High Specific Surface Area γ-Al2O3 Nanoparticles Synthesized by Facile and Low-cost Co-precipitation Method

Zahra Gholizadeh  
Semnan University

maryam aliannezhadi (✉ m_aliannezhadi@semnan.ac.ir)  
Semnan University

Mehrdad Ghominejad  
Semnan University

Fatemeh Shariatmadar Tehrani  
Semnan University

Article

**Keywords:** Alumina (Al2O3) nanoparticles, Co-precipitation method, Cu ion removal, Structural and optical properties, Precipitating agent concentration

**Posted Date:** September 26th, 2022

**DOI:** https://doi.org/10.21203/rs.3.rs-2085977/v1

**License:** This work is licensed under a Creative Commons Attribution 4.0 International License. 
Read Full License
High Specific Surface Area $\gamma$-Al$_2$O$_3$ Nanoparticles Synthesized by Facile and Low-cost Co-precipitation Method


*Faculty of Physics, Semnan University, PO Box: 35195-363, Semnan, Iran

**Correspondence: m_aliannezhadi@semnan.ac.ir;

Abstract:

Alumina (Al$_2$O$_3$) nanoparticles (NPs) are particularly adsorbent NPs with a high specific surface area (SSA) that may well be utilized to clean water. In this study, pure $\gamma$-alumina NPs are successfully synthesized by the co-precipitation method, and the effect of ammonium bicarbonate concentration on the synthesized NPs is studied to find the optimum concentration to provide the highest capacity of copper ions removal from water. The results declare that spherical alumina NPs with average diameters in the range of 19-23 nm are formed with different concentrations of precipitation agent, and the concentration has no significant effect on the morphology of NPs. Furthermore, the precipitating agent concentration influences the optical characteristics of the produced alumina NPs, and the bandgap energies of the samples vary between 4.24 and 5.05 eV. The most important impact of precipitating agent concentrations reflects in their SSA and the capacity of copper ion removal. Ultra-high SSA=317 m$^2$/g and the highest copper removal are achieved in an alkalis solution followed by a neutral solution. However, admirable copper removal of 98.2% is even achieved in acidic solutions with a given concentration of ammonium bicarbonate, so this sample can be a good candidate for Cu ions removal from acidic water.

Keywords: Alumina (Al$_2$O$_3$) nanoparticles, Co-precipitation method, Cu ion removal, Structural and optical properties, Precipitating agent concentrations

1. Introduction

The production of nanostructured metal oxide materials has recently received much attention due to their unique features, such as high surface-to-volume ratio, high surface reactivity, and unusual electric properties. Metal oxides are extremely used in electronic and photonic devices, medicine, and also as catalysts and photocatalysts. They found particular desirability in many scientific fields, including chemistry, material sciences, physics, medicine, and electronics. Aluminum oxide, commonly known as alumina, is one of the most frequent metal oxides used in industry. Alumina nanoparticles have wide usage in adsorption-based applications because of their interesting properties such as acid-base properties, high specific surface area (SSA), structural stability, low cost, mechanical and thermal stability, good mechanical strength, volatile acidity, thermal conductivity, stiffness, inertness to most acids and alkalis, adsorption capacity, wear resistance, oxidation, good electrical and chemical resistance, electrical insulation, high melting points, as well as being non-toxic. Among these features, the high surface area, and open porosity enable $\gamma$-alumina to be applied as catalysts and adsorbents in petroleum refining and petrochemical industries.
Unlike organic pollutants, heavy metals are not decomposed naturally and incline to gather in living organisms and many heavy metal ions are the most common toxic contaminants mostly summarized in industrial effluents. Toxic heavy metals of particular attention in the treatment of industrial effluents include copper, nickel, lead, mercury, zinc, chromium, and cadmium.

Copper ion (Cu\(^{2+}\)) is one of the harmful heavy metals, which abundantly and naturally present in municipal wastewaters and industrial effluents, and is very harmful to human health. Copper ion, as a toxic contaminant of potable water resources, should be eliminated because of its dangerous risks at unauthorized dosages (more than 2 mg/L) for human health problems such as headache, depression, and learning problems. Adsorption has been accepted as one of the most promising methods for the removal of toxic metals from aqueous solutions due to its simplicity, flexibility, and high efficiency in industrial applications.

The use of nanoscale materials in the field has attracted considerable attention due to their large specific surface area and excessive active groups.

