CO-PRECIPITATION SYNTHESIS AND CHARACTERIZATION OF ALUMINUM OXIDE NANOPARTICLES AS CATALYST FOR THE REMOVAL OF REACTIVE BLUE 4 DYE FROM AQUEOUS SOLUTIONS

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Abstract: Calcinations of aluminum hydroxide (gibbsite) leads to a series of phase transitions. These phase transitions affect the properties and activity of the resulting aluminum oxide. During this work, aluminum oxide nanoparticles were prepared by co-precipitation method with calcination of the resulting aluminum hydroxide at two different temperatures (600°C and 1000°C). The structural properties of the resulting aluminum oxides were investigated using X-ray diffraction, Fourier Transform infrared analysis, and Field Emission Scanning Electron Microscopy. The results indicate the formation of the amorphous γ -AlOOH and γ- Al_2O_3 phases upon calcination of aluminum hydroxide at 600°C, while the γ-Al_2O_3 and α-Al_2O_3 phases are formed at calcination at 1000°C. Also, a change in the shape and size of the formed crystals was observed with the increase in temperature. The efficiency of the prepared oxides at different temperatures was compared in removing the reactive blue 4 dye by adsorption method from the aqueous solution and it was found that amorphous aluminum oxide is more effective in removing the polluting dye.

Keywords: Aluminum oxides nanoparticles, Phase transition,Calcination temperature , Adsorption

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INTRODUCTION

Aluminum oxide (Al_2O_3) fundamentally prepare by calcinations of aluminum hydroxides precursors, which may be in gelatinous and crystalline forms. Essentially, the aluminum hydroxides with crystalline forms contain two type of AlOOH aluminum oxyhydroxides (diaspore and boehmite) and three type $Al(OH)_3$ aluminum trihydroxides (nordstrandite ,gibbsite and bayerite). The crystalline hydroxides can be obtaine in the nature and obtaind from synthesis in different methods or from bauxite[1].

Phase transformations and sequence of decompositions of the aluminum oxide provided by Calcinations of gibbsite $Al(OH)_3$ to the phases have more stable by higher temperatures. The series of transformations at increases the calcination temperature include aluminum trihydroxides → Boehmite/amorphous (gama -AlOOH) → gama- aluminum oxide → Delta- aluminum oxide → theta- aluminum oxide → alpha- aluminum oxide[2] .

When calcined γ-Al_2O_3 above 800 °C converts to δ- Al_2O_3 the latter transforms into θ- Al_2O_3 when increase calcined temperature above 1000 °C and when calcined θ- Al_2O_3 above 1100 °C converts to α- Al_2O_3.However,the existence of impurities changes the impediment transformations of phase, addion 3% platinum to γ- aluminum oxide is considered an impurity that reduces the degree of calcination lower 1100 °C [3]. The number of active sites and the surface area it is directly affected by the phase transformations ,which is of great importance in particles applications. Therefore, many studies focused on the effect of calcination temperature on phase transformations and change of aluminum oxide properties and applications [4].

Alumina is reported to exist in several phases but due to of the increased thermodynamic stability upon reaching the critical surface area, as well as the superior microstructural properties, alumina γ- phase is highly desirable [5].

Aluminum oxide is a traditional adsorbent and the phase of γ – Al_2O_3 is in prospect to be more effective in adsorption than α-Al_2O_3. Due to high specific surface, mechanical strength, reactivity and low temperature modification γ – alumina nanoparticles are suggesting material for adsorbent at solid phase [6].

Depending upon the preparation method aluminum oxides vary in their properties: ion exchange properties existent in β-Al_2O_3 ; deficit in crystals found in γ- Al_2O_3. The hydroxides of alumina i.e $Al(OH)_3$ and (boehmite) AlOOH have distinguished adsorptive forces such as ion-exchange, physical

