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Anion effect on obtaining nano-sized metal particules by reduction reaction

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ABSTRACT

The word “nano” means; one in a billion of a physical mass. Nanotechnology has been frequently beneficial branch of science in recent years by applying nanoparticules to various fields. Synthesis of particules in nano is size, has increased the covered surface area in unit volume and this made expanding of using nanoparticules in many different areas. Especially the metal nanoparticules have many advantages leading to development of many ways of synthesis. One of these methods of synthesis is “chemical reduction”. This work makes a research on the anion effects on the size mass nanoparticules of metals Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) after reduction to nano size of sodium bor hidrur which belongs to salt of acetate and chloride, nitrate, sulfate. Depending on the radius ratios and solubility values of metal cations and anions, the nanoparticule obtained from $Cu(CH_3COO)_2$ salt has the smallest radius. Nanometal particules with the largest radius were obtained by reduction of Cl^- ion salts. Size analysis and scanning electron microscope (SEM) analysis made about the characterization of synthesised nano particules.

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1 Introduction

Nanotechnology, which is an up-to-date science, covers the production and applications of particules smaller than 100 nm [1]. The synthesis of nanostructured materials, especially metallic nanoparticules, has attracted great attention over the past decade due to their unique properties that make them applicable in different fields of science and technology [2]. Nanoparticule research is a fascinating science. The largely dimensional properties of nanoparticules offer countless opportunities for surprising discoveries. The often unexpected and unprecedented behavior of nanoparticules has great potential for innovative technological applications [3]. Nanoparticules have a surprisingly long history. Their preparation is neither a specific result of modern research nor limited to man-made materials. Naturally occurring nanoparticules, organic (proteins, polysaccharides, viruses, among others) as well as inorganic compounds Contains (iron oxyhydroxides, aluminosilicates, metals, among others) and are produced by weather conditions, volcano eruptions, forest fires, or microbial processes [4,5].
Transition metal nanoparticules are essential for the possible application of radiating diodes and nano centric chemical sensors in catalysis in quantum computers or other electronic devices. In addition, nanoparticules have important applications in optics, electronics, and magnetic devices. [6].

Metal oxide nanoparticules (MONs) are made entirely from metal precursors [7]. MONs are distinctive materials with properties such as catalytic, magnetic, UV absorption, fluorescent quenching and dielectric properties, photocatalyst oxidative catalyst, and drug release, biocompatibility, biomedical imaging, detection [8-14].

There are many studies on nanoparticules that have gained great attention in the last decade due to their unique properties [15-17]. In vivo and in vitro studies have shown that nanoparticules have toxic effects on living things [15,18-20]. Considering that nanotechnology, which has such fantastic features, will be used more widely in the future, people will come into contact with nanoparticules more. For this reason, the possible negative effects of nanoparticules on human health, especially the respiratory system, should be further investigated in order to prevent the repetition of the "fearful dream of asbestos" by human beings.

In this study, nanoparticule synthesis was carried out by reducing the sulfate, nitrate, chloride and acetate salts of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) metals with the help of sodium borohydride compound and in this way, the effects of the anion on the size of the nanoparticules were investigated. There is a gap in the literature on this issue and we think that the results of this study are important for the scientists who are interested in nanotechnology. For the characterization of obtained nanoparticules, size analysis and scanning electron microscopy (SEM) analysis was performed.

2 Materials and methods

2.1. Chemicals

Sulfate, nitrate, chloride, and acetate salts of copper, nickel, cobalt, zinc, manganese, and sodium borohydride ($NaBH_4$) are supplied from Sigma-Aldrich. All other chemicals used in the study are of analytical purity.

2.2. Synthesis of Nanoparticules

In this study, metal oxide nanoparticule synthesis was applied following the processes. 0.001 mol of transition metal salt and 0.005 mol of $NaBH_4$ were dissolved in 100 mL of distilled water. The pH of the solution was brought to around 6.50 with HCl solution. The solution was then taken into a flask and placed in the assembly consisting of a water bath and a mechanical stirrer. The transition metal solution was stirred for 2.5 hours at 85 °C, 700 rpm. In the last stage, the large particules and unwanted impurities settled at the bottom were filtered under vacuum and the metal oxide nanoparticule solid remaining at the bottom of the flask after the water was removed by the evaporator device was dried with a vacuum oven.

