionized water was used to wash the column to remove the traces of adsorbate and adsorbent.

3.6 Mathematical Model.

The current study revolves around developing a predictive model to estimate the 'Time (min)' variable based on a multitude of features presented in the dataset.

These characteristics cover a range of variables, such as cycle counts, pH values, and other specifics. Through a thorough understanding of the complex correlations that exist between these factors and the 'Time (min)', the study seeks to develop a profound grasp of the underlying patterns, which will enable more precise forecasts.

3.6.1 Data Import and Inspection

Using the Pandas package, the dataset was imported into the Python programming language as the first stage in the study. Gaining a basic grasp of the structure and properties of the data depended heavily on this phase.

3.6.2 Data Cleaning

A thorough search was done during the data cleaning process to see whether there were any values that were missing in the dataset, but none were found. The Z-score approach was then used in an effort to identify any outliers. In spite of this, no outliers were found, suggesting that the dataset previously existed fairly stable and clean.

The Z-score is calculated using the formula:

$$Z = (X - \mu) / \sigma \tag{3.4}$$

where:

- Z: Z-score.
- X: Individual data point.
- μ: Mean of the dataset.
- σ: Standard deviation of the dataset.

3.6.3 Data Visualization

Histograms were created at the data visualization stage to show the average value of each variable. Additionally, scatter plots were employed to investigate the correlations among the variables in the dataset and the 'Time (min)' variable.

3.6.4 Model Development

The set of data was divided into dependent and independent variables throughout the model-development stage. All other variables were considered independent, with the exception of the 'Time (min)' column, which was designated as the dependent variable. Next, a train-test split strategy was used to create a model using multiple linear regression, with 20% of the data set aside for testing. The multiple linear regression model is represented by the equation:

$$Y = \beta 0 + \beta 1\ X1 + \beta 2\ X2 + ... + \beta n\ Xn + \varepsilon \tag{3.5}$$

where:

- Y: Dependent variable ('Time (min)').
- X1, X2, ..., Xn: Independent variables.
- β0: Intercept, - β1, β2, ..., βn: Coefficients for the independent variables.
- ε: Error term.

3.6.5 Performance Evaluation

It was crucial to thoroughly assess the model's performance after it was created. For the test set, the 'Time (min)' variables were predicted, and a number of metrics were computed to evaluate the precision and dependability of the model. The following is a description of the metrics used:

1. Mean Absolute Error (MAE)

$$MAE = 1/n \Sigma |y_i - \hat{y}_i| \tag{3.6}$$

2. Mean Squared Error (MSE)

$$MSE = 1/n \Sigma (y_i - \hat{y}_i)^2 \tag{3.7}$$

3. Root Mean Squared Error (RMSE)

$RMSE = \sqrt{MSE}$

4. R-squared (R^2)

$$R^2 = 1 - (SS_{res} / SS_{tot}) \tag{3.8}$$

where:

- SS_{res}: residual square sum $\Sigma (y_i - \hat{y}_i)^2$.
- SS_{tot}: total squared sum $\Sigma (y_i - \bar{y})^2$, - y_i: Actual value.
- $\hat{y}_i$: Estimated amount.
- $\bar{y}$: The average of the real values.
- n: Quantity of observations.

Chapter Four: Results and Discussion

4.1 Introduction

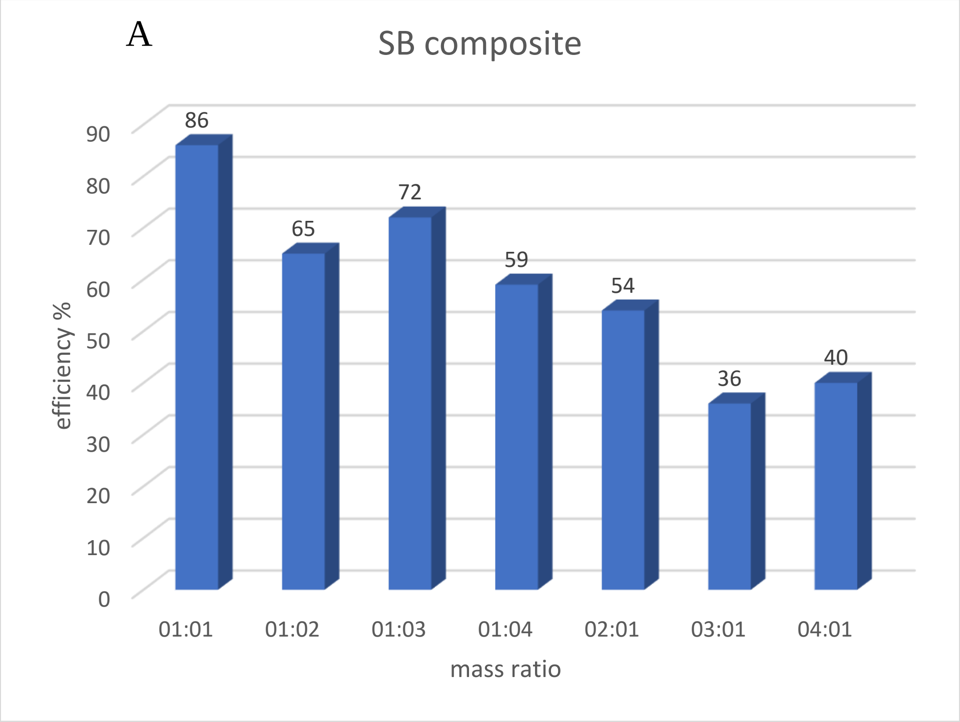
1. the adsorbent's preparation and characterization outcomes.

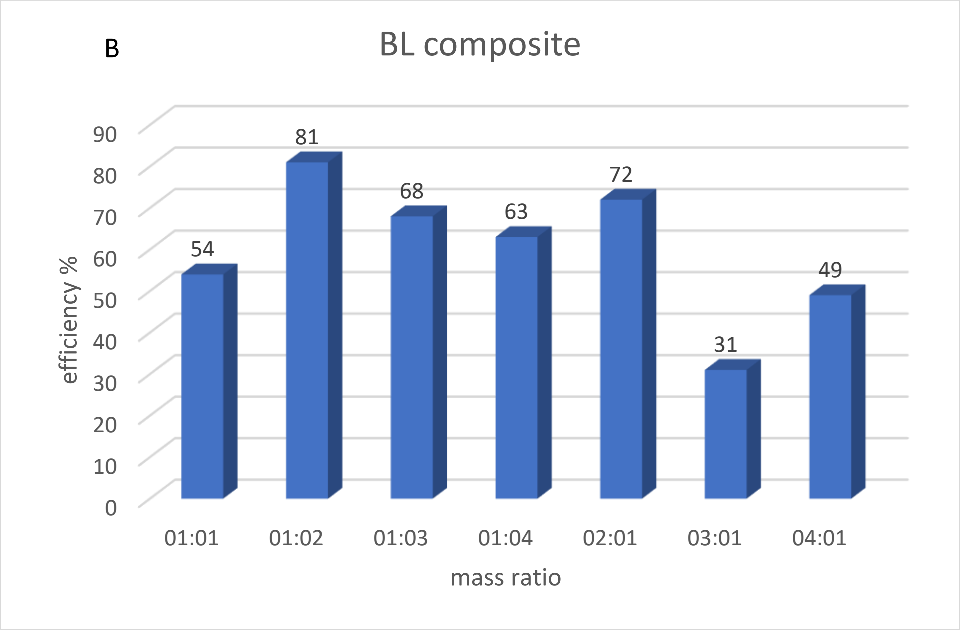
2.The results of experiments carried out in batch mode. The purpose of this part of the experiment was to assess how well the adsorbent removed sulfate from generated contaminated wastewater. The adsorption kinetics models (Pseudo-first-order and Pseudo-second-order) and adsorption isotherms models (Langmuir and Freundlich) were used to the experiment data in the batch experiment. The tests that are conducted in various conditions (contact time, pH solution, initial concentration, agitation speed, and adsorbent dosage) are represented in this section.

3. The results obtained from the continuous system by adsorption as a column bed. This part of results represent the experiments that carry out in different (cycle bed number, flow rate, pH of the solution, initial concentration of the adsorbate and bed height of the adsorbent).

4.2 Adsorbent Preparation

The adsorbent preparation was done by four stages, the sludge alone and three type composites are prepared; BL, BS, BLS. To check the ability of composites for sulfate removal with best mass ratio composition. the initial condition where the three composites are tested (C_o = 900 mg/l, PH =7.5, agitation speed = 200 rpm, contact time =60 min, adsorbent dose = 100 mg/50ml, temperature =25 C^o). the sludge removal efficiency alone is (57%), the figure (4.1) shows the result efficiency of BS and BL composite, and the figures (4.1) show the result efficiency of BLS composite. The best composite BLS with mixture mass ratio was 1:1:2 and the removal efficiency = 89 %, the increase of removal efficiency for this mass ratio composite was showed in characterization of adsorbent.





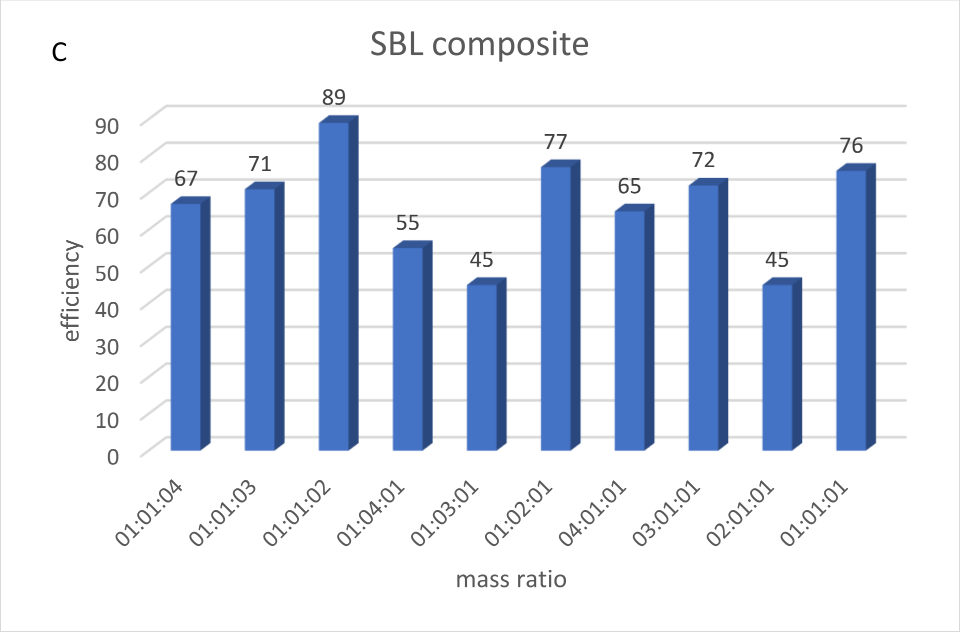


Figure 4.1 removal efficiency of A:SB, B: BL, C: SBL composites mixture mass ratio on sulfate.

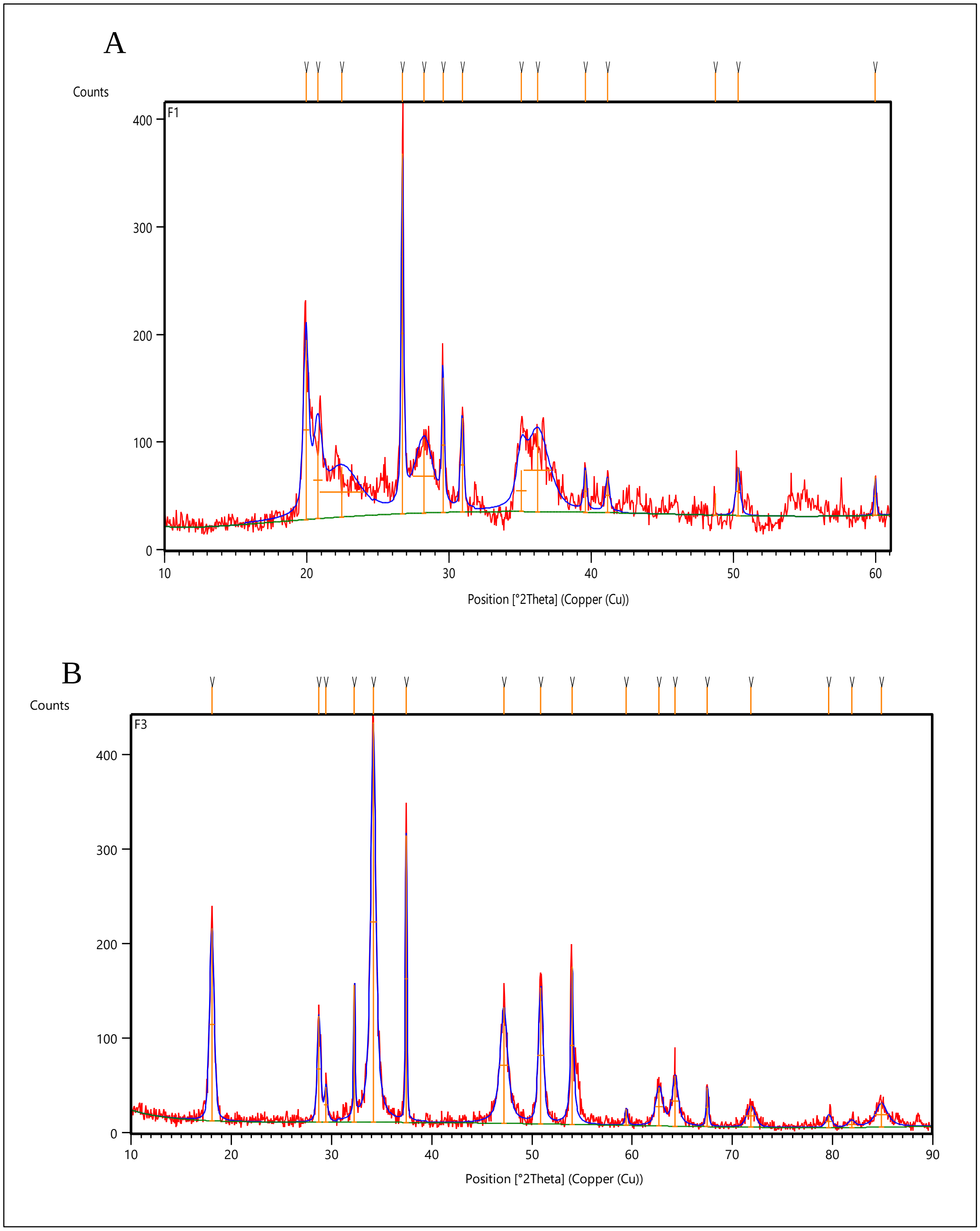
4.3 Characterization of the material and composite.