Alumina nanoparticles (Al\(_2\)O\(_3\) NPs) are important inorganic materials with a good adsorption capacity, high resistance to chemical agents, and excellent performance, which introduce them as a good catalyst candidate for many chemical reactions and the best candidate for water treatment. So, different research groups have synthesized alumina nanostructures and used them to remove a variety of contaminant ions from water. For example, S.M Siahpoosh et al. have synthesized alumina nanoparticles by sol-gel method and exploited them to remove nickel contaminants from water. Also, Mahdavi et al., Amin et al., and Shojaei Bahabad et al. have established nano alumina to remove some heavy metals such as Pb(II), Cu(II), Cd(II), and Ni(II) from aqueous solutions. Huimin Zhang et al. and Sara Al-Salihi et al. have also used the nano alumina to remove Congo red dye from water. Therefore, nano alumina is accepted as an excellent nanostructure for water treatment.

Alumina can be synthesized in several metastable transition phases depending on the preparation method as well as synthesis parameters like stirring times, calcination temperature, precursor, solution pH, and else. A well-known group of alumina like \(\eta, \chi, \rho,\) and \(\gamma\)-Al\(_2\)O\(_3\), which labeled as Al\(_2\)O\(_3\).\(n\) H\(_2\)O (n is a number between 0 to 6), is created at low-temperature by dehydration of boehmite and bayerite at ~600 °C. Meanwhile, other alumina groups like \(\theta, \delta, \kappa,\) and \(\alpha\)-Al\(_2\)O\(_3\), which are labeled as anhydrous Al\(_2\)O\(_3\), are mostly produced at high-temperature calcination in the range of ~900 to 1000°C. Phase transition in alumina follows the sequence \(\text{Boehmite} \rightarrow \gamma\)-Al\(_2\)O\(_3\) \rightarrow \delta\)-Al\(_2\)O\(_3\) \rightarrow \theta\)-Al\(_2\)O\(_3\) \rightarrow \alpha\)-Al\(_2\)O\(_3\). \(\gamma\)-alumina and \(\alpha\)-alumina are the only types of alumina that are commercially produced until now. Also, nano alumina can be synthesized by various routes, such as hydrothermal, mechanical milling, co-precipitation, vapor phase reaction, arc plasma, sol-gel, and homogeneous precipitation.

The co-precipitation method (CPM) is an easy, simple, and cost-effective synthesis method, which provides the ability to control the particle crystalline size, morphology, and numerous prospects of the NPs to customize the particle surface and properties by determining the relative rates of nucleation and growth during the synthesis process, especially when removing the solvent.

Also, different precipitating agents like sodium carbonate, sodium bicarbonate, ammonium carbonate, ammonium bicarbonate, ammonium hydroxide, and hexamethylene tetramine, and also different synthesis parameters have been used to synthesize high specific surface area (SSA) Al\(_2\)O\(_3\) nano-powders. Some reported SSA and synthesis conditions of the nano alumina are collected in Table 1 for comparison.

As you can observe, the precipitating agents and synthesis route have a significant effect on the SSA of the synthesized nano alumina, so using NH\(_4\)HCO\(_3\) in the co-precipitation method led to a higher value of nano alumina SSA than other precipitating agents. Therefore, this precipitating agent can be a good candidate to achieve high SSA nano alumina. Furthermore, the co-precipitation method is a simple, rapid, lower temperature, and low-cost method with the ability to easily control the sample.
crystalline size and morphology, well controllability over the stoichiometric, and overall homogeneity for synthesizing the nanoparticles.

Table 1 Method, precursor, precipitating agent, calcination temperature and time, and SSA of synthesized γ-Al2O3 nanoparticles.

