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kaolin and their application in removing heavy metals ions from real municipal wastewater.

M.M.EL-Rabiei[a] , A. A. Farghali[b] , Ghada M. AbdEl-hafez [a],N.Shehata[b] , M. M. Faisle[a]*

[a] *Chemistry Department, Faculty of Science, Fayoum University, El Fayoum 63514, Egypt.*
[b] *Faculty of postgraduates,, Beni souf University. Egypt.*

A R T I C L E I N F O

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A B S T R A C T

The global demand for clean water is greater than ever before, necessitating improved water treatment technology. According to the World Health Organization, each year, 2.2 million individuals lose their lives to diseases related to diarrhea, with many of these cases which caused by waterborne infections. Kaolin clay minerals, specifically those which belonging to the smectite group, that have a wide range of applications in the environment, chemical, industrial and other sectors. This paper focuses on the use of naturally occurring kaolin clay in batch experiments to assess its efficiency in removing Fe, Cu, Cr, and Zn ions heavy metals from real municipal wastewater. The results indicate that kaolin clay demonstrates effective removal efficiencies across different concentration ranges and pH levels ranging from 3 to 12. For the initial treatment, the maximum recovery efficiencies that reach79%, 96%, 75%, and 100% for Fe, Cu, Cr, and Zn respectively for the first treatment.

1. Introduction

As the world's population grows, the demand for clean potable water is constantly increasing. Also, the availability and pure surface and groundwater resources are not only limited but also consumed at an alarming rate. According to weakening of water quality was considered to be one of the seven greatest critical challenges of water. Numerous techniques have been employed to eliminate contaminants, remove or reduce contaminants, and prepare water for safe disposal into the environment. Most of these methods needed extensive handling of material and excessive time to reach removal of solids, oils and metal ions from the water. know, the most popular used techniques make use of numerous typed techniques make use of numerous kinds of material that are used to adsorb wastewater pollutants; among these, clays were found to have an observable affinity for heavy metal ions [1].

Environmental pollutants and their toxicity remain a global concern due to their negative effects and the serious health problems they pose. Water pollution has become a worldwide phenomenon, undermining the economic and environmental and deleterious health effects on humans. Water contamination is a result of contamination from natural and anthropogenic activities [2]. The primary types of pollutants found in sewage wastewater include biodegradable organic compounds, volatile organic compounds, metal ions, suspended solids, nutrients like phosphorous (P) and nitrogen (N), microbial pathogens, and parasites [3].

Clay minerals possess favorable characteristics that make them highly effective natural barriers. These include their fine grain size, significant specific surface area, large capacity, and the diagenetic processes they undergo, which result in high natural density. These properties enable clay minerals to effectively seal gaps and cracks that could potentially serve as pathways for leachates. Furthermore, their chemical reactivity allows for the immobilization of significant pollutants. Numerous studies have shown that natural materials, particularly clay minerals, can serve as excellent sorbents for toxic substances, including heavy metals[4]. Kaolin has promises of recognition as an adsorbent. Because of the large adsorption ability, lower cost, abundant several continents globally and ability for ions exchange. Kaolin clays, which are made up of metal oxides such as Aluminum oxide, Silicon dioxide, Magnesium oxide and Calcium oxide are globally abundant and naturally obtainable minerals [5].

*Corresponding author.

E-mail address: mm6193@fayoum.edu.eg (M.faisle); Tel.: +201092459274
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The use of clay as sorbent to remove toxic contaminants from contaminated water has been comprehensively investigated in developing countries [1]. The clay minerals possess a high cation-exchange capacity and can therefore contribute to water security by their ability to eliminate metals - organic and non-organic pollutants. The existence of heavy metallic ions and organics is the common cause of water contamination, making water unfit for domestic use [8] .Kaolin is a clay mainly composed of kaolinite (Al2Si2O5(OH)4), which has been widely applicated in numerous technological applications. Due to the low-cost and large abundance, the use of clays like kaolin converts the adsorption process into an attractive and promising technique [9].