and ion association which are quite explored in chromatographic separations. It is necessary to focus on these different and important phenomena of hydroxides /aluminum oxide nano size and develop easy, economical and environmentally friendly methods to treat water pollutants [7].
Sushmita Banerjee et al. synthesized and applyed of Al_2O_3 nanoparticles for removal of an anionic dye OrangeG from aqueous solutions. the results indecated that the material can be successfully used and re-used for the removal of anionic dyes from the aqueous solutions. [8].
Shokati Poursani et al[9]. Synthesized nano-γ-Al_2O_3 by sol-gel method and studied its sorption nature to the cations Cd^{2+}, Cr^{3+} , Pb^{2+} and Ni^{2+} at 25ºC. The results shown that the adsorption order: $Cr^{3+} > Cd^{2+} > Ni^{2+} > Pb^{2+}$
Hany H et al. prepared Al_2O_3 nano particles from waste alumnium metal and investigated the degradation of the reactive yellow 160 dye by prepared nano Al_2O_3 particles under different conditions Three heated samples are contained mainly of alumina crystalline phase in the nano scale. The order of adsorbability of the synthesized oxides were Alo-110> Alo-600 > Alo-800 > Alo-1050 . For Alo-110 percentage removal of reactive yellow 160 dye reached 100% [10].
Vijaya et al. prepared aluminum oxide nano particles by sol-gel method and has been studied the adsorption of Methylene Blue (MB) azo dye by prepared aluminum oxide nano particles .It was found that aluminum oxide is very effective in removing azo dyes from polluted water[11].
In this paper , the Al_2O_3 nanoparticles synthesized by coprecipitation process with two calcination temperatures (600 ºC and 1000 ºC) and utilized for removal of reactive blue 4 dye RB4 from aqueous solution by adsorption method.

EXPERIMENTAL

Synthesis of alumina nanoparticles
The Al_2O_3 nanoparticles were prepared by co-precipitation method using 0.1M aluminium sulfate $Al_2(SO4)_3$ and 0.2M sodium hydroxide NaOH precursors. Aluminium sulfate was dissolved in deionized water, and to complete the dissolution, it was kept under constant stirring for one hour, sodium hydroxide was slowly added to the aluminum sulfate solution while stirring continuously.
A white solution was obtained which left for one day, then the precipitate was removed and washed by deionized water for some time. With hot air, the precipitate was dried at 80ºC for 48 hour. The product be divided for two parts, one part was calcined at 600 °C and the second part was calcined at 1000 °C for 2 hours to obtain Al_2O_3 nanoparticles. The Al_2O_3 nanoparticles were then characterized using XRD to determine the phase formed and the crystal size .

Adsorption Experiments
The reactive blue 4 dye (RB4) was used as adsorbate in this study. 0.01 g RB4 was dissolved in deionized water to get a 100ppm stock solution. By diluting the stock solution were prepared different working solutions and their absorbance was measured by UV–visible spectrophotometer at wavelength 596 nm.
Effect of Contact Time: The influence of contact time was studied by using 100 ppm of RB4 dye concentration , 0.01 g/10 ml dosage of adsorbets and changing the shaking time between (5-30) minutes at a constant temperature of 25° C.
Effect of adsorbent weight : The adsorbent weight was varied between (0.01, 0.016, 0.023, 0.03 and 0.045) g using a volume of 10 mL of 100 ppm of dye solution at the equilibration time for each adsorbent.
Effect of initial concentration: The removal of RB4 dye was studied at different initial concentration of this dye solution (50-100) ppm at fixed dose of adsorbents 0.01g / 10 ml and contact time (30 min). The removal efficiency of RB_4 dye was calculated using Equation (1)

$$\text{Removal } \% = \frac{A_0 - A_e}{A_0} \times 100 \qquad (1)$$

where , A_0 is the initial absorption of a RB_4 dye solution and Ae is the equilibrium absorption of a RB_4 dye .

RESULTS AND DISCUSSION

Structural properties
FTIR Analysis
By comparing the FTIR spectra of alumina oxides after thermal treatment at 600°C (A) and 1000°C (B) Figure 1 . For both samples A and B FTIR spectrum shows a broad bands at 3458 cm^{-1} , 3425 cm^{-1} attributed to O-H stretching from hydroxyl groups and the band at 1637 cm^{-1}, 1645 cm^{-1} is associated with bending H-O-H bond groups of adsorbed H_2O. Also the broad band at 3458 cm^{-1} that is in the Infrared spectrum of sample A can be described to the Al-O-H vibrations of AlOOH and stretching vibration of OH group in the hydroxide structure in absorbed water. For both samples A and B the symmetric stretching vibration of the Al-O-H occurred at 1258 cm^{-1}, 1247 cm^{-1} and 1163 cm^{-1}, 1153 cm^{-1}, respectively . The peak at 1076 cm^{-1} in sample B was due to the asymmetric stretching Al-O vibration mode of γ-Al_2O_3 [12] and band at 1066 cm^{-1} observed in the A sample is due to the vibration mode of -OH groups on the boehmite.The strong bands between 400 and 800 cm^{-1} for both samples due to Al-O-Al band are assigned to Al_2O_3. Presented results confirm that the product of the synthesis of the sample A is boehmite AlOOH while for the samples B it is aluminum hydroxide $Al(OH)_3$[13].