4.3.1 XRD

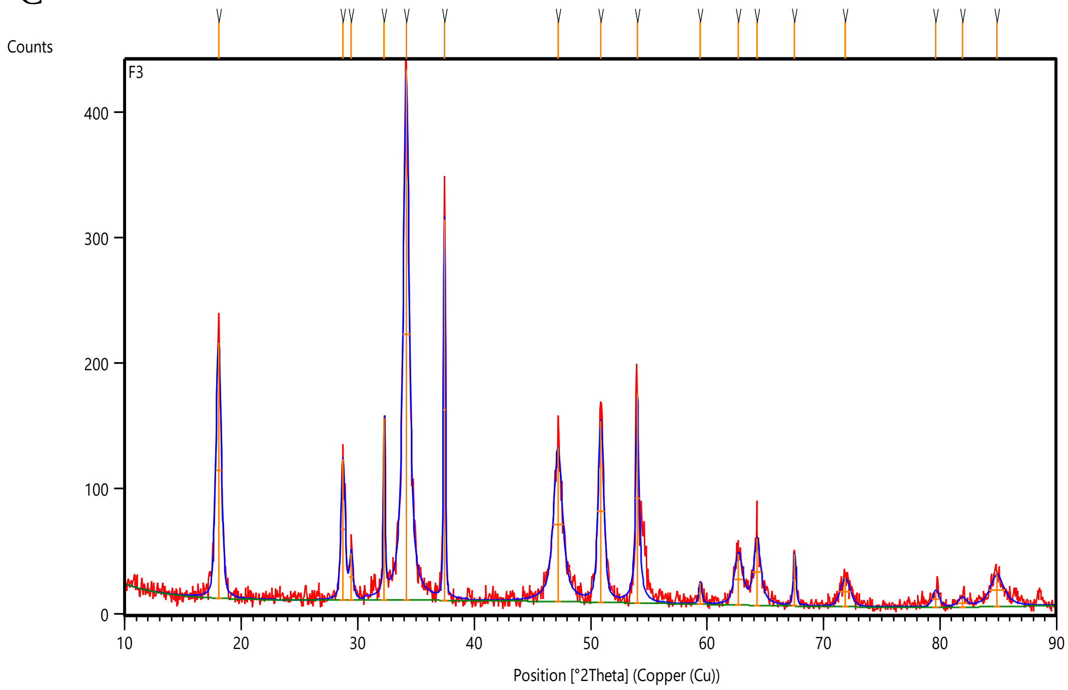
The SBL composite were characterized using X-ray diffraction (BRUKER) in the Physic Department / College of the Science/ University of Tehran. Using X-ray diffraction (XRD) analysis, the SBL composite was analysed before and after adsorption, and the result data was presented in Figure 4-2. From Figure 4.2, only diffraction peaks (2θ=15° and 23°) for the carbon and (2θ=24°, 26.5°, 42.1°, 45°, 51°,78° and 84°) for the graphite were observed in the SBL composite. The average crystallite size was 96.7 µm calculated by using Debye-Scherrer equation (Eq. 5.1) ***(Monshi et al. 2012)***.

$$D = 0.9\lambda/(\beta \cos \theta) \qquad (5.1)$$

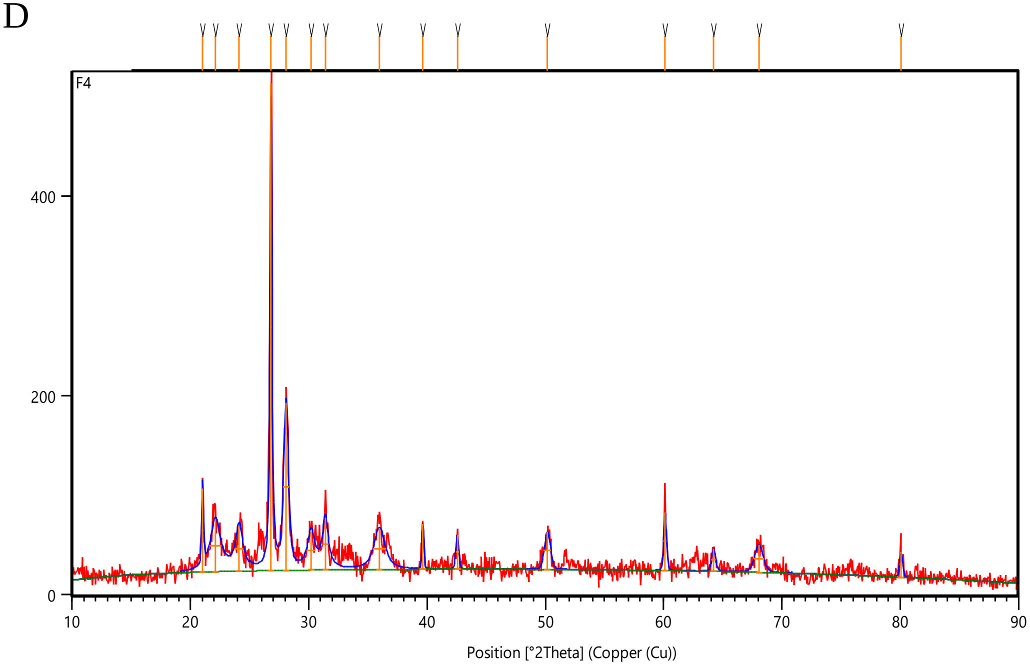
Where, $\boldsymbol{D}$ is the particle size, the X-ray wavelength is $\boldsymbol{\lambda}$, the full peak width at half-maximum intensity (in Rad) is $\boldsymbol{\beta}$, $\boldsymbol{\theta}$ is the half diffraction angle of $\boldsymbol{2\theta}$ of peak corresponding to interlayer spacing (in degree).



C


Counts
F3
400
300
200
100
0
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))

D


F4
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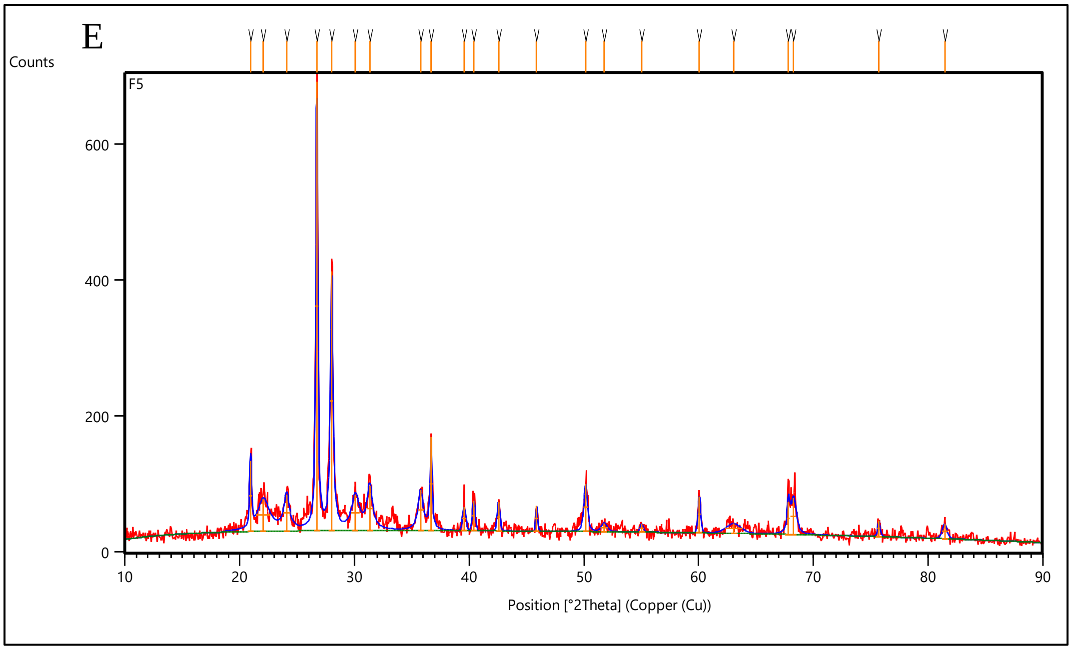


Figure 4.2 XRD patterns(a)for bentonite, (b)limestone, (c) sludge, (d)SBL before adsorption, (e) SBL after adsorption.

4.3.2 BET Analysis

The Brunauer-Emmett-Teller theory, which describes the physical adsorption of gas molecules on a solid surface, provides an analytical method for determining a material's specific surface area (Thommes et al. 2015). The pre-mix results for bentonite, limestone, and sludge were, in order, 11.2959 m^3/g, 15.0577 m^3/g, and 7.5571 m^2/g. The composite SBL's specific surface area of 22.1282 m^2/g shows how the activation process causes the specific surface area of SBL to expand from 22.1282 m^2/g to 42.1283 m^2/g. This indicates that a higher surface area results in a higher adsorption capacity.

4.3.3 Zeta Potential

Figure (4.3) shows the value of zeta potential in different pH solution and it was obvious that when the pH of solution equal to 6.3, the value of adsorbent isoelectric point (Zero-point charge (ZPC)) was founded. This mean that when the value of pH is above the Zero-point charge which founded to be equal to 6.3, the adsorbent surface is negative, and is positive when the value of pH is below 6.3. In addition, when the value of pH increases to 9, the negative adsorbent surface will be rose and this means that the adsorption of the contamiat is highest at this region because of the adsorbent-metals interaction had a smaller amount of electrostatic repulsion between them ***(Hong et al. 2016)***.

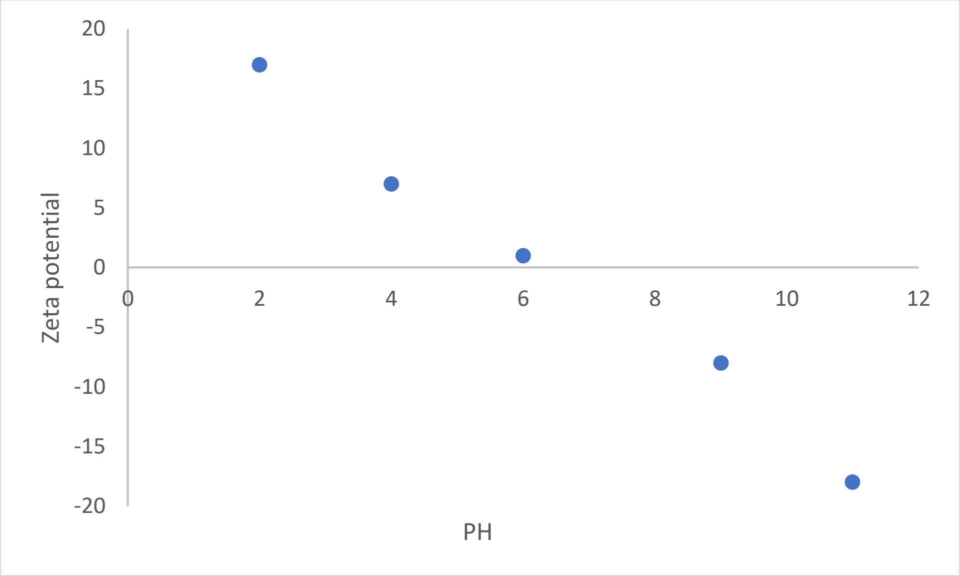


Figure 4.3 SBL Zeta potential.

4.4 Result of Batch Experiments

4.4.1 Adsorptions Studies

1) Equilibrium Time

As seen in Figure (4.4), the sulfate removal was impacted by the contact time. In order to remove $SO_4{}^{-2}$, 50 mL of the solution was placed at room temperature, with 0.1 g of the adsorbent added. The initial conditions were as follows: pH = 7.5, agitation speed = 200 rpm, dosage = 0.1 g/50 mL, Co = 900 mg/L, T = 25 C^o. Ion adsorption on the adsorbent usually occurs in two steps. Adsorption happens quickly in the first step but gradually slows down in the next. Adsorption slows down on the adsorbent surface when the number of adsorption sites decreases (Alkan et al. 2008). The proportion of SO4-2 according to the adsorbent and ion solution's contact time is displayed in Figure (4.4). As the amount of sulfate eliminated increases, the percentage increaseswith increased contact time. The fast adsorption at the initial stage is due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surfaces at the beginning ***(Bulut and Tez, 2007)***.

In an hour, over 90% were eliminated. Furthermore, the ion concentrations stayed largely stable for contact times longer than an hour. Sorption experiments in other batches were carried out at one hour, despite the fact that residual ion concentrations did not vary noticeably for up to three hours.