<table>
<thead>
<tr>
<th>Method</th>
<th>Precipitating agent</th>
<th>Precursor</th>
<th>calcination temperature and time</th>
<th>SSA (m²/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPM</td>
<td>sodium carbonate</td>
<td>Aluminum nitrate</td>
<td>550 ° (5 h)</td>
<td>140</td>
<td>23</td>
</tr>
<tr>
<td>CPM</td>
<td>sodium bicarbonate</td>
<td>Aluminum nitrate</td>
<td>550 ° (5 h)</td>
<td>185</td>
<td>23</td>
</tr>
<tr>
<td>CPM</td>
<td>Ammonium carbonate</td>
<td>Aluminum nitrate</td>
<td>550 ° (5 h)</td>
<td>179</td>
<td>23</td>
</tr>
<tr>
<td>CPM</td>
<td>Ammonium bicarbonate</td>
<td>Aluminum nitrate</td>
<td>550 ° (5 h)</td>
<td>190</td>
<td>23</td>
</tr>
<tr>
<td>Green method</td>
<td>ammonium hydroxide</td>
<td>Aluminum nitrate</td>
<td>650 ° (2 h)</td>
<td>217.02</td>
<td>31</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Hexamethylene tetramine</td>
<td>Aluminum sulfate</td>
<td>650 ° (2 h)</td>
<td>273.3</td>
<td>32</td>
</tr>
</tbody>
</table>

So, the co-precipitation method is selected to synthesize the high SSA alumina NPs. Also, NH₄HCO₃ is selected as the precipitating agent because the highest SSA has been achieved by using this material. To the best of our knowledge, there is no evidence to investigate the effect of NH₄HCO₃ molar concentration on the properties of synthesized alumina nanoparticles or any effort to achieve the optimal alumina nanoparticles with the highest SSA for water treatment in the literature. So, the synthesis of Al₂O₃ nanoparticles using different amounts of NH₄HCO₃ is done in the paper by co-precipitation method to consider the effect of NH₄HCO₃ molar concentration on the characteristic properties of nano alumina and the removal of copper ions as a toxic metal from aqueous solutions. The results declare that the molar concentration of NH₄HCO₃ is a significant parameter that affects the properties of alumina NPs and Cu²⁺ ion removal from water.

2. Material and method

2.1 Synthesis

Aluminum nitrate (Al(NO₃)₃, 95%), Ammonium bicarbonate (NH₄HCO₃, 98%), and NaOH were purchased from Merck company and used without further purification.

For the synthesis of Al₂O₃ nanoparticles, first 2.5 g of aluminum nitrate (Al(NO₃)₃) and a given value of ammonium bicarbonate (0.6, 0.8, 1, and 1.2 g of NH₄HCO₃) were dissolved in 60 mL of deionized water (DI water) separately on two different magnetic stirrers at ambient temperature for 15 minutes. Then, two previous solutions were inserted into 40ml deionized water and taken in a reaction vessel on an adjusted magnetic stirrer at a temperature of 70°C with two droppers to finish the solutions.
After that, 8 g of NaOH was dissolved in 100 ml of DI water for 15 minutes on a magnetic stirrer at ambient temperature and inserted into the previous solution with a dropper to adjust the solution pH at 8. The precipitate was left for 3 h on a magnetic stirrer adjusted at 70°C. Next, Al cations precipitate in the form of hydroxides. The white precipitate was washed with DI water (three times) and ethanol (two times) to remove all impurities including Na ions and else. Then the alumina production was transferred to an oven at 70 °C for 12 h to dry. Calcination of all alumina samples was carried out in a programmable furnace at 550°C for 2 h with a temperature rate of 30°C/min. The white calcined samples prepared using NH4HCO3 in different masses of 0.6, 0.8, 1, and 1.2 g were labeled according to the used mass of NH4HCO3 as RA-0.6, RA-0.8, RA-1, and RA-1.2, respectively.

2. 2 Characterization

Fourier transform infrared (FTIR) spectroscopy, Shimadzu spectrometer, model 8400S, was done by KBr disc technique in the range of 400–4000 cm−1 to investigate the structure, vibration modes, and the chemical bonding configuration of the alumina samples. The white powders were investigated by X-ray diffraction (XRD), ADVANCE-D8 model, with Cu-kα radiation source (λ = 1.5406 Å) in the range of 2θ =10–90° to identify the phases and the crystallinity of the alumina calcined samples. Field emission scanning electron microscopy (FESEM) and dispersive X-ray analysis (EDX), TESCAN-model MIRA3 microscope, were used to study the surface morphology and elemental analysis of the samples. The optical properties of the alumina samples were investigated using diffuse reflectance spectroscopy (DRS) by the Avaspec-2048-TEC device. The specific surface areas (SSA) of the samples were estimated from Brunauer-Emmett-Teller (BET) theory by using nitrogen adsorption-desorption isotherm data obtained at -196°C (77K) on a constant-volume adsorption apparatus with Micromeritics Gemini VII version 5.03. The samples were degassed at 200 °C for 3 h before BET analysis.