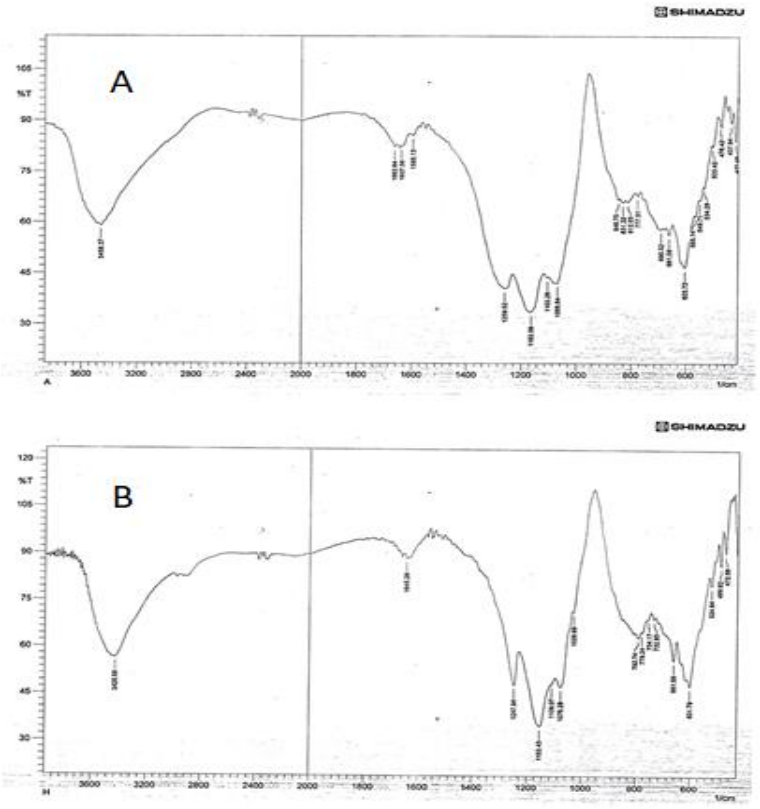

Figure 1. FT-IR spectra for alumina oxides calcined at (A)600°C and (B)1000°C

XRD Analysis

According to the XRD pattern fig.2A who appears result of sample A(calcined at 600ºC),the XRD peaks which observed at 13.32°, 21.4°, 24.2°, 28.67°, 29.62°, 33.1°, 35.2°, 38.35°, 40.3° and 44.2°showed mixed phases of pseudoboehmite γ-AlOOH, boehmite $Al(OH)_3$ and γ-Al_2O_3. There was a small protuberance at 13.32°, which revealed the existence of γ-AlOOH (JCPDS 21-1307)[14].

The XRD pattern for sample B (calcined at 1000 ◦ C) fig. 2B shown there was in addition to peak indicating γ-AlOOH formation at 13.32°, 18.7° and 21.46° that characteristic reflections at 2θ =31.88º, 37.3º, 45.8º,60.9º and 66.97º detect the cubic γ-Al_2O_3 formation. The achieved peaks give well agreement with (JCPDS card 00-029-0063) standards' database [15,16]. The XRD peaks which could be observed at 2θ =25.6º, 35.5º, 43.6º,52.52º , 59.3and 64.0º reveal the formation of the rhombohedral α-Al_2O_3 [16].

Debye-Scherrer equation (2) was used to determine the average size of the crystals[17]. The obtained value of zise of A and B samples are found to be 39 nm and 32 nm respectively

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

Where, K is the constant has value 0.9, D is the crystalline size, λ is the wavelength of incident beam , θ is the Bragg's angle ,β equal to (FWHM) represent the broadening half of its maximum intensity.

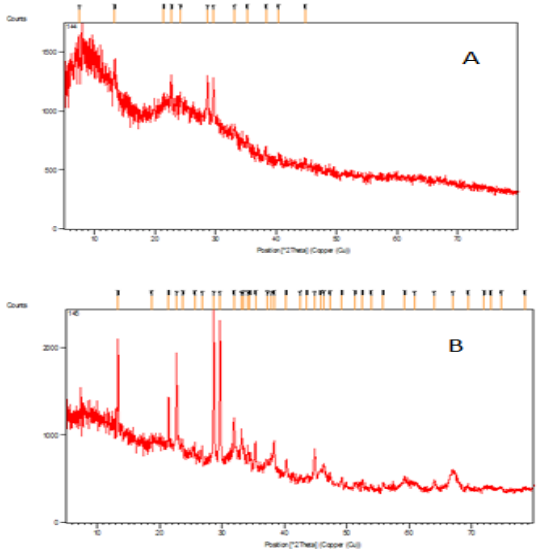

Figure 2. XRD pattern for alumina oxides calcined at (A)600°C and (B)1000°C

FE-SEM Analysis

Figure.3 show (FE-SEM) images of Al_2O_3 nanoparticles through two calcination temperature.It be able to seen from the fig. 3A Al_2O_3 nanoparticles when calcination at 600 ºC has large heterogeneous aggregation with mixture of spherical irregular and cylindrical shapes, this large aggregation of molecules is expected to give high energy to the surface [18].