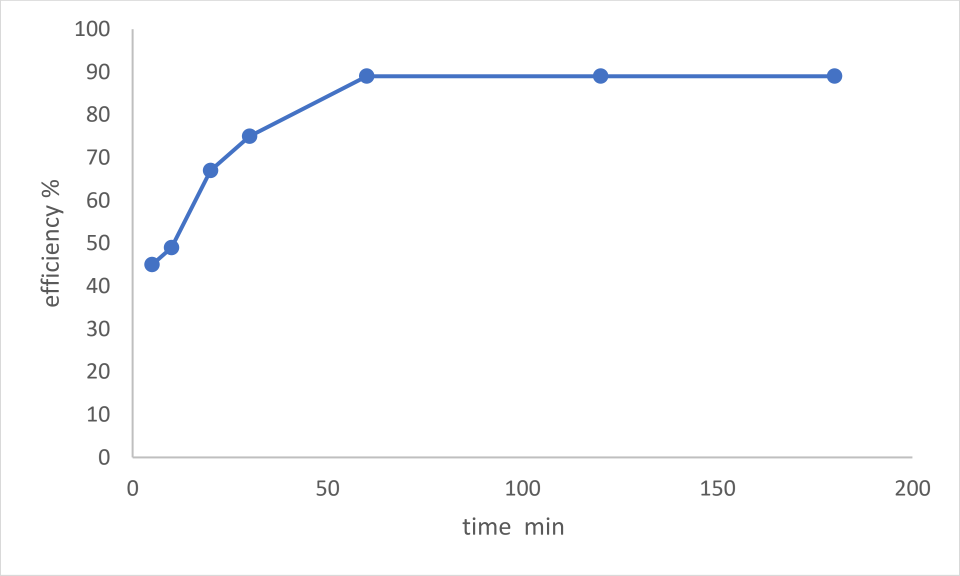


Figure 4.4 the variation sulfate removal efficiency with time.

2) The pH of the Solution

Due to its impact on the ionic forms of the pollutants and the surface characteristics of the adsorbent, the solution pH is the primary factor regulating the adsorbent's capacity for adsorption (Garg et al. 2007). Due to the sorbent's basic and acidic groups being protonated and deprotonated, which affects how ions interact with the surface structure of the adsorbent, the pH value has an impact on the adsorption behavior of the ions (Alkan et al. 2008). In Figure (4.5), the sorbent basic and acidic groups' deprotonation and protonation resulted in an increase in removal efficiency at doses of 0.1 g/50 mL, 900 mg/L, 1 h of contact time, 25 Cº, and 200 rpm of agitation speed. ***Al-Homaidan et al. 2014*** have documented a similar occurrence wherein an increase in the pH of the solution causes an increase in the ion's adsorption. The polarity reactive sets on the adsorbent surface were protonated under acidic circumstances.

This means that protons were taken up by the ions' binding sites, which decreased the adsorption of the ions ***(Areco et al., 2012)***. Figure (4.5) made it clear that there was competition between pollutants and H^+ ions on the adsorbent surface when the pH value rose, increasing removal efficiency.

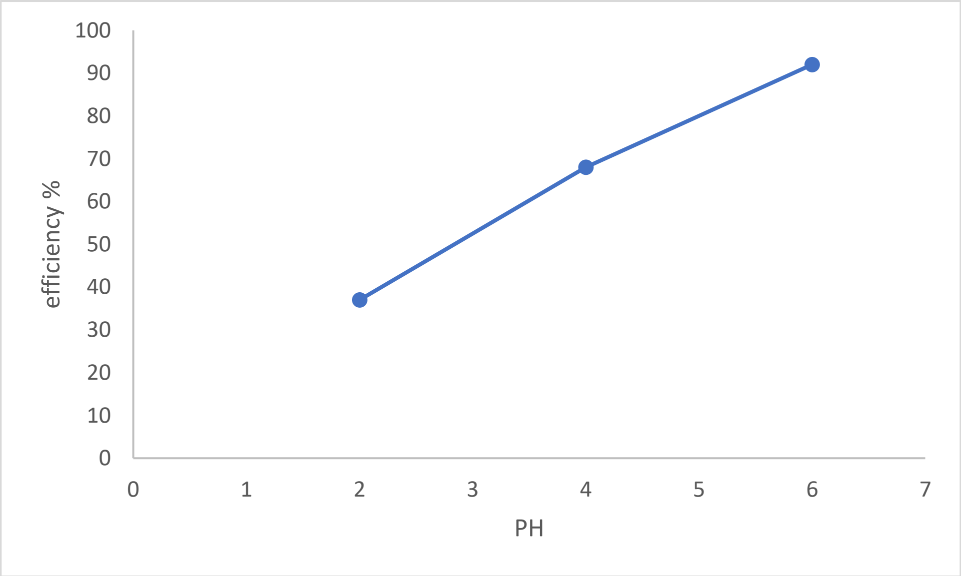


Figure 4.5 Shows sulfate removal efficiency effected by pH.

3) The effect of Initial SO_4^{-2} Concentrations

The effectiveness of removing sulfate was investigated experimentally at various ion initial concentrations. Initial sulfate concentrations in the range of 100 to 1000 mg/L, 0.1 g of the adsorbent per 50 ml of solution, agitation at 200 rpm for one hour, and a pH of 6 solution were employed in these tests. Figure (4.6) illustrates the relationship between the initial ion concentrations at equilibrium state and the ion removal efficiency at (contact time=1 h; agitation speed=200 rpm; dose=0.5 g/50 mL; pH=6; T= 25 ^{o}C). The outcomes demonstrate that the ion removal was greater at the initial concentration values. The elimination efficiency dropped as the initial concentrations increased. After 100 mg/L, there was no discernible change in the ion concentration. This results from the ions' inability to interact with the active sites on the adsorbent. This suggests that when ion concentrations rise in the solution, sites become less energetically favorable. ***(Buasri et al. 2008)***.

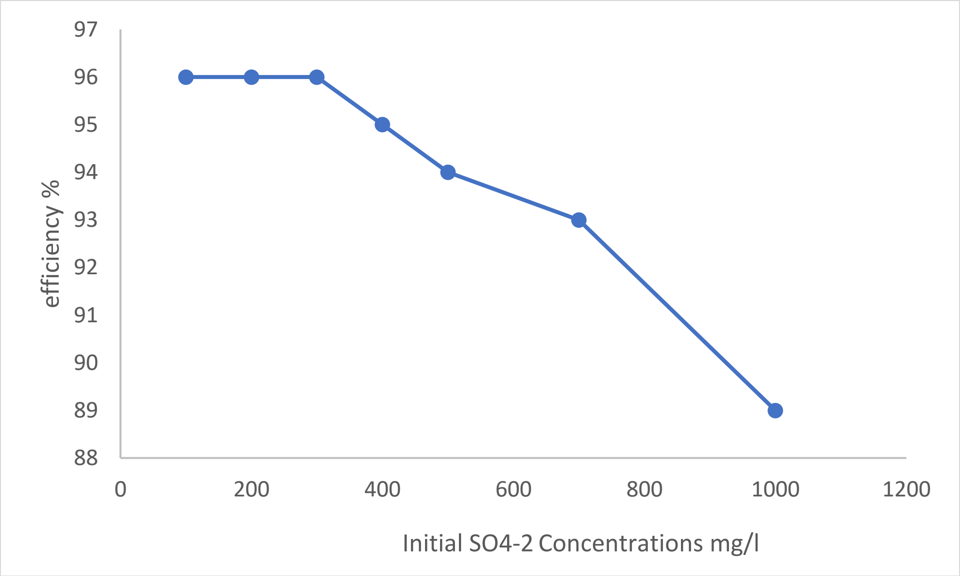


Figure 4.6 sulfate removal efficiency effected by initial concentration.

4) Agitation Speed

Several tests were conducted at varying agitation speeds raining from 0 to 250 rpm with contact time=1 h; Co=900 mg/L; dose=0.1 g/50 mL; pH=6; T= 25oC in order to investigate the influence of agitation speed on sulfate efficiency from contaminated wastewater. Prior to agitation, the SO_4^{-2} removal efficiency was to be 10%, as indicated in Figure 5.8. This efficiency was progressively raised when the agitation speed was increased from zero to 250 rpm, reaching 97%. This rise is explained by the fact that when the agitation speed increases, the ions diffusion on the adsorbent surface improves. Thus, sorbate ions in solution and adsorbent sites form a bond that allows the ions to transfer to the adsorbent sites efficiently (***Anwar et al., 2010)***.

As shown in Figure (4.7), at the agitation speed of 250 rpm, it was obtained the best equilibrium and higher removal efficiency of SO_4^{-2}ions as that all adsorbent sits at this speed for uptake sorbate ions are readily available. Also, when the required functional groups for the interaction between sorbate and adsorbent, which is located on the adsorbent surface, is greater availability, the binding capacity is improved and the processes are rapidly carry out ***(Parvathi et al. 2007)***.

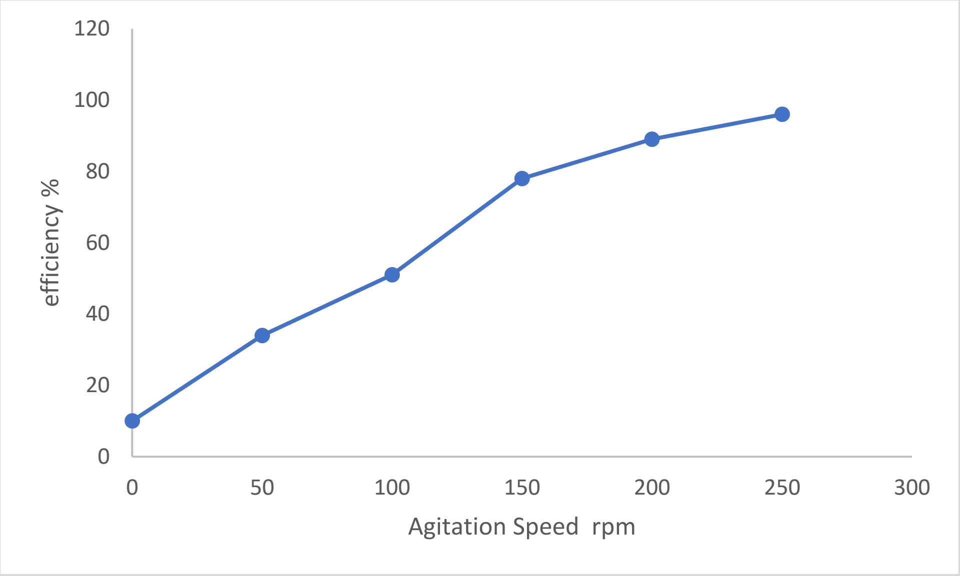


Figure 4.7 sulfate removal efficiency effected by the agitation speed.

5) The Effect of the Adsorbent Dosage

Different concentrations of the adsorbent, ranging from 0.05 to 0.6 g, were utilized in batch testing to investigate how the adsorbent dose impacts the sulfate adsorption. with a ions solution of 50 ml with fixing the other parameters (contact time=1 h; agitation speed= 250 rpm; pH=6; C_o=900 mg/L; T= 25°C). Figure (4.8) shows different amounts of the adsorbent related to sulfate removal efficiency. The sulfate removal efficiency grew because of the increased adsorbent dosage from 0.05 to 0.5 g/50 mL with the fixing of other parameters. The result described above was expected according to the fact, that, when the adsorbent dosage in a solution rises, subsequently more active sites are available ***(Vijayaraghavan and Yun, 2008)***.

The sulfate amount in the solution and its binding to the adsorbent remained fixed despite the increased adsorbent dosage until the maximal rate of sulfate removal was achieved with the adsorbent dosage of 0.5 g ***(Palaniswamy, R. Veluchamy, 2017)***.