2. 3 Application

Adsorption of copper ions by synthesized nano-alumina was studied by taking out 55 mL of Cu2+ ion solution (184 ppm) at room temperature. For investigation of copper ion removal from water, 0.050 g of synthesized nano-alumina were dissolved in this acidic solution (pH= 5.79) on a magnetic stirrer and the adsorption reactions were studied at different times of 2, 10, 20, 30, 40, 50, 60, 90, 120, 180, 1440 minutes. At the desired times, 5 cc of the solution was separated and filtered using a No. 4 sinter glass filter and was analyzed by atomic absorption spectrum (AAS) to evaluate the amount of copper in the water. Also, Agilent Technologies 240AA flame atomic absorption spectrometer was used to obtain the AAS of the simulated water and determine the copper ions concentration in the solution. The nano-alumina sample with the best removal efficiency of Cu2+ in acidic conditions was further studied under the same experimental conditions in neutral and alkaline solutions (pH= 7 and 8), too.

3. Result and discussion

3.1 FTIR

Fourier transform infrared (FTIR) spectroscopy was performed on the alumina samples to investigate the vibrational states and chemical structure of the samples. Figure 1 shows the FTIR spectra of the samples synthesized using different concentrations of ammonium bicarbonate in the range of 400-4000 cm−1. As can be seen, similar absorption peaks with small shifts are observed in the absorption spectrum of the samples, which demonstrate the same chemical structures
of synthesized samples at different concentrations of ammonium bicarbonate. The peak at 1623 cm\(^{-1}\) confirms the presence of water in the sample and is based on the H-O-H bending vibration of H\(_2\)O molecules. The wide peak in the region of 3200-3700 cm\(^{-1}\) is related to the stretching vibration of OH\(^-\), which is bonded to Al\(^{3+}\).

Also, the presence of broad absorption peaks in the range of 500-1000 cm\(^{-1}\) refers to the asymmetric stretching vibrations of the Al-O-Al bond. Therefore, Al\(_2\)O\(_3\) is created in all samples synthesized with different concentrations of ammonium and we will discuss about the formation of nano alumina in the next subsection.

3.2 The formation mechanism of nano-Alumina

The formation of Al\(_2\)O\(_3\) NPs occurs through the following chemical reactions, which indicates the formation of NH\(_4\)OH in the early stages of the synthesis process through the dissolution of ammonium bicarbonate in water (Equation 1). Therefore, the concentration of NH\(_4\)HCO\(_3\) has a direct relation with NH\(_4\)OH production:

\[
\text{NH}_4\text{HCO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} + \text{H}_2\text{O} + \text{CO}_2 \quad (1)
\]

\[
\text{Al(NO}_3)_3 + 3\text{NH}_4\text{OH} \rightarrow \text{Al(OH)}_3\downarrow + 3\text{NH}_4\text{NO}_3 \quad (2)
\]

\[
\text{Al(OH)}_3 \rightarrow \text{AlOOH} \downarrow + \text{H}_2\text{O} \quad (3)
\]

\[
\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad (4)
\]

According to references, the formation of Al(OH)_3 is essential for creating alumina, which is provided during the interaction of NH\(_4\)OH with Aluminum nitrate (Equation 2). In addition, in the present work, the addition of sodium hydroxide leads to the production of more Al(OH)_3. When NaOH is added to the solution to adjust the pH, it is separated into Na and OH ions. On the other hand, NH\(_4\)O\(_3\) salt (Equation 2) is present in the solution as NH\(_4\) and NO\(_3\) ions, which can react with sodium hydroxide ions to produce excess NH\(_4\)OH and NaNO\(_3\) salt in the solution. Therefore, NaOH can also play the role of a precipitating agent. According to Equation 3, more AlOOH precipitate is produced in the presence of NaOH, which ultimately increases the production yield of alumina nanoparticles. Therefore, we expect the formation of Al\(_2\)O\(_3\) in all the above synthesis conditions.

3.3 XRD Analysis

The crystalline structures of the synthesized alumina samples were investigated by X-ray diffraction (XRD) analysis and the results in the range of 2\(\theta\) = 10 to 90 degrees and with step sizes of 0.65 degrees are depicted in Figure 2.
According to the results, some partly broad and low-intensity peaks can be observed in the XRD patterns of all the alumina samples, which demonstrates the small size of the crystal. Moreover, identification of the crystal phase of the synthesized alumina samples by X’Pert high score software revealed that all samples were formed in the Cubic phase.