2.3. Characterization Studies

2.3.1. Scanning electron microscope (SEM)

The surface morphology of the synthesized nanoparticules was investigated using scanning electron microscopy (SEM; FEI / Quanta 450 FEG, USA). The sample attached to the SEM holder by double-sided carbon tape was then coated under vacuum with a thin layer of gold. Then the resulting SEM sample was placed in the device and the image was taken.

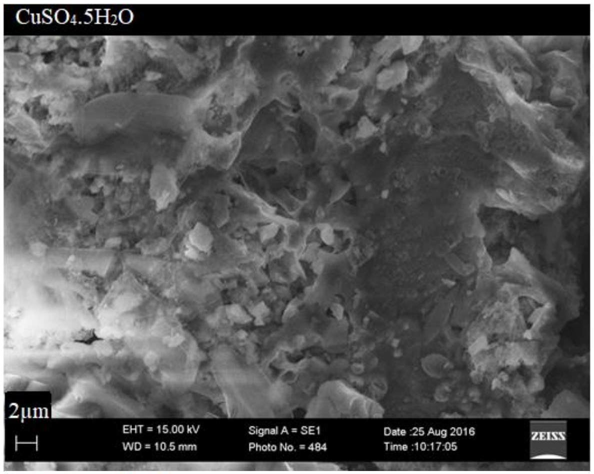
2.3.2. Size analysis

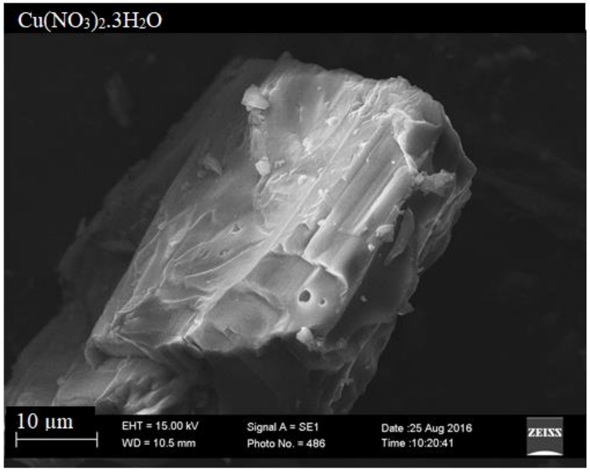
The size of the nanoparticules in the aqueous solution was analyzed. The scattering angle of the laser light passing through the particule depends on the particule size. As the particule size decreases, the scattering angle increases logarithmically. The scattering angles of large particules are low, and the intensity of the scattered laser light is high. In small particules, the scattering angle is high and the intensity of the scattered laser light is low.

3 Results and discussions

3.1. Scanning Electron Microscope (SEM)

SEM images of metal oxide nanoparticules are given in the figures (Fig. 1-5). The images of the nanoparticules obtained by reducing them in 2+ oxidation step with $NaBH_4$ by scanning electron microscopy are given.