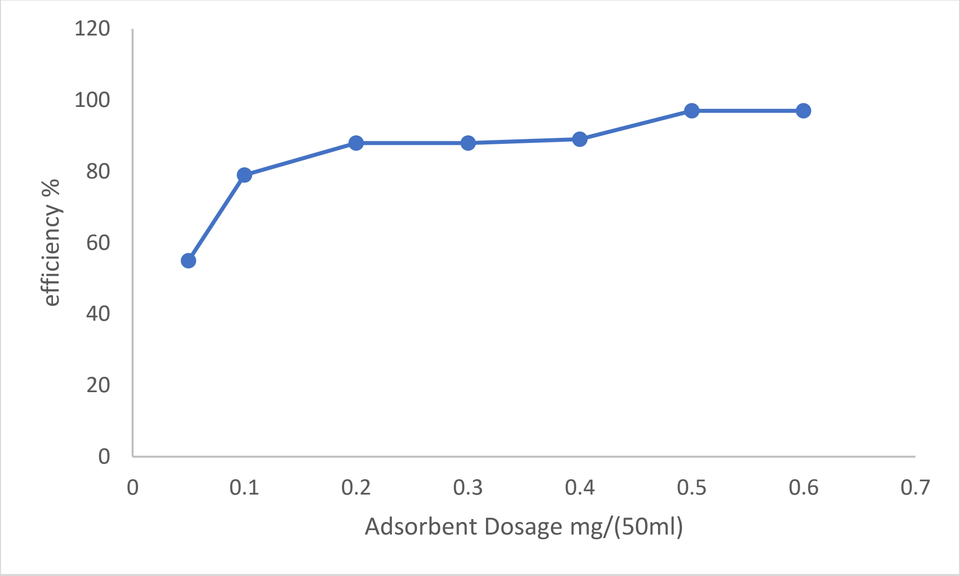


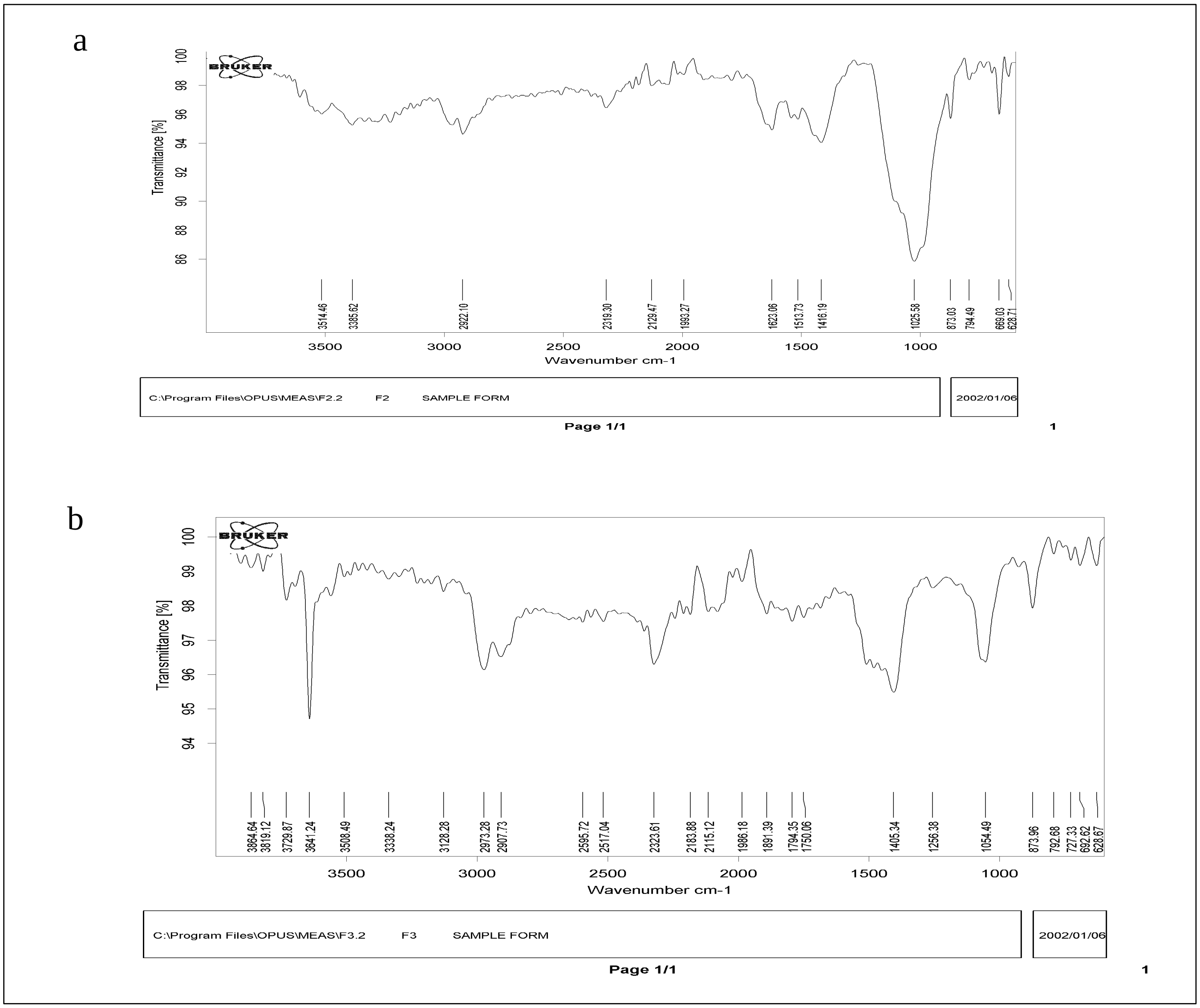
Figure 4.8 sulfate removal efficiency effected by the amounts of adsorbents dosage.

4.4.2 Adsorbent Characterization before and after Adsorption

1) Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra of bentonite, sludge, limestone, and SBL before and after the adsorption process are displayed in Figures (4.9), respectively. The samples' spectra reveal the existence of many functional groups. These spectra showed that following the alteration process, there was a decrease, broadening, disappearance, or development of new peaks. The effect of alteration was evident by the shifts in the spectra. The noticeable bands upon modification demonstrate the produced adsorbents' ability to effectively remove sulfate. The silicate characteristic bands, which are closely linked to the stretching vibrations of Si–O, are identified by the peaks seen at 1042.89 cm^{-1}, 1036.41 cm^{-1}, and 1029.58 cm^{-1}. These peaks coincide with those reported by Aroke et al. (2013) at 1150 cm^{-1}, 1060 cm^{-1}, and 1030 cm^{-1}.

The Si–O deformation bands are responsible for the peaks at 1036.41 cm^{-1} and 1007.92 cm^{-1}, which are more in line with the values published by Georges–IVO 2005 at 1033, 1032, and 1007 cm^{-1}. (IVO–Georges, 2). According to Bhasker and Gopalakrishnarao (2010), the peaks 912–937 cm^{-1} were attributed to Al–OH bending vibration of kaolin clay type, and they are more similar to the 914–936 cm^{-1} range. The Si–O stretching of the bentonite clay type was attributed to the peaks at 799.10 cm^{-1}, 757.78 cm^{-1}, and 797.78 cm^{-1}. Thes matched the ones noted by Georges–IVO 2 at 796 cm^{-1}, 754 cm^{-1}, and 695 cm^{-1}.



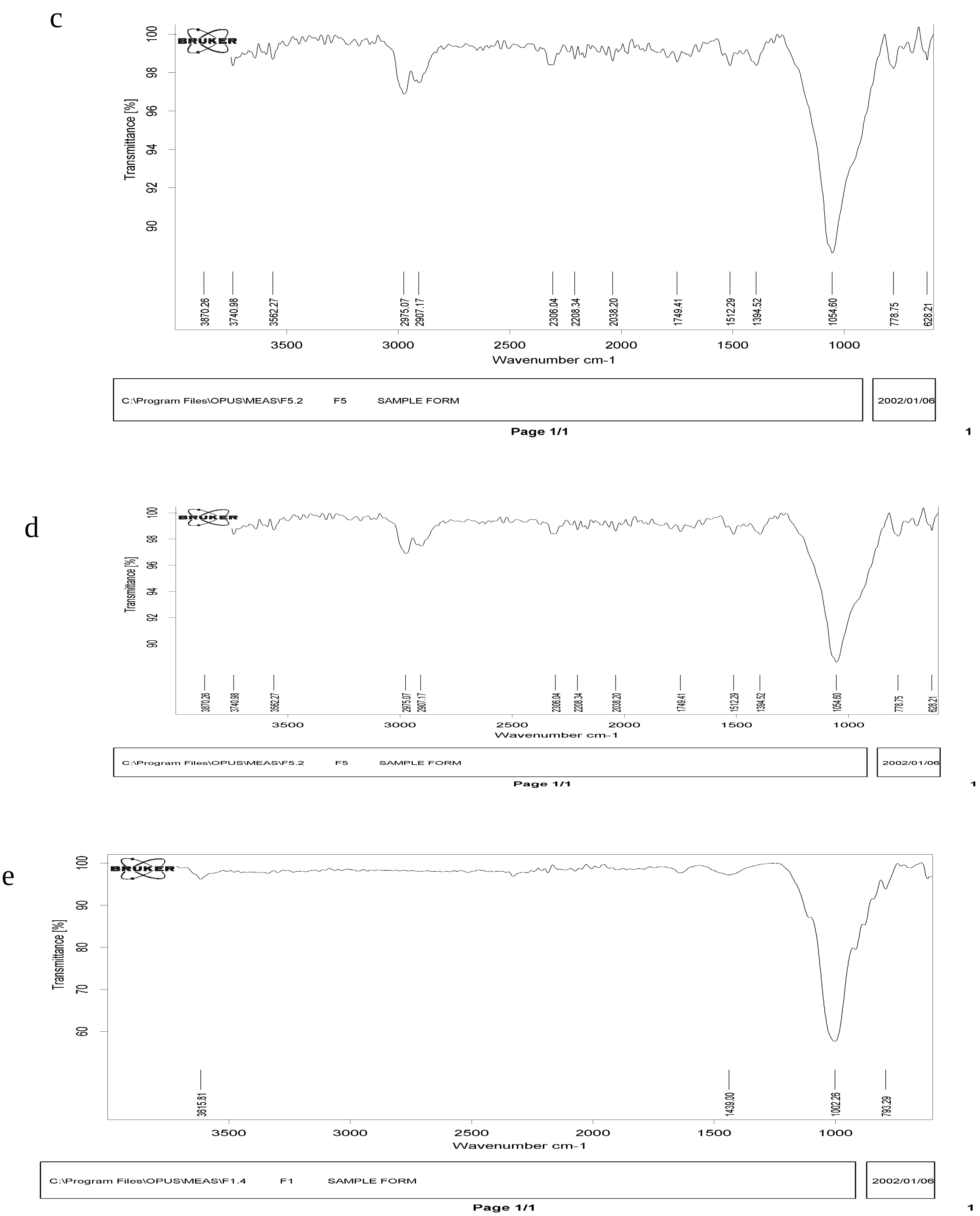
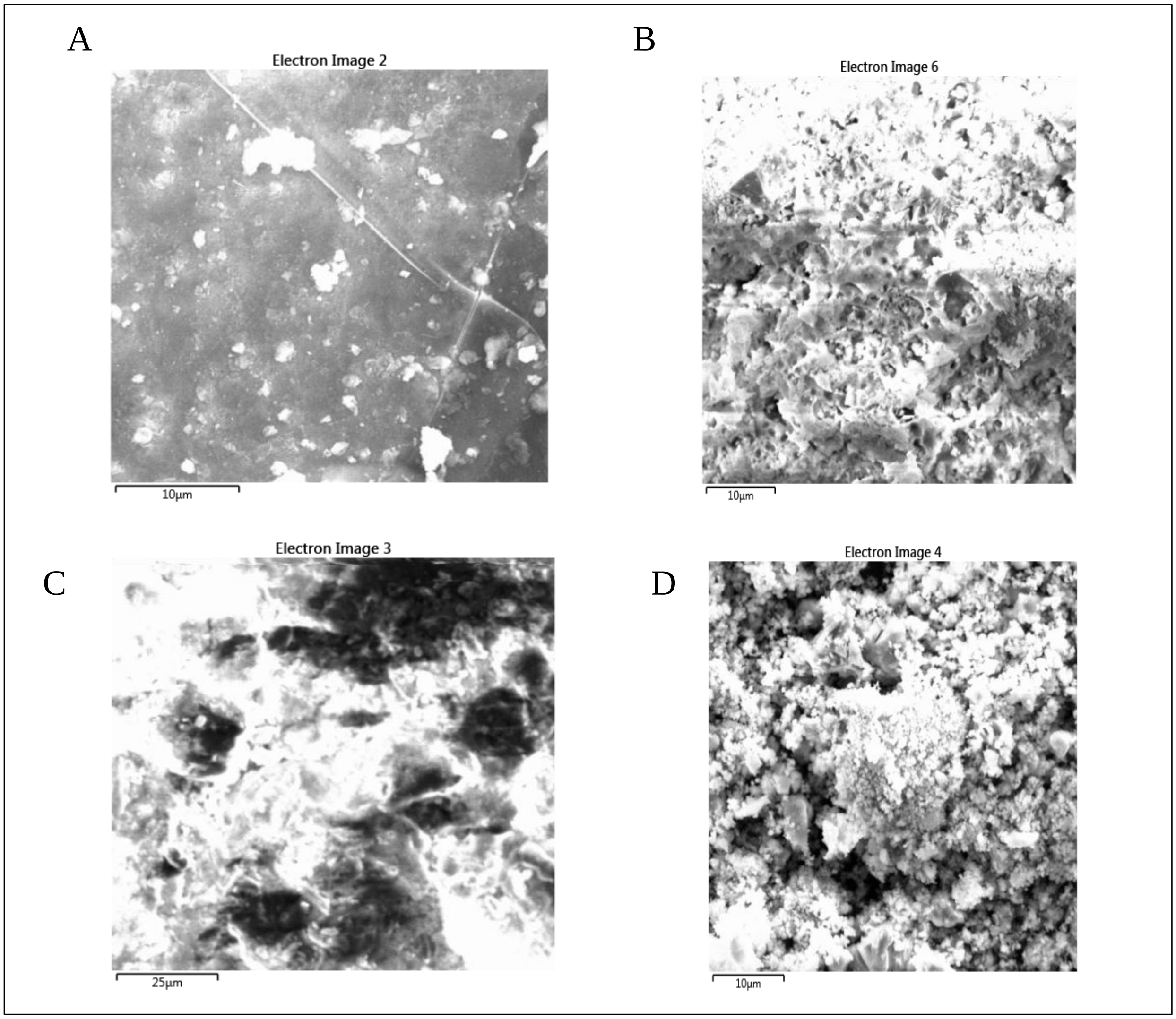


Figure 4.9 spectra of (a) sludge, (b) limestone, (c) bentonite, (d) SBL before, (e) and SBL after sulfate adsorption.

Surface morphology of SBL composite is shown in Figures (4.11). possess rough surfaces, edges, and sharp corners in addition to a compact and regular pore structure. SBL's huge surface area and structure. Its structure is typically lamellar.