![XRD patterns of alumina samples](image)

Figure 2: XRD patterns of alumina samples synthesized with different concentrations of ammonium bicarbonate including 0.6, 0.8, 1, and 1.2 g in 60 mL of deionized water.

Table 2. Crystalline properties of Al₂O₃ nanoparticles synthesized with different concentrations of ammonium bicarbonate including 0.6, 0.8, 1, and 1.2 g.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Card number</th>
<th>Phase</th>
<th>Space group</th>
<th>Calculated lattice constants (Å)</th>
<th>Scherrer crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA-0.6</td>
<td>96-201-5531</td>
<td>Cubic</td>
<td>F d -3 m</td>
<td>7.92</td>
<td>3.51</td>
</tr>
<tr>
<td>RA-0.8</td>
<td>01-073-2294</td>
<td>Cubic</td>
<td>F d -3 m</td>
<td>7.89</td>
<td>4.16</td>
</tr>
<tr>
<td>RA-1</td>
<td>96-120-0016</td>
<td>Cubic</td>
<td>F d -3 m</td>
<td>7.88</td>
<td>4.56</td>
</tr>
<tr>
<td>RA-1.2</td>
<td>96-120-0016</td>
<td>Cubic</td>
<td>F d -3 m</td>
<td>7.86</td>
<td>5.07</td>
</tr>
</tbody>
</table>

The XRD patterns of the samples are refined by using MAUD software as a reliable. The XRD data were used without any smoothing or filtering in the MAUD software and lattice constants were calculated, and the results are presented in Table 2. According to the results, a decreasing trend is observed in lattice constants with increasing the concentration of ammonium bicarbonate.

Also, the mean crystallite sizes of the alumina samples are calculated using Scherrer equation according to reference 37 and presented in Table 2. The results reveal that the crystallite size increases with the increasing concentration of the precipitating agent.

### 3.4 FESEM

Figure 3 displays the FESEM images of alumina samples synthesized at different concentrations of ammonium bicarbonate. It can be observed that the morphology of Al₂O₃ is independent of the concentration of ammonium bicarbonate, and spherical nanoparticles are formed in all alumina samples. Also, it seems the higher concentration of the precipitating agent leads to producing more uniform nanoparticles. For more quantitative analysis, the average
diameters and data dispersion of the alumina nanoparticles can be calculated using Digimizer software and fitting a log-normal fitting function in Origin pro software. The distribution histograms of nanoparticle diameters are depicted in the inset of the FESEM images for every synthesized alumina sample and the average diameters of nanoparticles are calculated and collected in Table 3.

Furthermore, increasing the concentration of ammonium bicarbonate leads to more uniform nanoparticles, and the least data dispersion is obtained with the highest investigated concentration of the precipitating agent in sample RA-1.2.

Table 3. The Average diameter size and Standard deviation of Al$_2$O$_3$ nanoparticles synthesized with different concentrations of ammonium bicarbonate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D (nm)</th>
<th>Standard deviation (nm)</th>
<th>Percentage of standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA-0.6</td>
<td>23.10</td>
<td>0.93</td>
<td>4.06</td>
</tr>
<tr>
<td>RA-0.8</td>
<td>21.22</td>
<td>0.95</td>
<td>4.29</td>
</tr>
<tr>
<td>RA-1</td>
<td>19.54</td>
<td>0.45</td>
<td>2.26</td>
</tr>
<tr>
<td>RA-1.2</td>
<td>19.45</td>
<td>0.33</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Also, elemental analysis of the samples was done using EDX technique by the FESEM machine and the results are presented in Figure 4. EDX spectra of all nano-alumina samples synthesized at different concentrations of ammonium bicarbonate have two strong signals at 1.5 keV and 0.5 keV, which confirm the existence of Aluminium (Al) and Oxygen (O), respectively.
Furthermore, no extra peaks are observed in the spectra, which indicates the purity of all synthesized nano-alumina. For more detailed information, the weight percentage and atomic percentage of the elements in the nano-alumina samples are collected in Table 4.