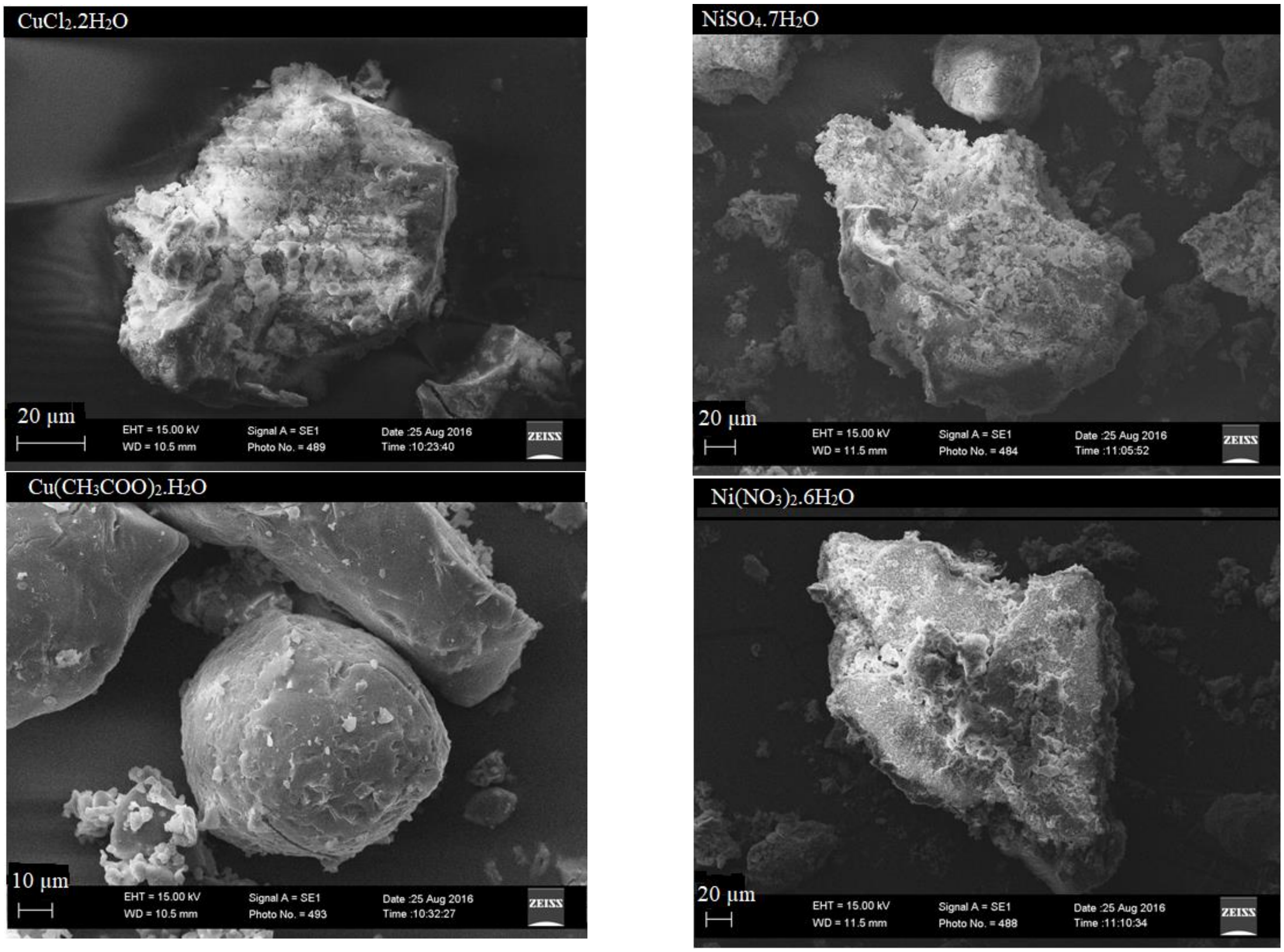


Figure 1. *SEM images of nanoparticules taken from Cu(II) salts.*

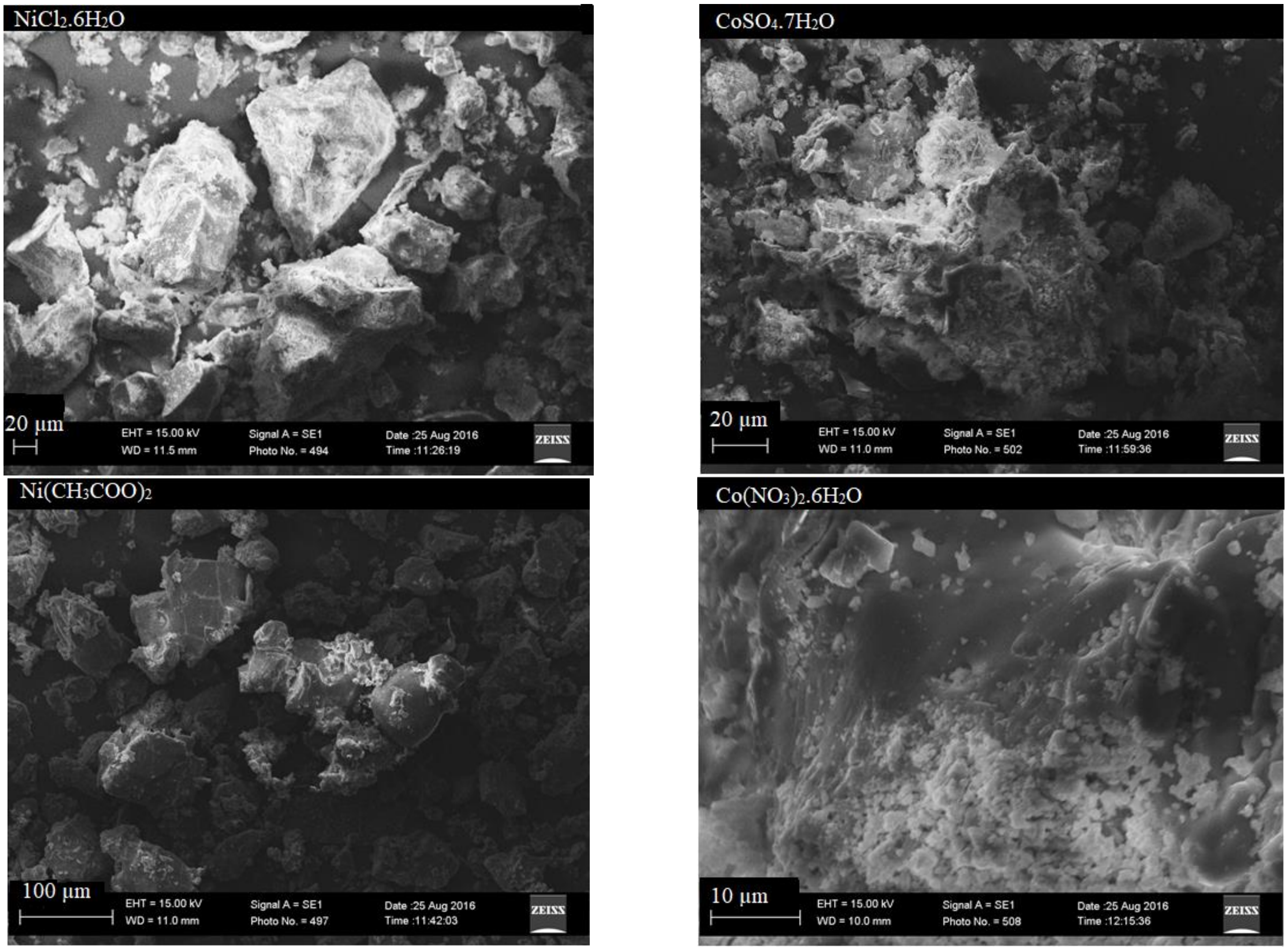


Figure 2. *SEM images of nanoparticules taken from Ni(II) salts*