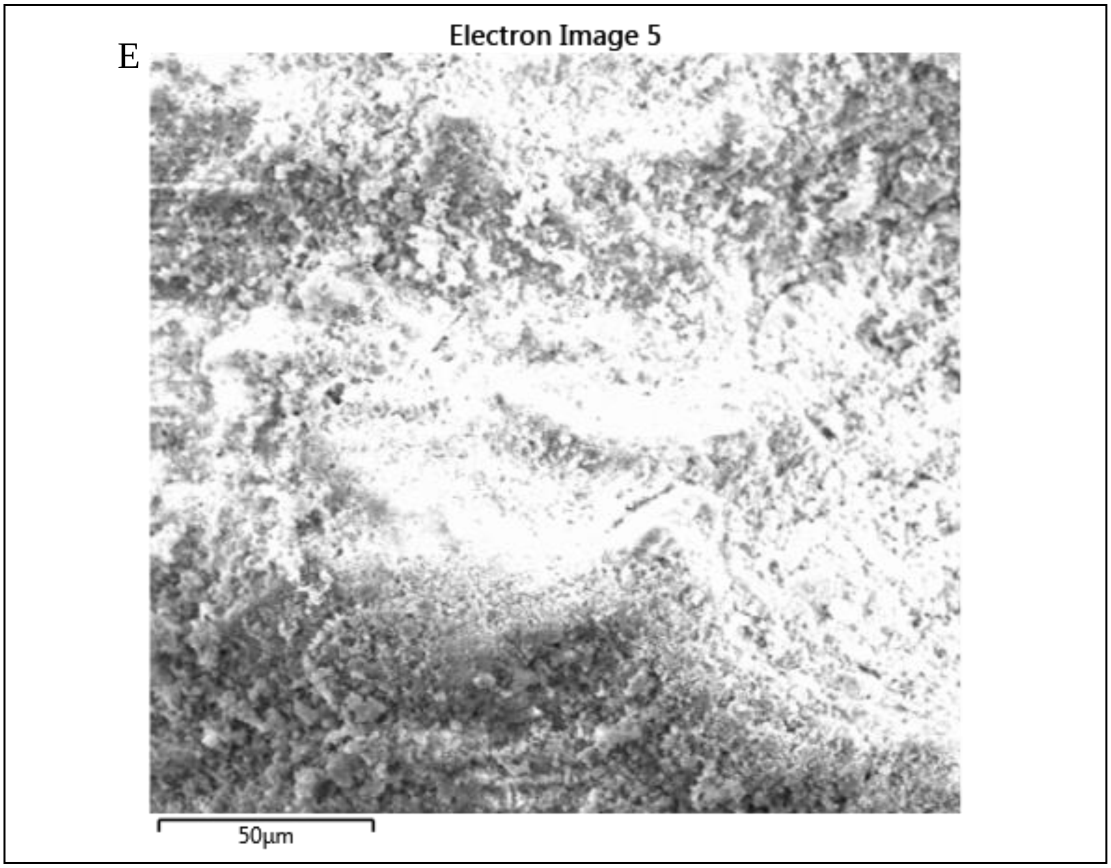
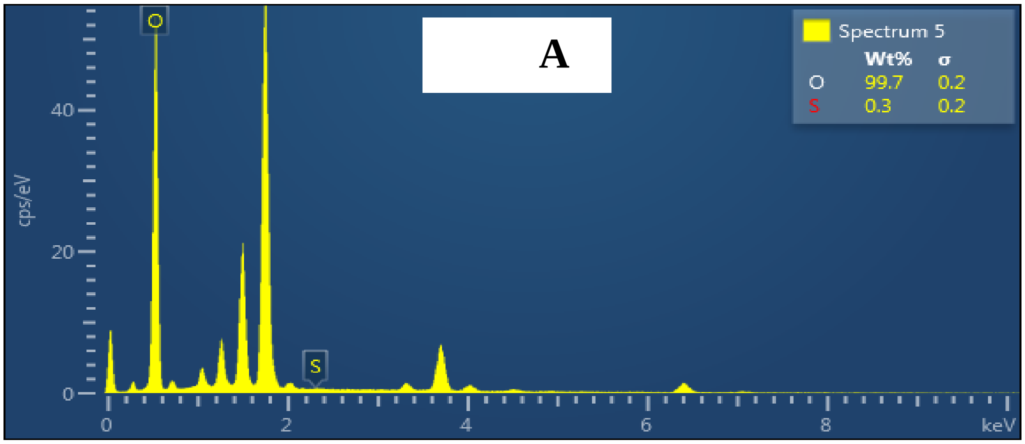


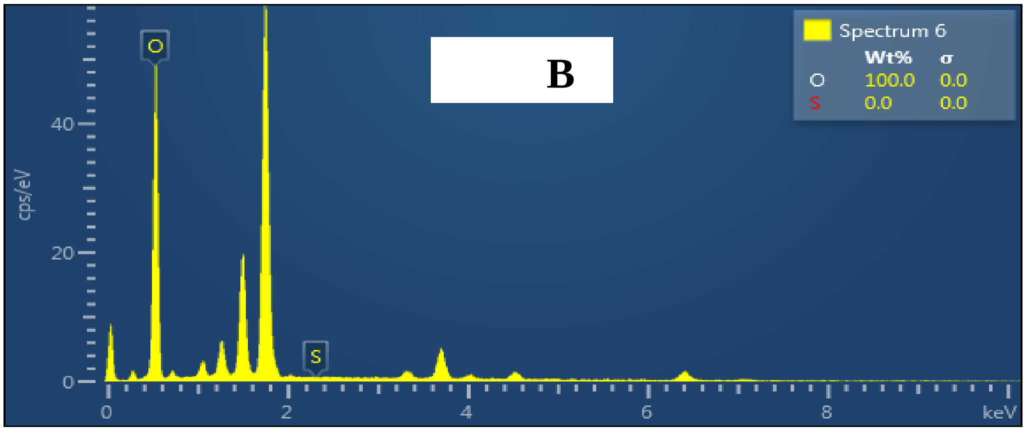
Figure 4.10 Images SEM for the: (A) sludge, (B) limestone, (C) bentonite, and ((D) SBL composite before adsorption and (E) SBL composite After adsorption).

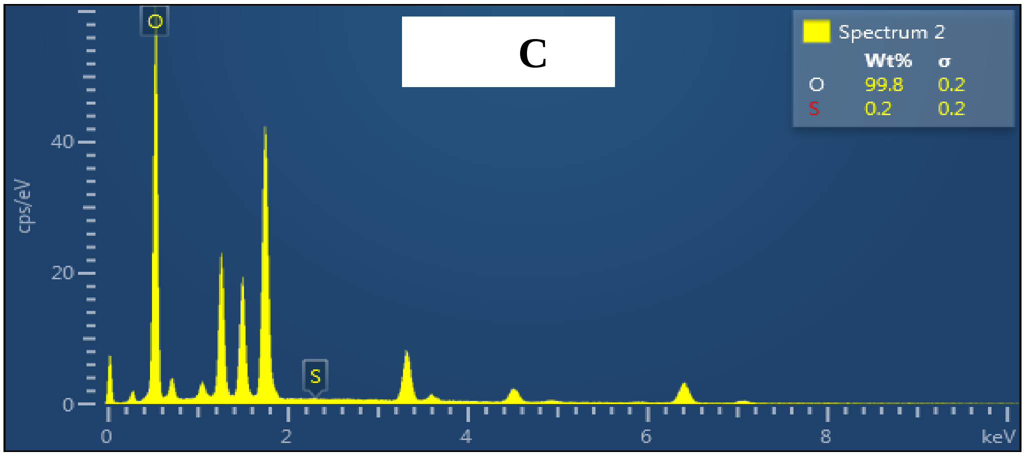
After the sulfate adsorption, as shown in Figures (4.10), the surface of the SBL composite has the similar morphology as SBL and increase dimeter of microparticle.

3) Energy Dispersive Spectroscopy (EDS)

From the Figures (4.11), it can saw that the SBL composite contain from O, S by the EDS spectrum. After modification, the contents of O and S increase dramatically, proving the successful activate of SBL by using physical method of synthesis.


A
Spectrum 5
Wt% σ
O 99.7 0.2
S 0.3 0.2
O
S
cps/eV
0
20
40
0
2
4
6
8
keV


B
Spectrum 6
Wt% σ
O 100.0 0.0
S 0.0 0.0
O
S
cps/eV
0
20
40
0
2
4
6
8
keV


C
Spectrum 2
Wt% σ
O 99.8 0.2
S 0.2 0.2
O
S
cps/eV
0
20
40
0
2
4
6
8
keV

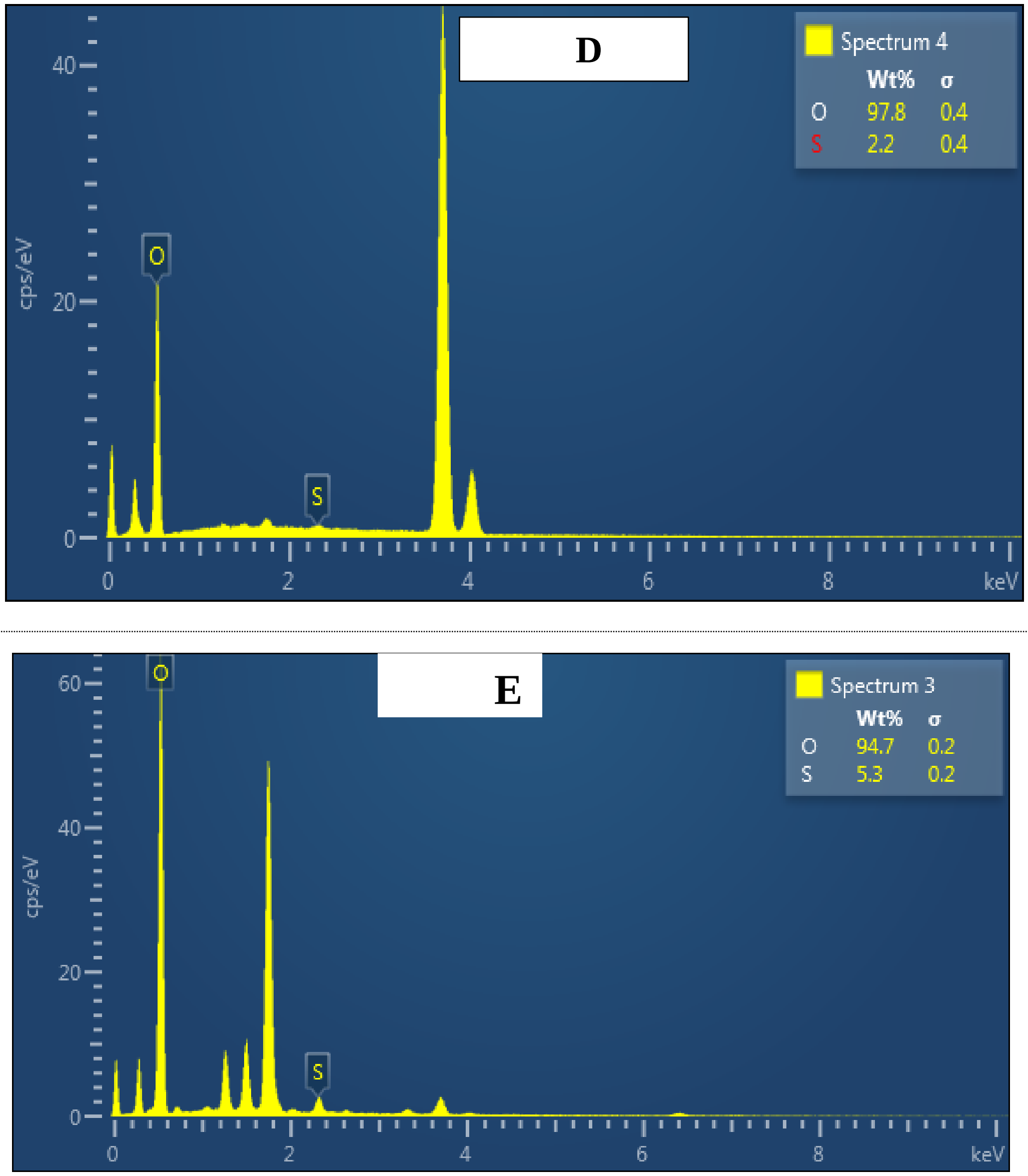


Figure 4.11 EDS spectrum for the: (A) sludge, (B) limestone, (C) bentonite, and ((D) SBL composite before adsorption and (E) SBL composite After adsorption).

From EDS spectrum as shown in Figures (4.11), after the sulfate adsorption, It is suggested that the adsorbent's adsorption impact on the contaminant is increasing as their content on the adsorbent significantly increases.

4.5 Adsorption Isotherm

The isotherms Langmuir, Freundlich model presented in Eq. 2.2, 2.3, were calculated respectively corresponded with the experimental data to check the most fitted isotherm to these data. Table 4.1 and Figure 4.12 show the results obtained for SO4-2adsorption onto the adsorbent (coefficient of determination (***R^2***) and isotherm parameters) at (25^{o}C, pH =6, 0.1 g per 50 mL, Time 1 h and 200 rpm). The parameter and model with the best fit are chosen using the R^2. The degree of concordance between the experimental and anticipated values by the proposed models is shown by the R^2. R^2 near 1 indicates that the model has a high degree of concordance between the actual and predicted values, with a range of 0 to 1.

The R^2 values for the two models were compared in this study. Due to its larger R^2 when compared to the other isotherm models, the Freundlich model generated better predictions for the adsorption processes. According to Figure (4.12), the isotherms' overall trend for sulfate is favorable.

