CHARACTERIZATION OF SYNTHESIZED $\gamma$-AL$_2$O$_3$
POWDER AS ADSORBENT MATERIAL FOR REMOVAL
OF COPPER FROM PRODUCED WATER

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Abstract

In this work, $\gamma$-Al$_2$O$_3$ powder as copper adsorbent material was synthesized from polyoxohydroxide aluminum (POHA) precursor using aluminum powder, potassium hydroxide and d-glucose dissolved in distilled water and ethanol, and calcined at 500 $^\circ$C. Prepared $\gamma$-Al$_2$O$_3$ powder was characterized using (XRD), (FTIR), (SEM), (LGI) and (BET) method. The copper ions concentration of oilfield produced water was determined using (ICP-OES). The parameters considered as $\gamma$-Al$_2$O$_3$ adsorbent dose, adsorption time and pH used in this work are (0.2 and 0.4 mg/l), (30-180 min) and (4-10 pH) respectively. The characterization results showed that $\gamma$-phase is the dominant phase of synthesized Al$_2$O$_3$ powder. The results also showed that high adsorption performance for copper ions with a high removal efficiency of 99.99% using synthesized $\gamma$-Al$_2$O$_3$ was obtained with an absorbed dose of 0.4 mg/l, adsorption time of 90 min and a pH of 7.

Keywords : $\gamma$-alumina, chemical method, adsorption, copper adsorption, removal efficiency

I. Introduction

Produced water is water enclosed in underground reservoir of rocks and transported to the surface through the production of crude oil and gas. It is the major volume of waste in the upstream petroleum production. In United States, the total volume waste of produced water is nearly 21 billion/year. The metals ions concentration in produced water is determined by the age and geological of the reservoir from which the gas and oil are produced [I].

In Iraq, the produced water is considered as a complicated problem with rising in water interruption assumed to be 8 barrels of produced water per barrel of oil produced [II]. Figure 1 shows produced water of West Qurna-2 oilfield in Iraq discharged into shallow lands. Discharge without proper
treatment of the produced water can cause severe environmental problem and thus affect human life [V].

**Fig. 1** Produced water from West Qurna-2 oilfield discharged into the shallow lands.

Heavy metals are non-biodegradable, toxic and easy in low concentrations gathered within organisms and in the human body; they can cause serious health problems, such as nerves, system damage, cancer and kidney problems and in high concentrations can be fatal [X]. The most general heavy metals commonly found in produced water include zinc, chromium, nickel, lead, silver, copper, arsenic, iron, uranium, and cadmium [I].

However, copper is predominantly existed at high level of concentration in produced water. Further more, copper ion is a very harmful metal even at very low concentration. Therefore, produced water contaminated with copper must be treated before discharge to the environment. Moreover, high copper concentration inside water determines the rapid deterioration of galvanized metallic fittings and aluminum utensils [VIII]. In industrial effluents, the particular permissible limit of copper ions was reported by the particular United State Environmental Safety Agency (USEPA) to become 1.3 mg/l although this has been stated simply by World Health Organization that the content of copper ions within drinking water should certainly not greater than 2 mg/l [III].

In the last few years, there have been many new methods and strategies that have been progressed to remove copper ions from produced water such as membrane filtration, adsorption, cementation, electro dialysis and photocatalysis [XI].

Alumina is a known metal oxide material used as adsorbents in environmental engineering. The asset of alumina includes low cost, relatively high surface area and good chemical and thermal stability [VII]. It has numerous structural phases, namely α, β, γ, η, θ, λ, K, and X. Among the alumina phases, γ-alumina is the most employed one for applications as industrial catalyst and adsorbent, because of its high surface area and good porosity parameters. In materials, the control of crystal linity and morphology is very important because of inherent relationship between microstructure and
function. Consequently, the search for synthetic or modified methods for obtaining candidate materials with preferred properties is highly attractive to researchers nowadays[IX].

In the present study, synthesis and characterization of $\gamma$-Al$_2$O$_3$ particles as adsorbent material for copper removal from produced water of East Baghdad oil field in Iraq was performed. The dose of $\gamma$-Al$_2$O$_3$, adsorption time and pH on copper ion adsorption to reach the best removal efficiency were studied.

II. Experimental work

Synthesis of $\gamma$-Al$_2$O$_3$ powder utilized as adsorbent material was performed using powder of aluminum (400mg), KOH(1.5g) in 40ml, ethanol: water at 3:1(V:v) and 50.0mg d-glucose. The sesubstances are added to the vial and sonicated in an ultrasonic bath(output 125W/20KHz). Two phases are formed after the aluminum has been dissolved completely. This shows that the formed gel is concentrated at the vial bottom. The gel was separated by decantation and ethanol (100ml) dropped gradually. The resulting solid (1g) was dried at 70°C in an oven. The resulting powder was calcined at 500°C for two hours in the furnace.