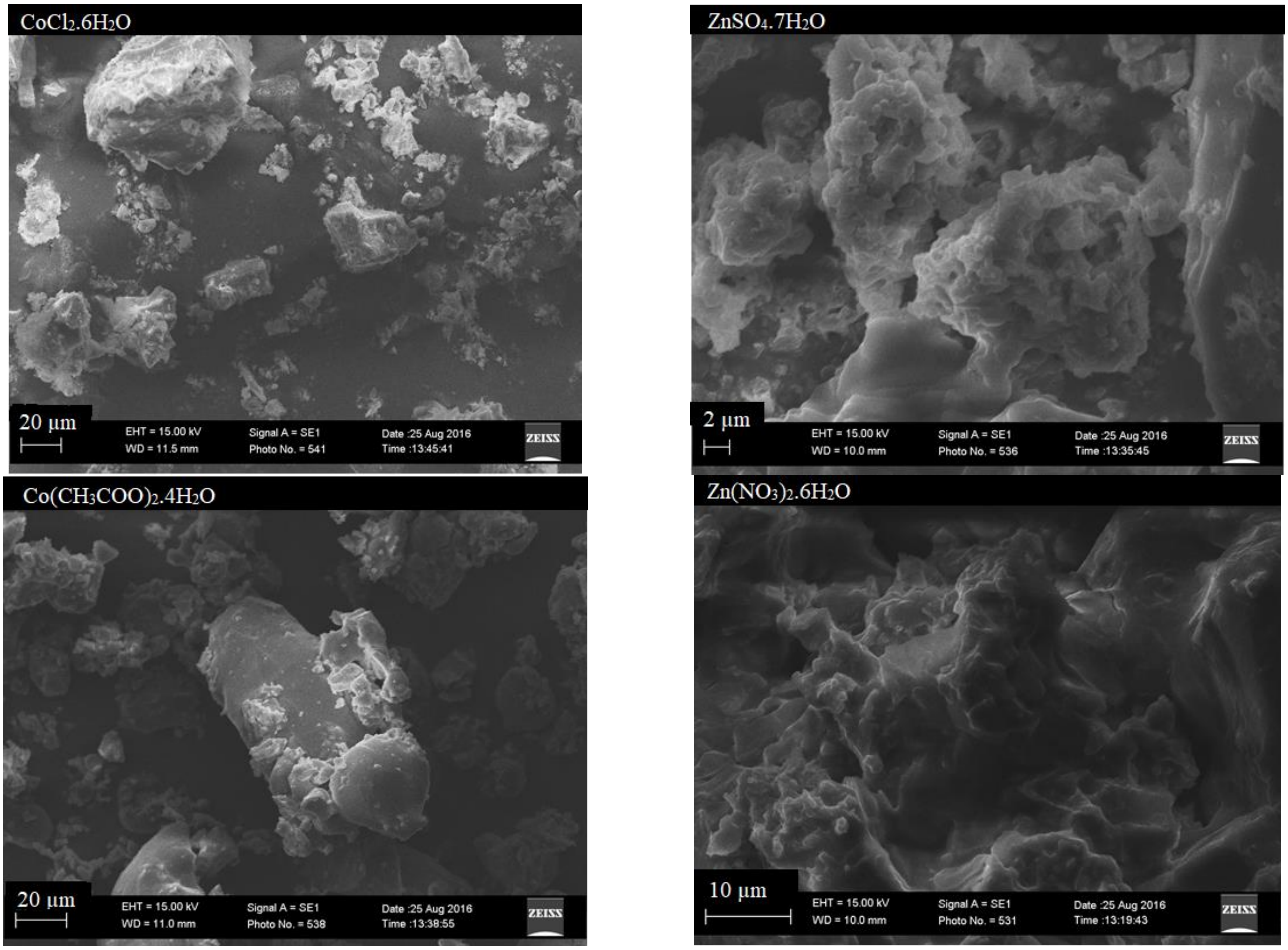


Figure 3. *SEM images of nanoparticules taken from Co(II) salts*

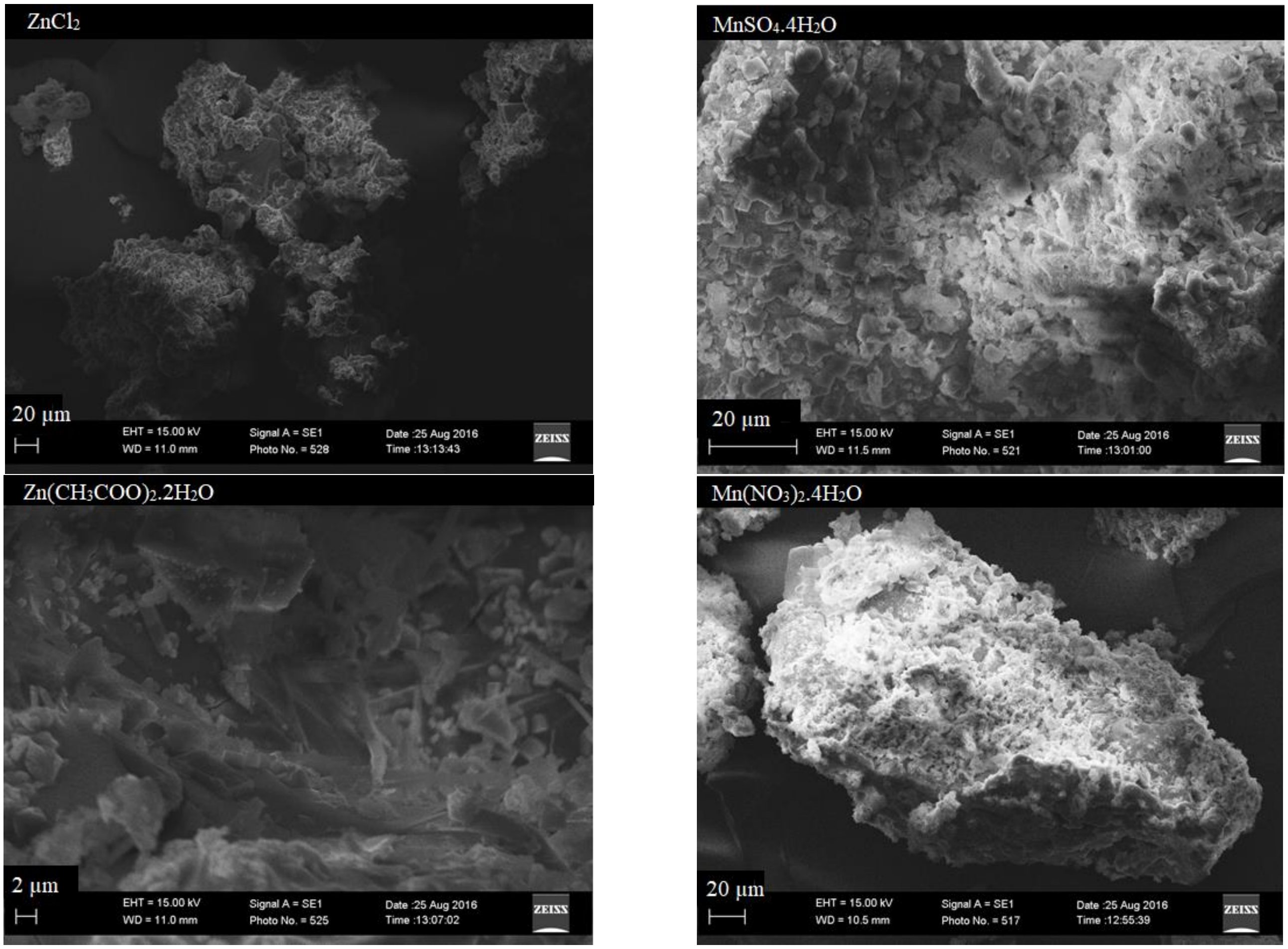