Table 4.1Adsorption isotherm models SO4-2 on adsorbent; 25oC, pH =6, dosage = 0.1 g/50 mL, Time= 1 h and agitation speed = 200 rpm.

Isotherm	Equation №	Calculated parameters	SO4-2
Langmuir	2.2	q_{max} *(mg/g)*	44.4
		b (L/mg)	0.93
		R^2	0.4705
Freundlich	2.3	K_F (mg/g)	17.1
		n	1.55
		R^2	0.9798

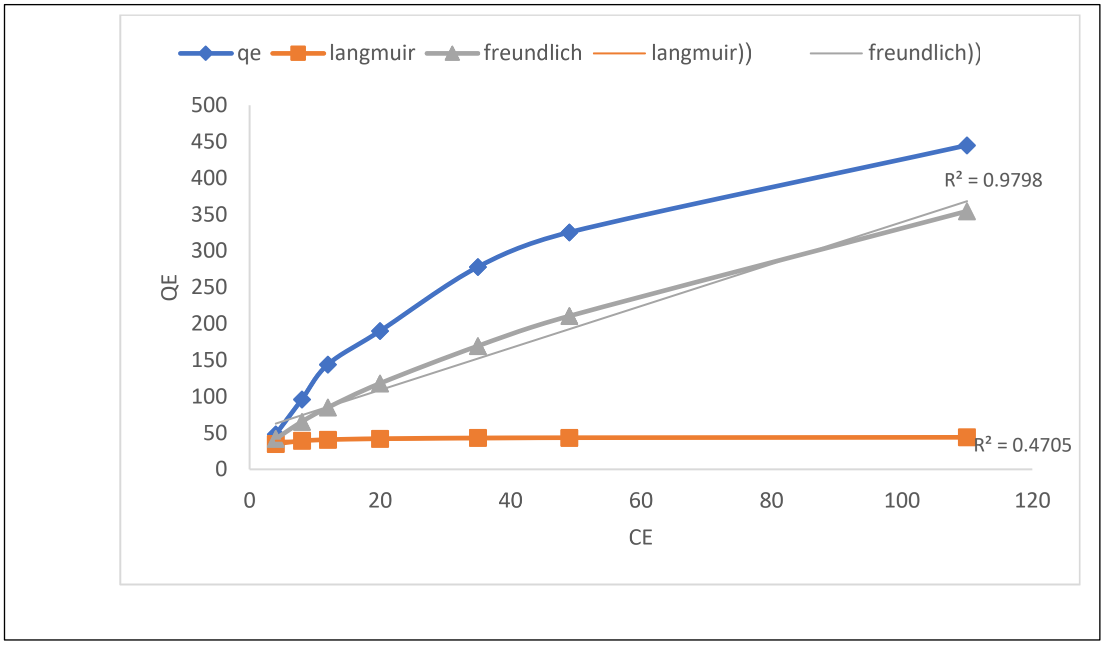


Figure 4.12 Adsorption isotherm models SO4-2 on the adsorbent at 25oC, pH =6, dosage = 0.1 g/50 mL, contact time = 1 h and agitation speed =200 rpm.

4.6 Adsorption Kinetics

The Equations 2.9 and 2.10, which were used to test the experimental results, provide pseudo-first-order and pseudo-second-order kinetics models, respectively, that can be used to compute the mechanism governing sulfate adsorption on the adsorbent as a chemical or physical process (Bulut and Tez, 2007). Nonlinear regression analysis was used to look at the nonlinear forms of the kinetics adsorption models. The pseudo-second-order and pseudo-first-order values for the SO4-2 adsorption on the adsorbent, as determined by experiment, are displayed in Figure (4.13) and Table (4.2) at (200 rpm, 0.1 g/50 mL, C_o = 900 mg/L, 25°C, contact time = 1 h and pH =6).

The values of determination coefficient (R^2) for the adsorption process of sulfate were greater than (Table (4.2)) if the pseudo-second-order kinetics model was employed and these values were higher than the values obtained from application the pseudo-first-order kinetics model. Consequently, the sulfate adsorption process can be thought of as a chemisorption process because it adheres to the pseudo-second-order kinetics model ***(Bulut and Tez, 2007)***.

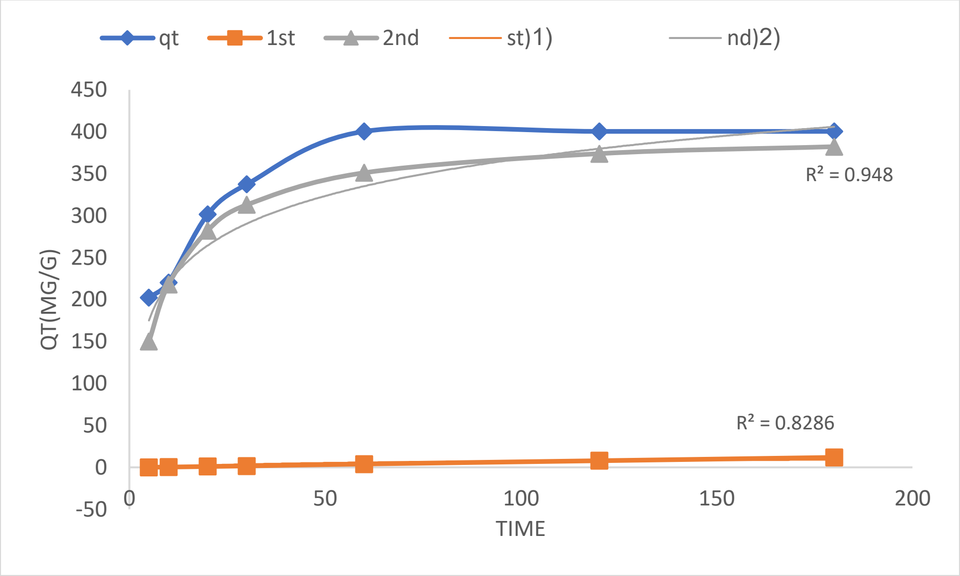


Figure 4.13 Adsorption kinetics models calculated using nonlinear regression analysis for So$_4^{-2}$ (200 rpm, 0.1 g/50 mL, Co = 900 mg/L, 25oC and contact time = 1 h and pH=6).

Table 4.2 Adsorption kinetics models coefficients for So4-2 on adsorbent.

Kinetic model	Equation №	Calculated parameters	SO4-2
Pseudo-first-order	2.9	$k_1(min^{-1})$	0.000167
		$q_e(mg/g)$	181.27
		R^2	0.8286
Pseudo-second-order	2.10	k_2 (g/mg.min)	0.0003
		q_e (mg/g)	400
		R^2	0.9480
Experimental		q_e	400.5

4.7 Experiments at Continuous System

4.7.1 The Flow Rate

The contact time between solution of the contaminant and the particles is effected by the liquid flow rate parameter, so according to that, this parameter is considered to be as a major parameter through adsorption column designing ***(Sulaymon et al., 2013)***. The system removal efficiency is lowered when the residence time is reduced, this reducing is caused by an increasing of solution volume flow in the same condition. So, this causing that the contaminant concentration becomes higher than usual in the effluent ***(Nelson et al., 2017)***.

Figures (4.14) show the results of adsorption SO4-2, effecting by different flow rate of the liquid (6, 9, 12 and 15 L/h) with constant (pH=6, C_o=900 mg/L and bed height=10 cm).

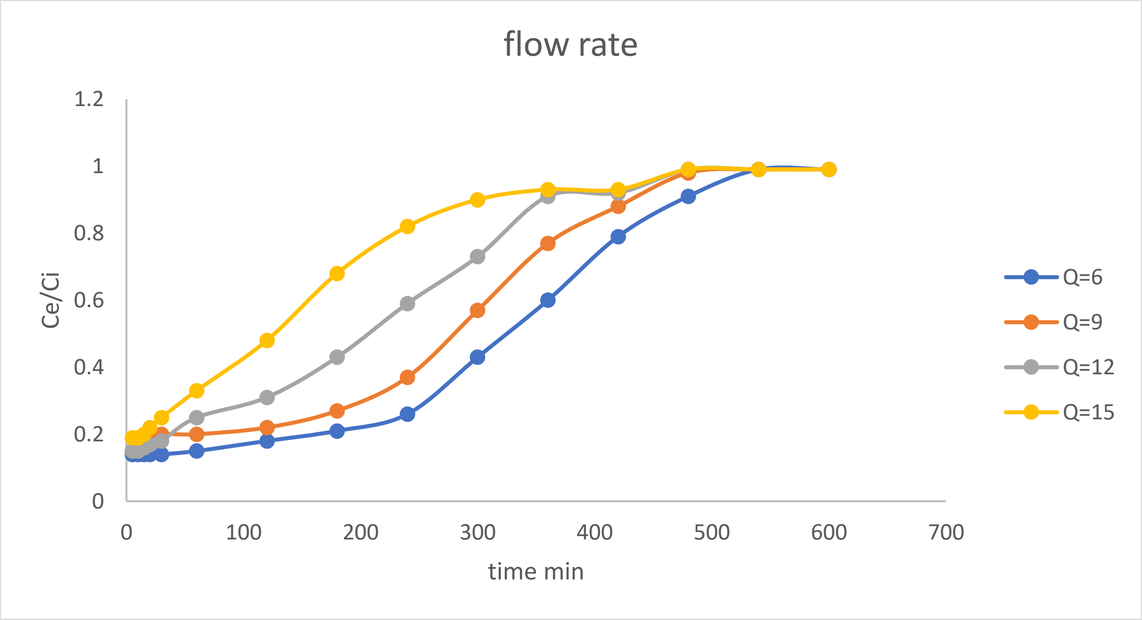


Figure 4.14 sulfate adsorption breakthrough curves at different flow rate (L/h) with constant of (pH=6, Co=900 mg/L and bed height=10 cm).

It is obvious that the increasing flow rate of liquid resulted in increasing the contaminant concentration in the solution. This behavior is related to contact time term. Adsorption time is reduced when the contact time is shorter that leads to increasing the concentration of the pollutant in the aqueous solution. The obtaining results by ***(Naja and Volesky 2006; Han et al. 2006)*** were agreed with the results above.

4.7.2 Effect of pH

In order to study the pH effect on the sulfate adsorption capacity in the continuous system, different values of the pH of the solution were used, and the breakthrough profile for these experiments with constant of (Q=6 L/h, C_o =900 mg/L and bed height = 10 cm) were shown in Figure (4.15).

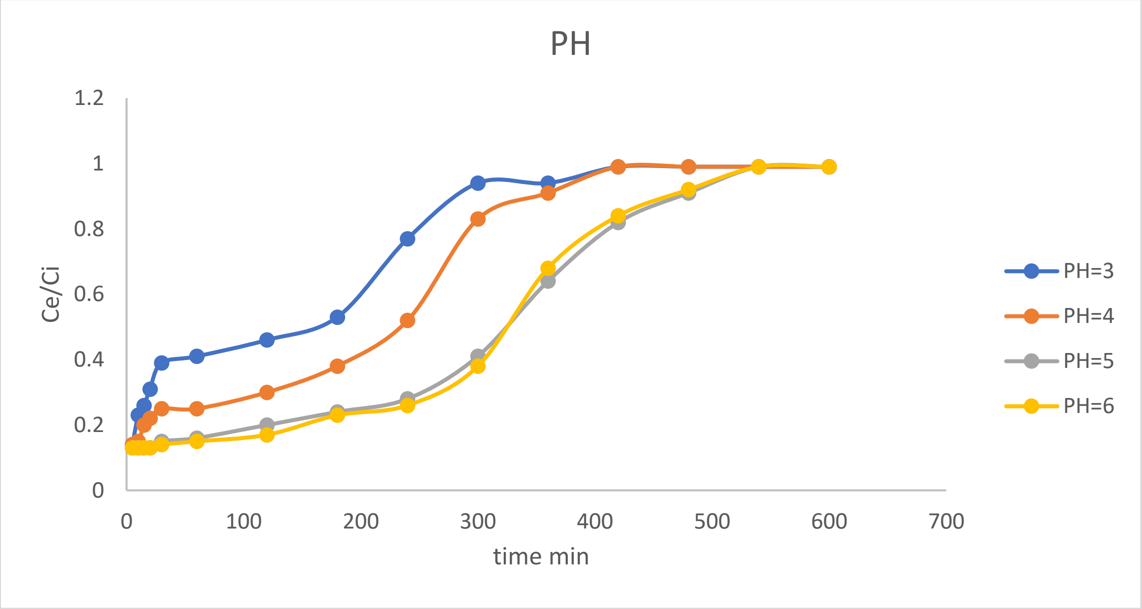


Figure 4.15 sulfate adsorption breakthrough curves at different pH with constant of (Q=6 L/h, Co =900 mg/L and bed height = 10 cm).

It is obvious in these Figures that the time required for reaching equilibrium is increased with increasing the value of the pH, which means that the time of the diffusion rate to reach saturation is increased also. As mentioned in the batch experiment, it is important to identified the value of adsorbent zero-point charge (pH_{ZPC}) for a good understanding of the pH effect on the mechanism of the adsorption. Generally, the anions, and cations adsorption are favored at $pH < pH_{ZPC}$, and $pH > pH_{ZPC}$ respectively ***(Hong et al. 2016)***.

Because of the H_3O^+ ions high concentration, the surface charge becomes positive at low pH. Therefore, at low pH sorption effectiveness becomes very low because of competition for binding sites with available protons is increased (because of higher number of protons). Also, these result agreed with ***(Srivastava et al., 2006; Esmail 2016)***.