X-ray diffraction of synthesized Al$_2$O$_3$ powder was performed to demonstrate $\gamma$– Al$_2$O$_3$ formation using X-Ray Diffractometertype ShimadzumodelAA-6800/Japan, with CuKα($\lambda=1.5418\text{Å}$). The $\gamma$-Al$_2$O$_3$ powder was also characterized by fourier trans for minfrared spectroscopy (FTIR) using Bomen model MB100 with KBr pellets in the range of 4000 to 500 cm$^{-1}$. Surface morphology of the synthesized $\gamma$– Al$_2$O$_3$ powder was assessed by Scanning Electron Microscopy(SEM) model Hitachi 3400 N instrument. The particle size distribution of synthesized $\gamma$-Al$_2$O$_3$ was measured by laser granularity instrument (LGI) model Brookhaven 90 Plus. The result of particle size distribution analysis as illustrated in figure 2 showed that the average diameter of synthesized $\gamma$– Al$_2$O$_3$ is 1476.6 nm. The specific surface area of $\gamma$-Al$_2$O$_3$ was calculated by method of Brunauer–Emmet–Teller (BET) adsorption to be 5 m$^2$/gm.
Electrolytic aqueous solutions (blank solutions) with pH of 3 to 12 were synthesized. A small amount (0.4 mg) of the γ-Al₂O₃ was added to the solutions. The obtained aqueous suspensions were reached to equilibrium at 24 h. Digital pH meter device was used to measure the difference in the pH through equilibration [IV]. ∆pH was defined as
\[
\Delta pH = pH_1 - PH_2
\] (1)

where pH₁ and pH₂ represent the initial and final pH of solution respectively. Point zero charge was determined which is similar to the lowest ∆pH value [IV].

Oil field produced water applied in the current research was provided from Petroleum Research and Development Center associated with Middle Oil Company (East Baghdad). The copper content and pH of produced water utilized in this study were 139 ppm and 6.6 determined using inductively coupled plasma optical emission spectrometry (ICP-OES) type Thermo Fisher ICAP 6500/USA with detection limit of ≤ 0.01 μg/l and pH meter model Hanna Bench pH 211 Meter /UK respectively.

The influence of pH on copper ions adsorption at different adsorption times of 30, 60, 90, 120, 150, and 180 min was investigated using 0.2 and 0.4 mg of γ-Al₂O₃ adsorbent dose in 1 liter of produced water. The resulting solutions were adjusted to pH of 4, 7, and 10 by adding 0.1 M HCl and 0.1 M NaOH for 30 minutes with magnetic stirring of 50 rpm at room temperature. After the predetermined time period elapsed, the mixture of adsorbent and adsorbate was directly separated using a 0.42 μm filter. A sample of the filtered solution was collected for copper ions analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). The removal efficiency (%) of copper was calculated by Equation (2) [VI].

\[
R\% = \frac{C_i - C_f}{C_i} \times 100\% \tag{2}
\]

Where \( C_i \) and \( C_f \) are initial and final concentration of copper.
III. Results and Discussion

The phases of synthesized γ-alumina powder, calcined at 500°C were determined using x-ray diffraction method as shown in figure 3. The peaks of γ-alumina phase are clearly determined at 2θ of 38.5°, 44.48°, 44.76°, 47.34°, and 65.15°. This result was matched by F. Segala as reported elsewhere [IX]. Other peaks indicate other phases are created and relate to various types of impurities presented in the sample.

![X-ray diffraction of synthesized alumina calcined at 500°C.](image)

Figure 4 shows FTIR spectrum of the γ-alumina acquired from POHA after calcination at 500°C. The peaks at 3404.96 and 1639.91 cm⁻¹ are referred to the modes of stretching and bending of water that strongly adsorbed. The intense bands positioned at 690.13 and 667.85 cm⁻¹ were assigned to aluminum coordinates of AlO₄ and AlO₆ which are typical of γ-Al₂O₃. In addition, the calcination process triggered the decomposition of d-glucose.

The aluminum oxidation with a higher fraction of ethanol in an aqueous mixture (i.e. 3:1, v:v) in H₂O-EtOH under sonication was necessary to accelerate the precipitation of aluminum trihydroxide (bayerite) [IX]. The existence of d-glucose had essential effect in achieving the POHA because the bulk condition was the same, i.e., 1:3 water-ethanol. Since d-glucose is able to make hydrogen bond, it can occur in concert with the interlayers of the initial oligomeric structures or with the cation of fresh aluminum and therefore favor the premature aggregation of the aluminate species.
Scanning electron microscopy (SEM) was utilized in this work to create a high-resolution image of synthesized $\gamma$-Al$_2$O$_3$. Figure 5 showed that irregular shape of synthesized $\gamma$-Al$_2$O$_3$ particles is dominated. The surface of synthesized $\gamma$-Al$_2$O$_3$ particles was displayed a micro-rough structure, which can enhance the adsorption of copper ions.