![Figure 4: EDX spectra of Al2O3 nanoparticles synthesized using different concentrations of ammonium bicarbonate labeled as (a) RA-0.6, (b) RA-0.8, (c) RA-1, and (d) RA-1.2.](image)

Table 4: The weight percentage and atomic percentage of the elements (Al and O) in the Al2O3 nanoparticles synthesized with different concentrations of ammonium bicarbonate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th>W%</th>
<th>A%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA-0.6 g</td>
<td>Al</td>
<td>66.84</td>
<td>54.45</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>33.16</td>
<td>45.55</td>
</tr>
<tr>
<td>RA-0.8 g</td>
<td>Al</td>
<td>58.8</td>
<td>45.84</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>41.2</td>
<td>54.16</td>
</tr>
<tr>
<td>RA-1 g</td>
<td>Al</td>
<td>61.05</td>
<td>48.17</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>38.95</td>
<td>51.83</td>
</tr>
<tr>
<td>RA-1.2 g</td>
<td>Al</td>
<td>65.22</td>
<td>52.65</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>34.78</td>
<td>47.35</td>
</tr>
</tbody>
</table>

### 3.5 DRS

As you can observe, the concentration of ammonium bicarbonate significantly affects the optical properties of the synthesized alumina nanoparticles, so that the sample RA-0.6 has the highest reflectance in the visible and NIR regions and can be used as an HR material in the regions. As shown in Figure 5(b), absorption of the synthesized nano-alumina in the range of 500-850 nm experiences an increase with increasing the concentration of ammonium bicarbonate. The lowest reflectance/absorbance of all samples is located in UV-region around. However, the absorption peak experiences a red-shift with increasing the concentration of ammonium bicarbonate, and the highest absorption peak is observed for sample RA-1.2.

To determine the direct and indirect bandgap values of the alumina nanoparticles, Tauc method (Equation 5) can be used 39.
\[ (F(R)E)^n = B(E - E_g) \]  \hspace{1cm} (5)

where Kubelka-Munk function, \( F(R) = (1-R)^2/(2R) \), is used in the equation as a measure of the nano-alumina absorption coefficient. \( E \), \( B \), and \( E_g \) are photon energy, a constant, and the material bandgap, respectively. \( m \) is 2 or \( \frac{1}{2} \) for the calculation of the direct or indirect bandgap energy, and the direct and indirect bandgap energy can be determined from the intercept of \( (F(R)E)^2 \) and \( (F(R)E)^{1/2} \) versus photon energy plots as shown in Figure 6. The results declare that the concentration of ammonium bicarbonate significantly influences the direct and indirect bandgap energy of the synthesized nano-alumina, however, all synthesized alumina NPs have bandgap energy of more than 4.24 eV (between 4.42 and 5.05 eV) and they can mostly be considered as a semiconductor. Also, the lowest bandgap energy is obtained in the RA-1 sample. The bandgap energies of our synthesized samples are in the range of other reported studies. For example, Amirsalari et al. obtained the direct bandgap energy of 5.25 eV for alumina nanoparticles synthesized using a chemical wet method at pH=8 and calcined temperature of 550°C. Koopi et al. also reported the energy bandgap of 5.46 eV for nano-alumina samples synthesized using a green method.

3.6 Specific Surface Area

The specific surface area (SSA) of the alumina samples can be estimated using XRD data in dense, monodisperse, and spherical particles approximation as follows:

\[ \text{SSA} = \frac{6000}{\rho \times d} \]  \hspace{1cm} (6)

where \( \rho \) is the particle density of the alumina samples, which is determined using X’Pert high score software and \( d \) is the mean crystallite size calculated from XRD data. SSA values of the samples were calculated using Equation (6) and the results are gathered in Table 2. Also, the SSA values of the alumina nanoparticles were measured by the multipoint BET (Brunauer-Emmett-Teller) method from \( N_2 \) sorption-desorption data and the results are presented in Table 5.