Kaolin was mined for the first time near Yau-chau Fu in China The name Kaolin originates from the word kau-ling or high ridge that was specified to a hilltop, where. Kaolin generally known as Chinese clay containing 10-95 per cent of the minerals kaolinite and is usually mainly composed of kaolinite (85 to 95 per cent). Kaolinite (figure1) is usually comprised of quartz, mica, and rare feldspar; illite; montmorillonite; ilmenite; anatase; hematite; bauxite; zircon; rutile; kyanite; sillimanite; graphite; attapulgite; and halloysite [10].

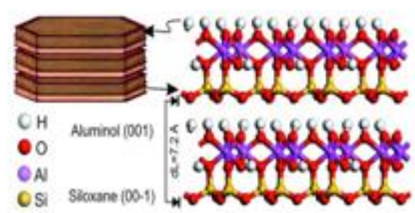

Fig .1. Molecular simulation model of kaolinite structure (1x2x2 unit cells) showing siloxane and aluminol surfaces [5].

These minerals found abundantly in nature and play a crucial role in removing pollutants from wastewater through processes like ion-exchange and adsorption. As depolluting agents, they effectively scavenge toxins from wastewater. Additionally, these minerals are non-toxic. The adsorption processes occur on the solid surface when interacting with ionic solutions, leading to the adsorption of counter ions. This results in the surface acquiring a positive or negative charge relative to the charge originating from the crystal lattice [1]. Significant economic deposits of sedimentary kaolin (figure 2) in Egypt can be found in three main regions: Aswan, the Red Sea, and Sinai. These deposits can be classified into two groups based on their possible origins. The first group is likely derived from the crystalline rocks of the Arabian Nubian Shield (ANS), which includes the Carboniferous and lower Cretaceous deposits in Sinai, as well as the lower Cretaceous deposit in the Red Sea area. The second group may have originated from the crystalline rocks of the East Sahara Craton (ESC) (figure3) and includes the lower Cretaceous deposit in the Aswan area [11].

Fig. 2. kaolin deposits

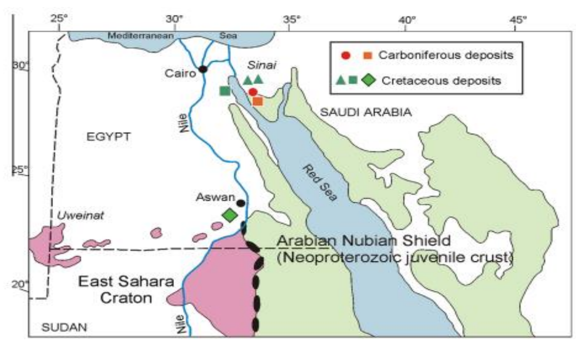

Fig. 3. in Egypt, Position of the sedimentary Kaolin occurrences from the Carbon Cretaceously and Lower Cretaceously in relationship to the cryogenic rocks of the Eastern Sahara crater (EPC) and the Arabic-Nubian shield (ARN)[12].

According to the World Health Organization [13]. The metals of most immediate concern are lead, cadmium, copper, cobalt, aluminum, chromium, manganese, iron, nickel, zinc and mercury. The most common heavy metals that can be found in surface and ground water supplies are cadmium, copper, lead and zinc. There are many other metals found in water sources; however, the lead is the metals that will be focused on for this study. these four metals are regulated by the United States Environmental Protection Agency's (U.S.EPA) national primary drinking water standard Table 1[14].

Heavy metal pollution is a main environmental because of the poisonousness, non-biodegradability, carcinogenicity, and environment fixation of the heavy metals, that cause them accumulate inside the living body via the food chain system [15]. Clay has gained great attention in heavy metals sorption from polluted water as a result of their acceptability and applicability. Syntheses of clay minerals have varied silicates and aluminates groups that have active sites contain hydroxyl groups. Substitution reactions occurred by displaced H2O molecules in the interlayer space of clay by polar molecules [16] .