The sample calcinated at 1000ºC figure.3B was composed of less aggregated spherical submicronsized particles due to the influences of evaporation of absorbed water and reorganization of the grains [19].The EDX of the synthesized oxides showed peaks confirming the presence of Al, and O elements.

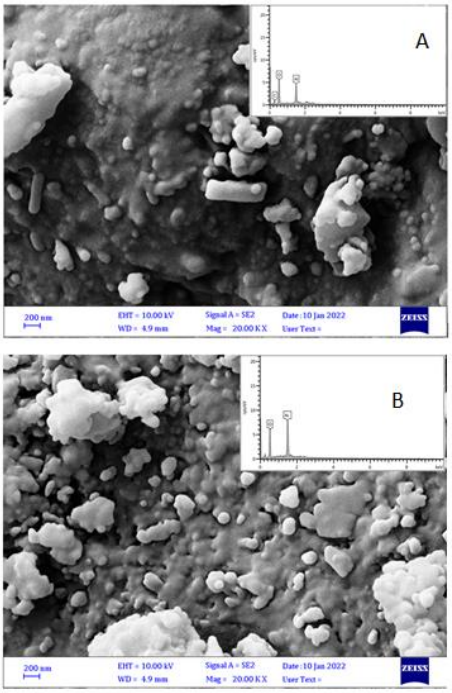

Figure 3. FE-SEM images and EDX of alumina oxides calcined at (A)600°C and (B)1000°C

Activity of Al_2O_3 in the removal of RB4 dye solution

As shown in Figure 4, Al_2O_3 that calcined at 600ºC (A) have more activity than Al_2O_3 sample that calcined at 1000ºC (B) under a presented weight loading (0.01 g/L) although B sample has a crystal size (32nm) less than that of form sample A(39nm) . It was found that the adsorption capacity decreases with the decrease in the size of the nanoparticles (Al_2O_3). This is due to a factor other than crystal size, amorphous Al_2O_3 have considerably defect density on surface compared to crystalline Al_2O_3 since its structure is not periodic .These defects act as effective sites on the surface[20]. Therefore, amorphous Al_2O_3 particles calcined at 600ºC have a higher adsorption efficiency compared with crystalline Al_2O_3 particles.

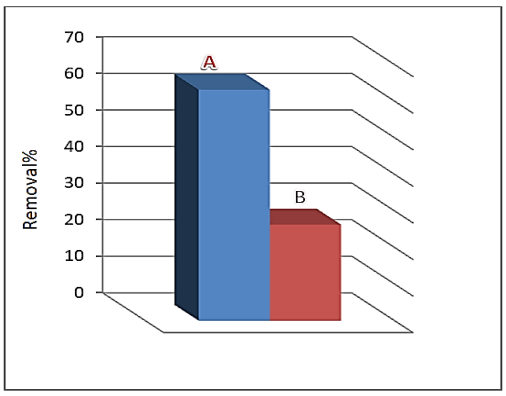

Figure 4. Comparison of the adsorption efficiency of RB4 dye for alumina oxides calcined at (A)600°C and (B)1000°C.

Effect of Initial Concentration

The effect of initial concentration of RB4 dye solution on adsorption efficiency was shown in figure 5. By using initial concentration (50 , 60, 70, 80,90 and 100) ppm with constant all other condition. The removal efficiency of dye decreases with an increase in its initial concentration because of the deficiency of ready active sites in elevation concentration of dye [21] for two aluminum oxides type , but surface that calcined at 600ºC was more active than aluminum oxides calcined at 1000ºC, the high activity of amorphous sample A was attributed to the rich defective unsaturated sites, which enhanced the dye adsorption[22].