As we expected, the specific surface area of the alumina samples significantly depends on the concentration of ammonium bicarbonate used in the synthesis process.
Also, the BET SSA and calculated SSA using XRD data has the same trend with increasing the concentration of ammonium bicarbonate. However, the estimated SSA values of the samples with these two methods are different, which can be due to the invalidity of the applied approximation. Indeed, the trend of SSA changes with increasing the concentration of ammonium bicarbonate, and setting the pH value to 8 can be due to two competitive phenomena. First, increasing the ammonium bicarbonate leads to an increase in the SSA value. Second, setting the pH value while increasing the ammonium bicarbonate decreases the NaOH concentration in the solution and subsequently decreases the concentration of hydroxyl groups in the liquid. Also, according to reference 31, the SSA value of alumina nanoparticles directly relates to the concentration of hydroxyl groups in liquid and therefore falls with decreasing the NaOH concentration.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Density (m²/g)</th>
<th>BET SSA (m²/g)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA-0.6</td>
<td>3.59</td>
<td>317</td>
<td>473.51</td>
</tr>
<tr>
<td>RA-0.8</td>
<td>3.98</td>
<td>168</td>
<td>286.6</td>
</tr>
<tr>
<td>RA-1</td>
<td>3.64</td>
<td>264</td>
<td>394</td>
</tr>
<tr>
<td>RA-1.2</td>
<td>3.66</td>
<td>225</td>
<td>311</td>
</tr>
</tbody>
</table>

### 3.7 Copper adsorption experiment

Most nanoparticles have no desirable operation in acidic conditions. First, we investigate the Cu ions removal from the simulated water to investigate the effect of ammonium bicarbonate concentration on the water treatment in acidic conditions (pH = 5.79), and the results are presented in Figure 5. The following equation was used to calculate the efficiency of Cu ions removal.

\[
\text{Removal efficiency} \% = \left(1 - \frac{C_t}{C_0}\right) \times 100
\]  

where, \( C_0 \) and \( C_t \) are the initial concentration of copper in solution and its concentration at time \( t \), respectively.
According to Figure 7, concentration of ammonium bicarbonate significantly affects the ability of Cu ions removal by the synthesized alumina nanoparticles, and the highest efficiency is obtained using the sample RA-0.6, and copper ions removal% reaches 98.2% in 120 mins. Also, copper ions removal% at the same time is 73.5%, 57.8%, and 51.2% for RA-0.8, RA-1, and RA-1.2, respectively, which is an acceptable Cu$^{2+}$ removal from water.

The efficiency of Cu ions removal of RA-0.6 from water is interesting efficiency compare to reported results for Cu removal% by alumina nanoparticles in the literature. For example, Ren. yu Wang et al. have synthesized alumina nanostructures by sol-gel method and used it to absorb copper metal contaminants from water $^{43}$. The maximum adsorption capacity of alumina nanoparticles for copper metal was 88.7 mg/L (about 65%), which indicates the greater capacity of sample RA-0.6 for Cu$^{2+}$ removal from water.

The difference in Cu removal% of the synthesized nano-alumina samples can be related to the high SSA of the RA-0.6. High specific surface area (SSA) leads the high active sites, which requires adsorption, which is one of the most significant adsorbent characteristics. The direct relation between the performance of material adsorption and surface area was previously reported in Reference $^{44}$.

As mentioned, the RA-0.6 sample has the highest Cu ions adsorption at the investigated acidic condition. So, the Cu ions removal of the RA-0.6 sample was studied in neutral, acidic, and alkaline conditions (pH=5.79, 7, and 8), and the results are depicted in Figure 8. According to the results, the efficiency of the sample in neutral and alkaline conditions are significantly higher than the acidic condition and most Cu ions are removed from water in less than 10 min in neutral and alkaline conditions while it takes 120 mins to reach the efficiency of 98.2% in acidic condition.

Previous works on alumina nanoparticles have been reported and shown a better Cu ions removal of the nanoparticles in alkaline conditions $^{45}$. However, our efficiency in acidic, normal, and alkaline conditions is significantly admirable and the alumina nanoparticles can be an excellent candidate for water treatment and Cu ions removal from water in every condition.

The kinetics of Cu adsorption on the Al$_2$O$_3$ nano-particles are explored using pseudo-first-order and pseudo-second-order kinetics to further understand the adsorption mechanism. The pseudo-first-order and pseudo-second-order kinetics are based on the
The adsorption capacity of the adsorbent. The pseudo-first-order reaction can be calculated by the following equation:

\[-\ln \left( \frac{C_t}{C_0} \right) = k_{\text{app}} t\]  

(8)

where \(C_0\) is the initial concentration and \(C_t\) is the time-dependent residual concentration of Cu ion solution and \(k_{\text{app}}\) is the rate of Cu removal from water.\(^{46}\)

The pseudo-second-order reaction model is presented as follows:

\[\frac{t}{Q_e} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}\]  

(9)

where \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is a rate constant of the pseudo-second-order kinetic model, and \(Q_e\) and \(Q_t\) (mg g\(^{-1}\)) are the amount of Cu adsorbed per unit mass of the nano alumina samples at the equilibrium and time \(t\), respectively. \(Q_e\) can be calculated using the following equation:\(^{18}\)

\[Q_e = (C_0 - C_e) V / W\]  

(10)

where \(V\) (L) is the volume of Cu solution, \(W\) (g) is the mass of inserted adsorbent in the experiment, and \(C_e\) is the concentration at the equilibrium.