Table 1 U.S. EPA drinking water standards, potential health effects, and contamination sources for heavy metals

Contaminant	*MCLG (mg/L)*	*MCL or TT (mg/L)*	*Potential Health Effects from Long-Term Exposure*	*Sources of Contaminants in Drinking Water*
Cadmium	0.005	0.005	Kidney Damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Copper	1.3	TT; Action Level = 1.3	Gastrointestinal distress; Liver or Kidney damage	Corrosion of household plumbing systems; erosion of natural deposits
Lead	zero	TT; Action Level=0.015	Infants and Children: delays physical or mental development Adults: kidney problems; high blood pressure.	Corrosion of household plumbing systems; erosion of natural deposits.
Zinc	5	5	Fever; Gastrointestinal distressb	Corrosion of household plumbing systems, pesticidesb

MCLG = Maximum Contaminant Level goal, MCL = Maximum Contaminant Level MCL, TT = Treatment Technique, a Secondary Drinking Water Regulation (not regulated as primary contaminant), b Information is referenced from World Health Organization (WHO)(WHO 2005)

2. Experimental part

2.1. Synthesis

During this study, untreated wastewater samples were gathered from wastewater treatment plants located in Fayoum Governorate, Egypt. The objective was to identify the primary range Fe, Cu, Cr, and Zn ions heavy metals from real municipal wastewater contaminants. Characterization Egypt, according to the global statistical Mundi Index (2007), holds the distinction of being the top kaolin producer in Africa and the Middle East[5] . Kaolinitic sandstone formations can be found in various regions of Egypt, including Sinai, the Eastern Desert, and the southern Western Desert. Wadi Qena, located in the Eastern Desert, is among the largest wadis in Egypt. For this study, a sample was collected from the high Dam in Aswan governorate. The kaolin sample was washed with distilled water to eliminate soluble impurities and subsequently dried for 24 hours at a temperature range of 103-105°C [2]. Figure 4 illustrates the microscopic particle size in micrometers (μm). It is worth noting that smaller particles exhibited greater effectiveness compared to larger ones due to their larger surface area and higher adsorption capacity. Finally, the kaolin was stored in a glass container and made ready for use.

Fig .4. kaolin powder that used in this search Prepared at Temperatures 103-105°C.

2.2. Characterization

The initial step involved the analysis of the kaolin powder using XRD (X-Ray Diffraction). The structure of the kaolin powder was characterized using a diffractometer with Cu kα radiation at a wavelength of 1.5406Å, operating at 40 kV and 30 mA. To examine the surface morphology of the prepared materials, a field emission scanning electron microscope (FESEM) model (ZEISS, Gemini, Sigma 300 VP, Germany) was utilized. The electron beam was accelerated at a voltage of 30 keV.

3. Results and discussion

3.1. Characterization

3.1.1 X-ray diffraction

The X-ray diffraction (XRD) technique finds wide application in mineral characterization, including density determination, assessment of residual stress/strain, phase transformation analysis, crystal structure and size determination, phase identification, analysis of crystallographic orientation, and determination of lattice parameters, dislocation, and thermal expansion coefficient. This technique is highly regarded as a powerful non-destructive method within various domains [17]. Each crystalline mineral or solid possesses a unique set of interplanar spacing and relative intensities, resulting in a distinct XRD pattern that acts as a fingerprint. Therefore, the diffraction intensities and peak positions obtained through XRD analysis enable the determination of characteristics of a sample [17]. The structure of the kaolin sample was characterized using X-ray diffraction (XRD). X-ray diffraction patterns were obtained by using a diffractometer with Cu Kα radiation and a wavelength of 1.5406Å. The patterns were recorded at 2θ degrees with a scan speed of 0.03 degrees [18]. The XRD patterns of kaolin exhibited sharp and intense peaks at 2θ = 28.53°, while the peaks at 2θ = 11, 19, 21, 23, and 25.56° were less intense [18].as seen in figure 5.