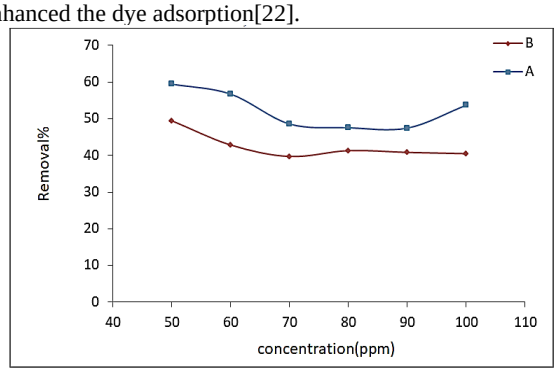

Figure 5. Effect of Initial Concentration of RB4 dye on adsorption efficiency of alumina oxides calcined at (A)600°C and (B)1000°C

Effect of adsorbent dosage

When Al_2O_3 amount increases with remaining concentration of dye solutions , temprature and contact time at constant value efficiency of removal initial increases, reaches the maximum and next decreases for alumina oxides calcined at 600°C and 1000°C figure.(6) because with increase in adsorbente amount numeral of active sites is lower where aggregation of particles happen, as a result of this efficiency decreases[23]. Sample Al_2O_3 calcined at 600ºC gave maximum efficiency at 0.016 g but Al_2O_3 calcined at 1000ºC at 0.03g

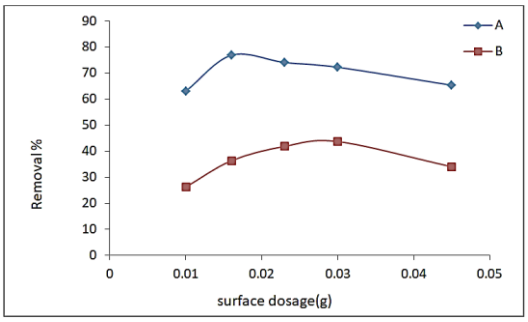

Figure 6. Effect of adsorbent dosage of alumina oxides calcined at (A)600°C and (B)1000°C on removal efficiency of RB4 dye solution

Effect of Contact Time

Figure 7 shown the relation between the removal efficiency and the contact time at 100ppm initial RB4 dye concentration,0.01g of surfaces dosage and 25ºC. Efficiency first time increased from 34 to 71% after 20 minute for Al_2O_3 sample that calcined at 600ºC and then it dropped to 65% and remained almost constant just when of adsorption is varied from 5 to 30 minutes. When using Al_2O_3 sample that calcined at 1000ºC, the removal percentage increased with time from 25 to 30% after 20 minute, and then it was fixed at 29%. The increase in adsorption initially indicates the abundance of active sites available on the Al_2O_3 surface for adsorption the dye molecules[24].

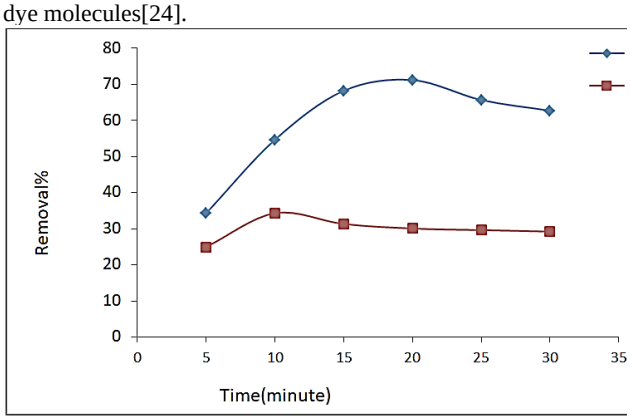

Figure 7. Effect of Contact Time on adsorption efficiency of alumina oxides calcined at (A)600°C and (B)1000°C on removal efficiency of RB4 dye solution

CONCLUSION

Al_2O_3 nanoparticles were synthesized through coprecipitation method and calcined at two different temperatures (600°C and 1000 °C) . Amorphous γ-AlOOH , γ- Al_2O_3 phase of aluminum oxide were formed at 600°C and γ- Al_2O_3, α-Al_2O_3 formed at 1000°C . Crystallite size are affected by calcination temperature and decreases with its increase. By increasing the calcination temperature the removal efficiency of reactive blue dye solution was decreases.

Ethical approval: The research includes the preparation of aluminum oxide nanoparticles in different temperatures and its use in the purification of water from reactive blue dye. It does not include any in vitro or in vivo experiments, so it does not require ethical approval.

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Conflict of interest:N/A

Informed consent: The study does not include a case in which researchers need to use and submit an informed consent form.

Authorship

Hanaa Kadtem Egzar: wrote the manuscript with support from Nuha Abdul-Saheb Ridha.

Eman Hassan Sahap : carried out the experiment with support from Hanaa Kadtem Egzar. **Amer Muosa Juda** : conceived of the presented idea.

All authors discussed the results and contributed to the final manuscript

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