The plots of \(t / Q_e\) versus contact time are depicted in Figure 9 for synthesized nano alumina at pH=5.79 and straight lines are fitted to find some information about the kinetics of Cu adsorption on the synthesized nano alumina in the range of 2 to 1440 min. Also, the plots of \(-\ln \left( \frac{C_0}{C_t} \right)\) versus contact time are represented in the inset of Figure 9 for the samples, and straight lines are fitted to the data. Rate constants of the pseudo-first and pseudo-second-order kinetic model (\(k_{\text{app}}\) and \(k_2\)) of the samples for Cu removal from acidic water are calculated and gathered in Table 6. As it can be observed, the kinetics of Cu adsorption on the Al\(_2\)O\(_3\) nanoparticles does not match with pseudo-first-order but the adsorption process is well-matched with pseudo-second-order with the \(R^2\) (correlation coefficients) greater than 0.994. Previously, Ren. yu Wang et al. reported the pseudo-second-order kinetics model for Cu adsorption by their synthesized alumina nanoparticles\(^{43}\) and the results are consistent with this study in the case of the adsorption mechanism. It is also worth mentioning that the largest value of \(k_2\) in the acidic condition is obtained for the sample RA-06 and this Al\(_2\)O\(_3\) sample can be a good candidate for Cu ions removal from alkaline, normal, and even acidic water.
Table 6: Parameters of the adsorption isotherm model for copper adsorption by our synthesized nano-alumina in acidic simulated water (pH=5.79).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$k_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA-0.6</td>
<td>0.00237</td>
<td>0.436</td>
<td>16.9</td>
<td>0.999</td>
</tr>
<tr>
<td>RA-0.8</td>
<td>0.00577</td>
<td>0.996</td>
<td>4.51</td>
<td>0.998</td>
</tr>
<tr>
<td>RA-1</td>
<td>0.00206</td>
<td>0.968</td>
<td>3.50</td>
<td>0.994</td>
</tr>
<tr>
<td>RA-1.2</td>
<td>5.21E-04</td>
<td>0.699</td>
<td>8.32</td>
<td>0.997</td>
</tr>
</tbody>
</table>

**Conclusion**

In summary, the alumina nanoparticles were prepared by the Co-precipitation method with high specific surface areas (SSA) and were employed as adsorbents for Cu adsorption. In this work, ammonium bicarbonate was used as a precipitating agent in different masses, and the effects of ammonium bicarbonate concentration on the structural and optical properties of the synthesized nano-alumina were investigated. In all concentrations of the precipitating agent, Al$_2$O$_3$ nanoparticles were successfully produced. Also, the concentration of the precipitation agent affects the nanoparticles and crystallite sizes. Furthermore, the highest specific surface area (317 m$^2$/g) (SSA) as well as the highest percentage of pollutant adsorption in acidic simulated water were obtained with nano-alumina synthesized with the precipitating agent mass of 0.6 g. Indeed, the adsorption of copper ions and removal efficiency depends on the contact
time and pH of the solutions. It rises with the increase of contact time and the best Cu removal is obtained in neutral and alkaline conditions. However, the removal efficiency of the nano-alumina samples synthesized by the precipitating agent mass of 0.6 g is significantly high in the acidic medium and reaches 98.7% in a contact time of 120 min, which is a high value in the acidic condition and suggests the nano-alumina as an excellent candidate for even acidic water treatment. Also, the study of the adsorption mechanism declares that all synthesized nano-alumina follows the pseudo-second-order kinetics model.

availability of data

All data included in this paper are available upon request by contact with the contact corresponding author.

References:

14. Mahdavi, S., Jalali, M. & Afkhami, A. HEAVY METALS REMOVAL FROM AQUEOUS SOLUTIONS
USING TiO$_2$, MgO, AND Al$_2$O$_3$ NANOPARTICLES Heavy Metals Removal from Aqueous Solutions. 6445, (2016).