4.7.3 Initial Concentration Effect

Adsorption of in SO4-2 different initial concentration (100, 200, 300, 400, 500, 700 and 900 mg/L) with constant of (Q=6 L/h, pH=6, and bed height=10 cm) are shown in Figure (4.16).

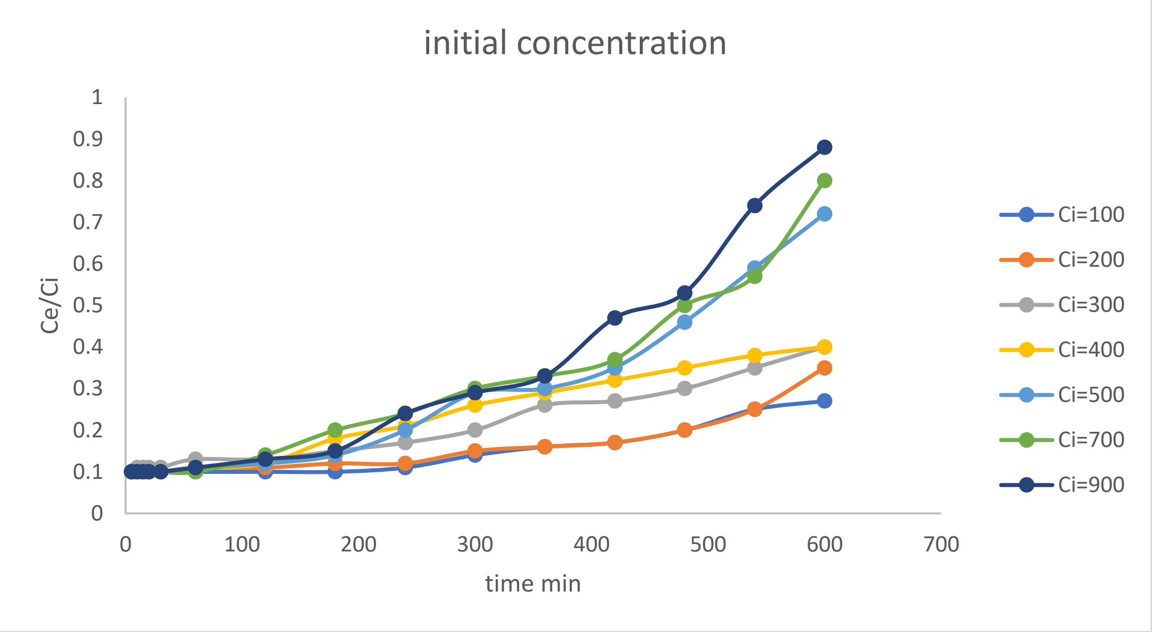


Figure 4.16 sulfate adsorption breakthrough curves at different initial concentrations (mg) with constant of (Q= 6 L/h, pH=6 and bed height=10 cm)

From these Figures, it is clear that the contaminant concentration in the effluent increase than usual at increasing the concentration in the feed from 100 to 900 mg/L because of increasing of the concentration gradient which controlled the diffusion rate ***(Patel 2019)***. Figure (4.16) show that the breakthrough curves were steeper and the breakpoint time was lower when increasing initial concentration.

The time of the diffusion rate for reaching saturation has to be longer in low initial concentration of the pollutant, which means that the initial concentration was related to the breakpoint inversely. The explaining of this behavior, that the high difference, which is referred to the adsorption driving force, between the solute concentration and the available binding sites on the adsorbent surface was caused an increasing in solute mass transfer rate for attaching a free sites on the adsorbent ***(Li, P. et al. 2001)***. Moreover, at initial concentration, the breakthrough curve slop and the bed saturation are higher and faster respectively ***(Al-Baidhany and Al-Salihy, 2016)***. The obtaining conclusion by ***(Naja and Volesky 2006)*** were agreed with the results above.

4.7.4 Bed Height Effect

The effect of the bed height on the adsorption process for SO4-2was shown in Figure (4.17) with using different heights (5, 10, 15 and 20 cm) and constant value of (Q=6 L/h, pH=6, and C_o =900 mg/L).

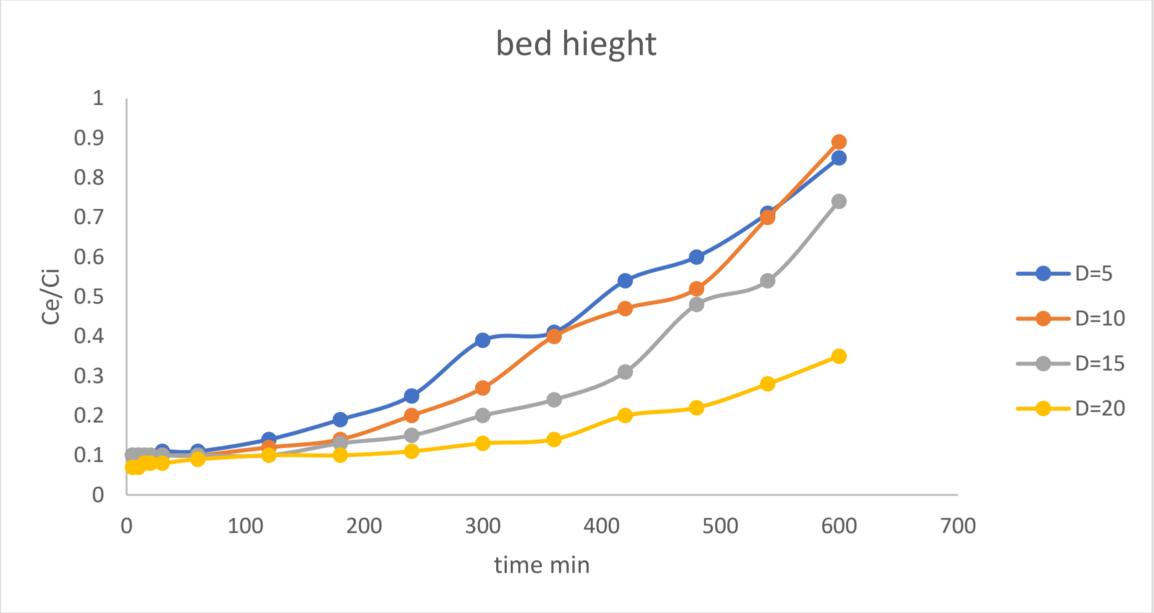


Figure 4.17 sulfate adsorption breakthrough curves at different bed heights (cm) with constant of (Q=6 L/h, pH=6 and Co =900 mg/L).

It is obvious in the figure that the time required for reaching equilibrium is increased with increasing bed height. This behavior can be expressed as the contact time between the adsorbent particles and the contaminants become high when there is an increasing in the bed height. The ratio of adsorbate concentration in the effluent with low bed height can be increase very quickly than that with high bed height, so a less time is required for saturation a low bed height. In addition, the adsorption sites or surface area is increased as the bed height increase and this will improve the process of the adsorption. The obtaining results by ***(Sivalingam et al., 2011; Al-Musawi, 2012;)*** were agreed with the results above.

4.7.5 Multi cycle bed column.

The outcomes are displayed in Figure (4.18), which illustrates how effective CFB is at removing SO4-2 ions. Consequently, the CBC produces better results and lasts for over five hours before the adsorbent runs out.

Compared to conventional fluidized beds, a CBC circulates solid particles between the riser and the downer at higher velocities, improving phase-to-phase contacting efficiency. Additionally, CBCs can achieve higher mass transfer, making them a more desirable reactor type.

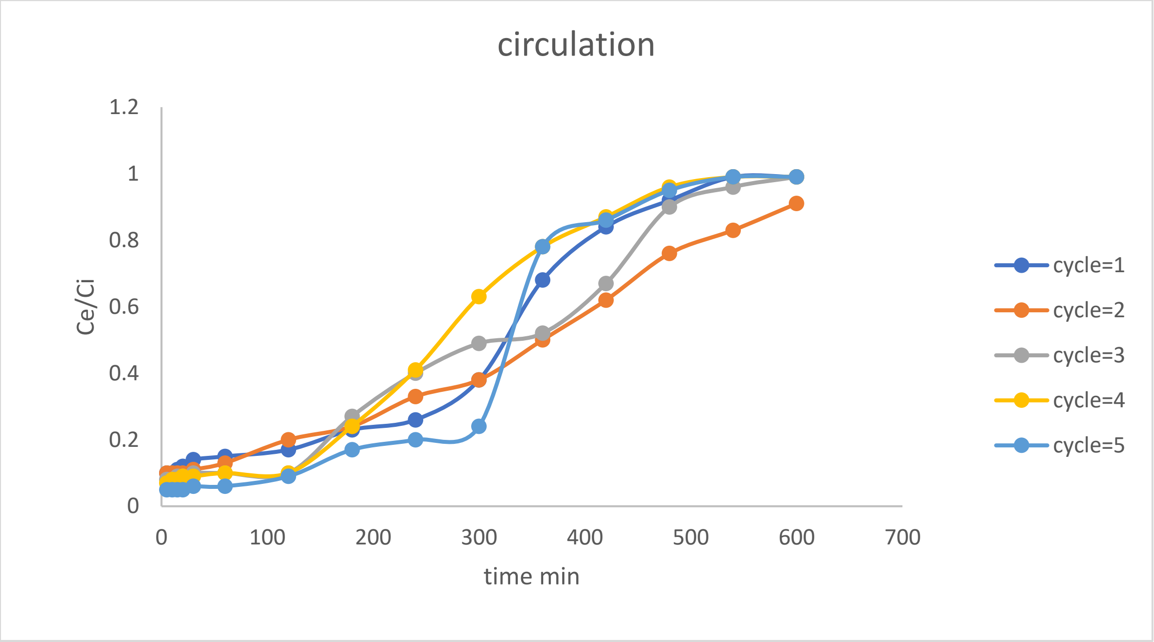


Figure 4.18 Sulfate adsorption breakthrough curves at different cycle with constant of (Q=6 L/h, pH=6, bed height=20 cm and Co =900mg/L).

From these Figure, it is clear that it was used five different circle to retreating the water more times. The result shows, the efficiency increase for 95% and be constant for 120 minutes, the 180 minutes fallowed the efficiency decrease for 80%, but still acceptable by using circle number (5). After 300 minutes the removal efficiency decreases for 20%, rezone of that the adsorbent be saturated with contaminants (Atta et al., 2009).

4.8 Data Analysis

Following the performance evaluation, the next step entailed the presentation of the final regression equation. This equation was derived by incorporating all the coefficients and the intercept obtained through the regression analysis, effectively serving as a mathematical representation of the predictive model.

This equation (appendix C) can be utilized to predict the 'Time (min)' based on the values of the independent variables in the dataset. In the final step of the procedure, visual representations were made to shortly illustrate the results derived from the analysis. This included a scatter plot representing the actual versus predicted 'Time (min)' values and a heatmap to design the correlations between the different features in the dataset, with smaller annotation sizes to facilitate readability. As shown in figure below.

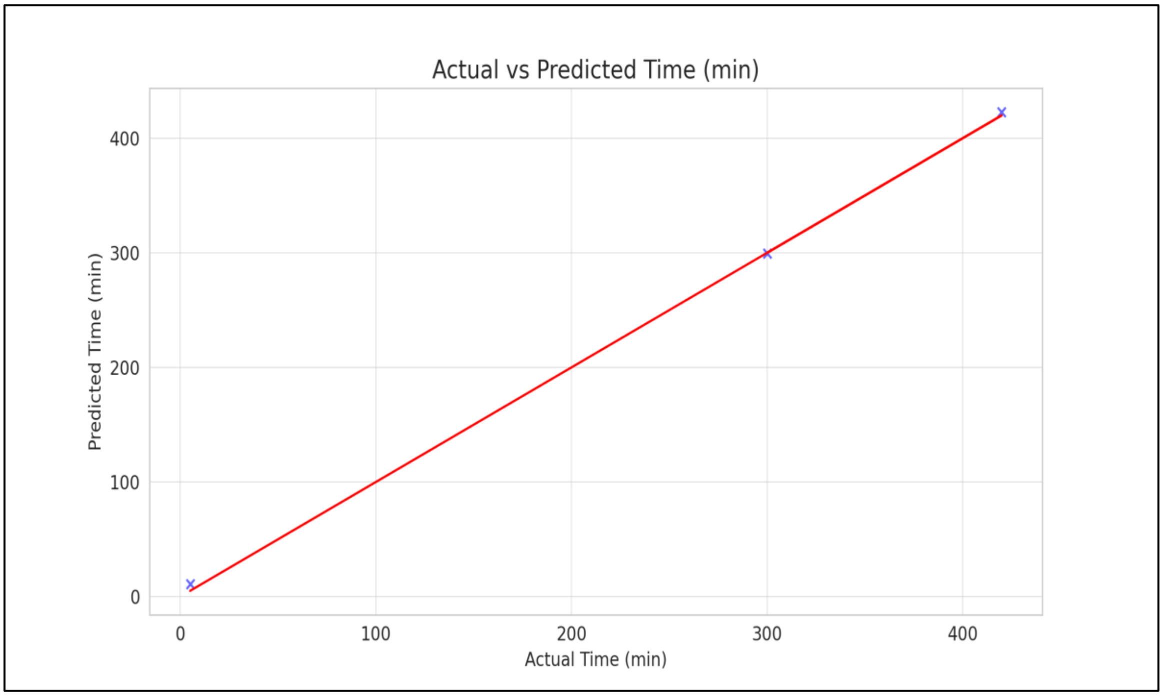


Figure 4.19 Visual Representations of data.