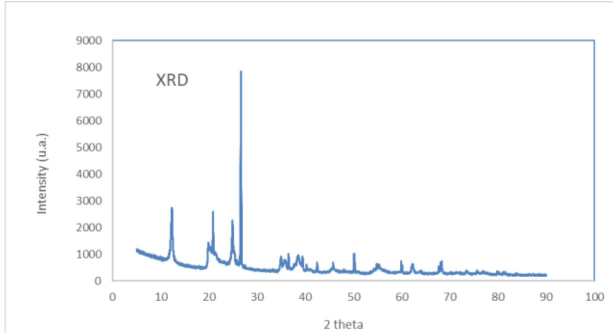

Fig .٥. XRD for kaolin. (author)

3.1.2 SEM

The crystal size and external morphology of the kaolin specimen were analyzed using scanning electron microscopy (SEM). Figure 6 (a,b,c) illustrates the results obtained from this technique. The SEM images revealed the presence of variable clusters of different sizes, as well as the occurrence of particles in spherules and the presence of pores on the surface of the kaolin. These observations indicate the exciting adsorbent properties of kaolin and its capacity for adsorption of ions [19].

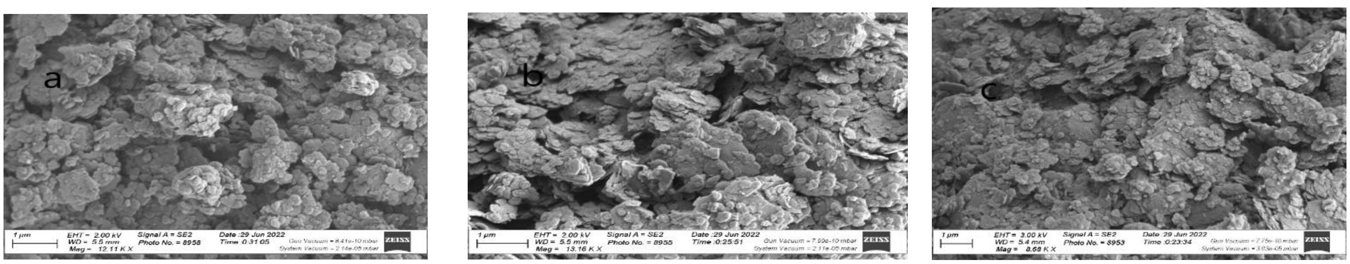

Fig.6. SEM photos for kaolin sample used.

3.2. Effect of pH on the heavy metals removal

Heavy metal pollution poses a significant environmental concern due to the toxic nature, non-biodegradability, carcinogenicity, and environmental persistence of these metals. This leads to their accumulation within living organisms through the food chain system, presenting a potential threat to the ecosystem [20]. Water pollution caused by heavy metal ions has emerged as a critical environmental concern, primarily due to their toxic nature and ability to accumulate in living organisms [21]. These heavy metal ions not only pose a threat to aquatic organisms but also have detrimental effects on land animals, including humans, through the transfer of contaminants along the food chain. Within living organisms, heavy metal ions can specifically bind to nucleic acids, proteins, and small metabolites. This interaction leads to the disruption or alteration of biological functions in organic cells, resulting in severe health issues [14]. The release of significant quantities of heavy metals into the natural environment, such as through the agricultural use of wastewater, presents numerous environmental challenges. Wastewater containing heavy metals is non-biodegradable, lacks sustainability, and has the potential to accumulate in the food chain, thereby posing a significant risk to human health. Therefore, it is imperative to remove these hazardous heavy metal ions from wastewater before it is discharged into the ecosystem, mitigating the potential environmental and health hazards associated with their presence[20]. Figure 7(A,B) represented the results for the heavy metals removal with factors constant (i.e., time – 180 -240 minutes, dose 0.8g/l, temperature - 20°C, mechanical mix for 4 hours),that exhibit removal efficiency increase with different initial concentrations of raw wastewater. And reach 79%, 96%, 75%, and 100% for Fe, Cu, Cr, and Zn respectively for the first treatment. The adsorption of Fe, Cu, Cr, and Zn ions onto kaolinite material exhibits an increase as the pH of the solution rises from 2 to 12. This enhanced adsorption can be attributed to various factors that contribute to the interaction between the ions and the kaolinite surface. At lower pH values, the surface of the kaolinite material possesses active sites that become positively charged. Consequently, the positive charge on the kaolinite surface is pH-dependent and intensifies with decreasing pH values. This leads to the presence of Al-O-H+2 species. As a result, there is a competition between H+ ions and the metal ions for available adsorption sites. However, as the pH increases, this competition diminishes due to the neutralization or increased negative charge of these active sites on the kaolinite surface. This facilitates the enhanced adsorption of positively charged metal ions through the electrostatic force of attraction [22]. Additionally, these results can be attributed to the release of hydrogen (H+) ions from the edge sites of the mineral during the adsorption process. It is also possible for adsorption to occur on the exposed flat planes of the silica and alumina sheets [23].