Point zero charge (pzc) of synthesized $\gamma$-alumina is described as the suspension conditions beneath which the surface charge density makes zero. Figure 6 shows that the pH$_{pzc}$ of the $\gamma$-alumina is equal to 6.5. At low pH value (less than 6.5), the $\gamma$-alumina powder carries a positive charge because the value of pH is lower compared with the point of isoelectric or point of zero charge. Adsorption is at least the weakest at the low value of pH and is caused by charging on the $\gamma$-alumina. The $\gamma$-alumina at pH value of greater than 6.5 is negatively surface charged rising to a high value of adsorption. This is related to the fact that when the copper ions are in a solution, they are positively charged and will be attracted to the negatively charged surface of $\gamma$-alumina,
for this reason, a pH greater than $\text{PH}_{\text{pzc}}$ is preferred for adsorption.

![Graph](image)

**Fig. 6** $\Delta \text{pH}$ versus $\text{pH}_1$ of synthesized $\gamma$-alumina.

The predominant factor is the pH for every kind of metal ion adsorption from an aqueous solution. The merits of $\gamma$-$\text{Al}_2\text{O}_3$ as adsorbents surface, ionic state of functional groups and metals nature are depending on pH status. Controlled experiments of pH were performed in this work and the result of experiments is shown in figure 7. It is evident that copper ion adsorption was detected to increase with an increase in pH from 4 to 10. Values obtained of copper removal efficiency of (21%, 38% and 24.2%) were carried out at a pH of 4, 7 and 10 respectively using $\gamma$-$\text{Al}_2\text{O}_3$ adsorbent of 0.2 mg/l. Copper removal efficiencies of (31%, 55.4% and 38.5 %) at a pH of 4, 7, and 10 respectively were obtained by using $\gamma$-$\text{Al}_2\text{O}_3$ adsorbent of 0.4 mg/l. Therefore, one can decide that at a pH of 4, an acidic solution, the adsorption mechanism is only an active site and the competition between the $\text{Cu}^{2+}$ ions and $\text{H}^+$ ions was present on the surface of adsorbent site. On the other hand, due to positive charge of hydrogen ions, the surface of the $\gamma$-$\text{Al}_2\text{O}_3$ will be positively charged and therefore the removal efficiency of $\text{Cu}^{2+}$ ion at a lower value. At pH of 7, although $\text{Cu(OH)}^+$ is activated due to increased surface negative charge, the maximum removal efficiency rate is obtained . At pH of 10, the alkaline solution of produced water, a gradual increase in the removal of Cu ions is established compared with 4 pH solution.

It can be concluded that $\gamma$-$\text{Al}_2\text{O}_3$ exhibits amphoteric properties according to a pH of point zero charge which is 6.5. In addition, $\gamma$-$\text{Al}_2\text{O}_3$ powder shows anion exchange in the produced water with a pH below 6.5, while cation exchange arises at a pH greater than 6.5.
Effect of pH on the removal efficiency of copper

The increase in metal ion adsorption with increasing adsorbent dose is attributed to the enhanced adsorption sites. The effect of adsorbent dose was examined with copper concentration of 139 mg/l of produced water by the addition of two adsorbent doses representing 0.2 and 0.4 mg/l on copper removal efficiency as shown in figure 8. The percent of copper removal efficiency was found to increase with an increase in adsorbent material dose. Highest copper removal efficiencies of 38 % and 55.4 % were obtained at adsorbent material dose of 0.2 mg/l and 0.4 mg/l, respectively.

Figure 8 Effect of γ -Al2O3 adsorbent dose on the copper removal efficiency (%).

Figure 9 shows the relationship between the removal efficiency (%) of copper ions with adsorption time. Clearly, the rate of copper removal efficiency increased very rapidly in 30 min. This is due to the availability of vacant effective sites on γ -Al2O3 adsorbent surface. The experimental results also showed that increased adsorption time increased the amount of copper ion...
removal. The maximum copper ion adsorption on $\gamma$-$\text{Al}_2\text{O}_3$ was reached to 99.99% and 99.2% for 0.4 mg/l and 0.2 mg/l respectively after 90 minutes.

**Fig. 9** Effect of adsorption time on the removal efficiency (%) of copper.

**IV. Conclusions**

The practical steps in this work were effective in preparation the $\gamma$-$\text{Al}_2\text{O}_3$ powder as adsorbent material from polyoxohydroxide aluminum (POHA) using chemical method. This study also showed that the copper removal efficiency using synthesized $\gamma$-$\text{Al}_2\text{O}_3$ particles was increased with increasing adsorption time from 30 to 60 min regardless the $\gamma$-$\text{Al}_2\text{O}_3$ adsorbent dose. The maximum copper removal efficiency of 99.2% and 99.99% were obtained using 0.2 and 0.4 mg/l of $\gamma$-$\text{Al}_2\text{O}_3$ adsorbent doses respectively at adsorption time of 90 minutes and pH of 7.

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