Upon completion of the regression model development, a series of insights were garnered. The R-squared value of approximately 0.9995 denotes a high degree of accuracy in the predictive model, explaining about 99.95% of the variance in the 'Time (min)' variable. This indicates a robust model with a significant predictive capability.

The performance metrics further substantiate the model's reliability. The values obtained were as follows:

- Mean Absolute Error (MAE): 3.1786
- Mean Squared Error (MSE): 15.2105
- Root Mean Squared Error (RMSE): 3.9001

These metrics affirm the model's capability to make predictions with a minimal margin of error. However, it is essential to note that while the model exhibits high accuracy, a meticulous examination of the individual coefficients is necessary to interpret the relationships between different variables accurately and to harness the full potential of the predictive model.

Moreover, the visual representations crafted facilitate an intuitive understanding of the model's performance and the relationships between different variables, serving as a pivotal tool in the presentation and interpretation of the results.

Chapter Five: Conclusions and Recommendations

5.1 Conclusions

- When compared to adsorption utilizing alternative adsorbents, such as inexpensive local adsorbent, the novel composite adsorbent (SBL) that was developed for adsorption of sulfate demonstrated a high capacity for adsorption.
- The characterization of the new composite adsorbent (SEM/EDS, FTIR and XRD) confirm successfully coating the low-cost local adsorbent by the nanoparticles that increasing the surface area 3 times of the novel composite adsorbent than the low-cost local adsorbent.
- Sulfate higher removal efficiency in batch test were achieved at best values of (contact time =1 h, pH 6, agitation speed 250 rpm, initial concentration 900 mg/L and dosage 0.5 g/50 mL) respectively was 96%.
- The sulfate adsorption process follows the pseudo-second-order kinetics model that indicating the mechanism of this process to be a chemisorption. Also, when compared to the other isotherm models, the Freundlich model yielded superior predictions for the adsorption processes because of its greater R^2 and lower SSE.
- From the results of the continuous system, the optimum values of parameters were (Q=6 L/h, pH=6, C_o=900 mg/L bed=20 cm, and circle number = 5) respectively was 95%.

5.2 Recommendations

- Comparison the removal efficiency of the low-cost adsorbent prepared by physical activation of another agriculture waste material, with the removal efficiency of the composite adsorbent which prepared in the present study.

- Comparison the cost of the low-cost local adsorbent prepared by present study, with the cost of the adsorbent which prepared by same method with another materials.

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Appendices

Appendix (A)

(Data for Batch Experiments)

Table A.1: sulfate adsorption Efficiency % by sludge.

sludge	Ci	Cf	% removal
	900	387	57

Table A.2: sulfate adsorption Efficiency % by (BL) composite with different mass ratios with initial condition at (T=25C^o, dosage= 0.1 g/50 mL, pH = 7.5, SO4-2 concentration= 900 mg/L, adsorption time =1h, and agitation speed =200 rpm).

Composite	NO	Mass ratio B+L	Efficiency %
Bentonite, limestone composites	1	1:1	54
	2	1:2	81
	3	1:3	68
	4	1:4	63
	5	2:1	72
	6	3:1	31
	7	4:1	49

Table A.3: sulfate adsorption Efficiency % by (BS) composite with different mass ratios with initial condition at (T=25Cº, dosage= 0.1 g/50 mL, pH = 7.5, SO4-2 concentration= 900 mg/L, adsorption time =1h, and agitation speed =200 rpm).

Composite	NO	Mass ratio B+S	Efficiency%
Bentonite, sludge composites	1	1:1	86
	2	1:2	45
	3	1:3	55
	4	1:4	59
	5	2:1	54
	6	3:1	36
	7	4:1	40

Table A.4: sulfate adsorption Efficiency % by (SBL) composite with different mass ratios with initial condition at (T=25Cº, dosage= 0.1 g/50 mL, pH = 7.5, SO4-2 concentration= 900 mg/L, adsorption time =1h, and agitation speed =200 rpm).

composite	NO	Mass ratio B+L+S	Efficiency %
Bentonite, limestone, sludge composites	1	1:1:4	67
	2	1:1:3	71
	3	1:1:2	89
	4	1:4:1	55

	5	1:3:1	45
	6	1:2:1	77
	7	4:1:1	65
	8	3:1:1	72
	9	2:1:1	45
	10	1:1:1	76

Table A.5: sulfate efficiency removal on the adsorbent related to contact time (pH=7.5; agitation speed= 200 rpm; dose= 0.1 g/50 mL; C_o=900 mg/L; T= 25◦C).

NO	Time (min)	Efficiency %
1	5	45
2	10	49
3	20	67
4	30	75
5	60	86
6	120	84
7	180	85

Table A.6: sulfate removal efficiency effected by initial pH (dose= 0.1 g/50 mL; C_o= 900 mg/L; contact time=1 h; T= 25°C; agitation speed= 200 rpm).

NO	PH	Efficiency %

1	2	37
2	4	68
3	6	80
4	9	71
5	11	64

Table A.7: sulfate removal efficiency effected by initial concentration (contact time=1 h; agitation speed= 200 rpm; dose= 0.1 g/50 mL; pH=6; T= 25◦C).

NO	Initial concentration(mg/L)	Efficiency %
1	100	92
2	200	87
3	300	79
4	400	69
5	500	58
6	700	36
7	1000	23

Table A.8: sulfate removal efficiency effected by agitation speed (contact time=1 h; pH=6; C_o=900 mg/L; dose= 0.1 g/50 mL; T= 25◦C).

NO	Agitation speed (rpm)	Efficiency %
1	50	34

2	100	51
3	150	68
4	200	85
5	250	88

Table A.9: sulfate removal efficiency effected by the amounts of adsorbents dosage (contact time=1 h; agitation speed= 250 rpm; pH=6; C_o=900 mg/L; T= 25◦C).

NO	adsorbent dosage (mg/50ml)	Efficiency %
1	0.05	55
2	0.1	79
3	0.2	84
4	0.3	84
5	0.4	85
6	0.5	87
7	0.6	87

Appendix (B)

(Column Bed System)

Table B.1: Effect of flow rate of solution at temperature 25°C, pH =6, bed height = 10 cm, initial concentration of SO4-2 = 900 mg/L.

Time (min)	Efficiency %			
	Q=6	Q=9	Q=12	Q=15
5.00	86	85	85	81
10.00	86	84	85	81
15.00	86	84	84	80
20.00	86	82	83	78
30.00	86	80	82	75
60.00	85	80	75	67
120.00	82	78	69	52
180.00	79	73	57	32
240.00	74	63	41	18
300.00	57	43	27	10
360.00	40	23	9	7
420.00	21	12	8	7
480.00	9	2	1	1
540.00	1	1	1	1
600.00	1	1	1	1

Table B.2: Effect of pH of solution at temperature 25°C, bed height =10 cm, initial concentration of SO4-2 = 900 mg/L, and flow rate = 6 L/h.

Time (min)	Efficiency %			
	PH= 3	PH=4	PH=5	PH=6
5.00	86	86	87	87
10.00	77	85	87	87
15.00	74	80	87	87
20.00	69	78	87	87
30.00	61	75	85	86

60.00	59	75	84	85
120.00	54	70	80	83
180.00	47	62	76	77
240.00	23	48	72	74
300.00	6	17	59	62
360.00	6	9	36	32
420.00	1	1	18	16
480.00	1	1	9	8
540.00	1	1	1	1
600.00	1	1	1	1

Table B.3: Effect of initial concentration of SO4-2, temperature 25°C, bed height =10 cm, flow rate = 6 L/h and pH=6.

Time (min)	Efficiency %						
	Ci=100 mg/L	Ci=200 mg/L	Ci=300 mg/L	Ci=400 mg/L	Ci=500 mg/L	Ci=700 mg/L	Ci=900 mg/L
5.00	90	90	90	90	90	90	90
10.00	90	90	89	90	90	90	90
15.00	90	90	89	90	90	90	90
20.00	90	90	89	90	90	90	90
30.00	90	90	89	90	90	90	90
60.00	90	89	87	89	89	90	89
120.00	90	89	87	88	88	86	87
180.00	90	88	85	82	86	80	85
240.00	89	88	83	79	80	76	76
300.00	86	85	80	74	71	70	71
360.00	84	84	74	71	70	67	67
420.00	83	83	73	68	65	63	63
480.00	80	80	70	65	64	60	57
540.00	75	75	65	62	61	57	47
600.00	73	65	60	60	58	46	38

Table B.4: Effect of bed height of the adsorbent at temperature 25°C, flow rate = 6 L/h, pH=6, and initial concentration of SO4-2 = 900 mg/L.

Time (min)	Efficiency %			
	D=5 cm	D=10 cm	D=15 cm	D=20 cm
5.00	90	90	90	93
10.00	90	90	90	93
15.00	90	90	90	92
20.00	90	90	90	92
30.00	89	90	90	92
60.00	89	90	90	91
120.00	86	88	90	90
180.00	81	86	87	90
240.00	75	80	85	89
300.00	61	73	80	87
360.00	59	60	76	86
420.00	46	53	69	80
480.00	40	48	52	78
540.00	29	30	46	72
600.00	15	11	26	65

Table B.5: Effect of Cycling on the adsorbent at temperature 25°C, flow rate = 6 L/h, pH=6, bed height =20 cm, and initial concentration of SO4-2 = 900 mg/L.

Time (min)	Efficiency %				
	Cycle =1	Cycle =2	Cycle =3	Cycle =4	Cycle =5
5.00	90	90	92	93	95
10.00	90	90	92	92	95
15.00	90	90	91	92	95
20.00	90	90	91	91	95
30.00	90	90	90	91	94
60.00	90	90	90	90	94
120.00	88	90	90	90	91
180.00	87	88	90	90	80
240.00	85	87	86	90	63
300.00	85	82	81	77	40
360.00	84	80	78	62	22
420.00	77	78	73	53	18
480.00	73	74	60	41	15
540.00	70	67	54	33	11
600.00	66	59	43	20	7

Appendix (C)

Data Analysis

Time (min) = -102.88822 + Q=6 * (72.85542) + Q=9 * (-70.00920) + Q=12 * (83.82713) + Q=15 * (265.68688) + PH= 3 * (-9.91691) + PH=4 * (10.24442) + PH=5 * (162.24173) + PH=6 * (-38.90318) + Ci=100 * (-8.42446) + Ci=200 * (32.71417) + Ci=300 * (-11.33259) + Ci=400 * (-153.96124) + Ci=500 * (31.22973) + Ci=700 * (96.89520) + Ci=900 * (88.62155) + D=5 cm * (64.23340) + D=10 cm * (131.15156) + D=15 cm * (-30.41896) + D=20 cm * (81.50268) + Cycle =1 * (75.28432) + Cycle =2 * (-52.79919) + Cycle =3 * (47.51196) + Cycle =4 * (53.91323) + Cycle =5 * (-89.59296)

الخلاصة

باستخدام مادة ماصة مركبة جديدة منتجة محليًا، تم التحقيق في إزالة الكبريتات من محلول ملوث في هذا العمل على قسمين العمل المختبري والعمل المقارب لمحطة المعالجة. تم تصنيع هذه المادة الماصة من النفايات والمواد المتوفرة محليا كممتاز محلي منخفض التكلفة عن طريق التنشيط المادي للحمأة والبنتونايت والحجر الجيري) مركب (SBL (بجرعة مثالية تساوي 0.5 جم / 50 مل) وتم فحصها باستخدامFTIR ، SEMو EDSوتحليل حيود الأشعة السينية. (XRD) وBET

تم تحديد القيم المثلى لهذه المعاملات لتكون (60 دقيقة، 250 دورة في الدقيقة، 900 مجم / لتر، 0.5 جم / 50 مل) على التوالي بناءً على كفاءة الإزالة الأعلى التي تم تحقيقها. تم فحص دراسات الامتزاز للمحلول مختبريا من خلال تجارب مكررة بقيم مختلفة من المعاملات مثل وقت التلامس، وسرعة الخلط او التحريك، ودرجة الحموضة، والتركيز الأولية للملوثات، وكمية المادة الممتزه. بينما كانت القيم المثلى لهذه المعاملات هي 6 لتر / ساعة، 6، 900 مجم / لتر، 20 سم، ورقم الدورة الخمسة على التوالي،

في عمل (المستمر) المحطة معالجة مصغره تم دراسة تأثير المعاملات التأليه: كمية التصريف والتركيز الابتدائي للملوث وتأثير الحامضية وسمك طبقة المادة الممتزه ودوران المياه عدة مرات على منحنى اختراق في هذا الجزء من العملي.

أربع موديلان متساوية الحرارة طبقت لفحص نتائج التجارب وكان الموديل الاكثر مطابقه هو موديل (Freundlich) اعتمادا على اعلى (R^2) (0.9798). المعادلات الحركية من الدرجة الاولى والثانية تم تطبيقها على النتائج وكانت أكثر مطابقه مع الموديل الحركي من الدرجة الثانية ومن خلال النتائج يمكن استنتاج ان عمليه الامتزاز هي عمليه كيميائية.

جمهورية العراق

وزارة التعليم العالي و البحث العلمي

جامعة كربلاء

كلية الهندسة

قسم الهندسة المدنية

معالجة الكبريتات المنتجة من مياه الصرف الصحي باستخدام الامتزاز بمواد محلية

رسالة مقدمة الى مجلس كلية الهندسة / جامعة كربلاء وهي جزء من متطلبات نيل درجة الماجستير

في علوم الهندسة المدنية

المؤلف:

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ربيع اول - 1445 ا.م.د معد فاروق تشرين الأول - 2023