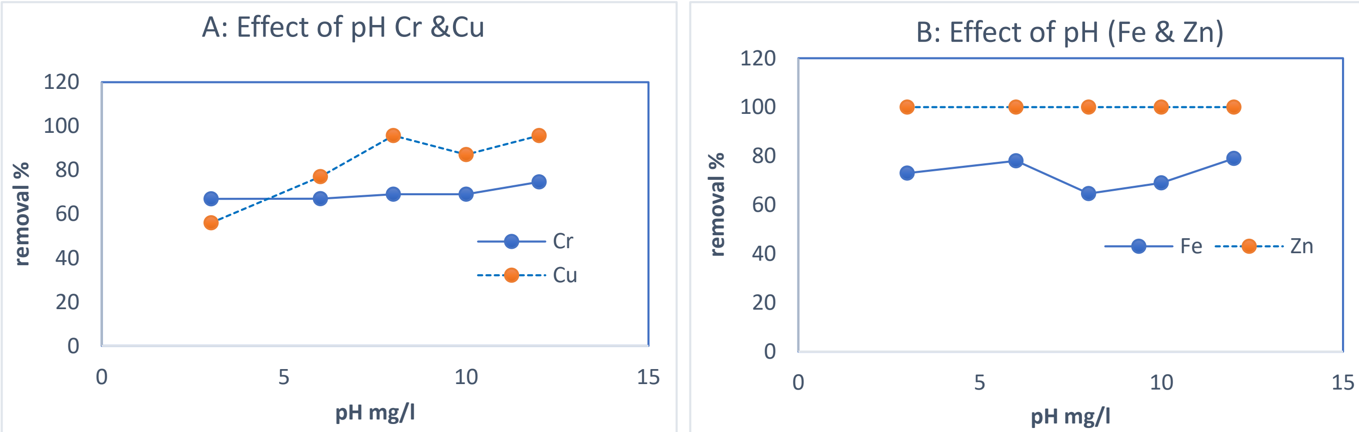

Fig 7. effect of PH (A) on Cr & Cu removal, (B) on Fe & Zn removal.

4. Conclusions

Removal of Fe, Cu, Cr, and Zn ions heavy metals from real municipal wastewater. was investigated using naturally occurring kaolin clay minerals in wastewater, the results indicate that kaolin demonstrates effective removal efficiencies across different concentration ranges and pH levels ranging from 3 to 12. For the initial treatment, Kaolin was chosen as the adsorbent material due to its non-toxic nature, high specific surface area, cation exchange capacity, availability, and cost-effectiveness. The results demonstrated that kaolin exhibited effective removal efficiencies across a range of concentrations and pH values from 3 to 12. the maximum recovery efficiencies 79%, 96%, 75%, and 100% for Fe, Cu, Cr, and Zn respectively for the first treatment. These findings highlight the effectiveness of kaolin in removing various pollutants from wastewater.

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Author Contributions
All authors contributed to this work. M. faisle prepared the samples and completed the experimental measurements., Ghada AbdEl-hafez, Nabila Shehata, with M. faisle shared writing and followed the performance of the experiments. Mohammed el Rabee, Ahmed farghali helped the author complete the sample preparation. completed the paper writing, analyzing the data, and validation. Mohammed el Rabee, Ahmed farghali, Ghada AbdEl-hafez, Nabila Shehata followed the revision and submission of the manuscript for publication.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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