Figure 4. *SEM images of nanoparticules taken from Zn(II) salts*

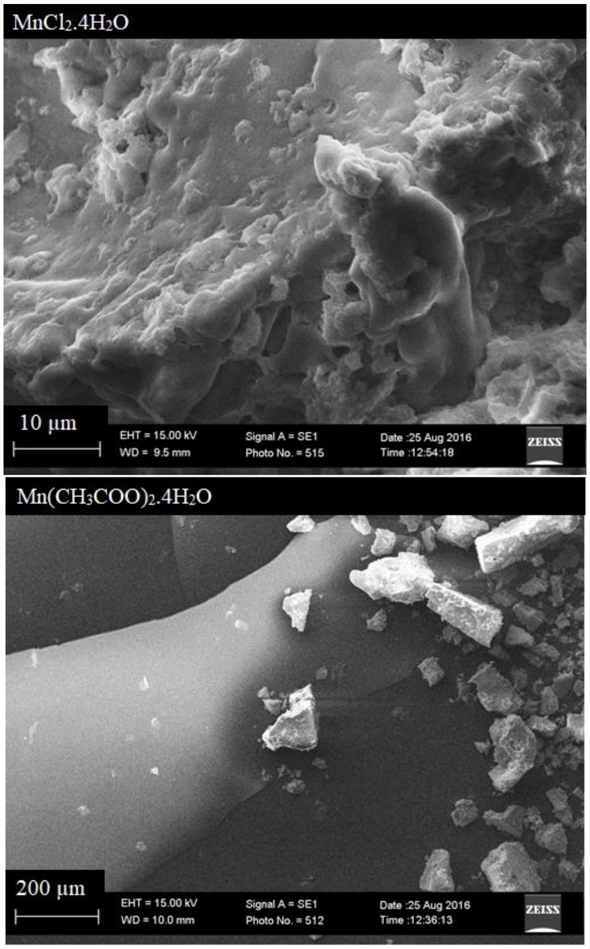


Figure 5. *SEM images of nanoparticules taken from Mn(II) salts*

3.2. Size Analysis

The results of the size analysis of nanoparticule metal powders performed by the Zeta-Sizer method are given in Table 1. The smallest size nanoparticule Zeta-Sizer plots are shown in Figure 6. The largest size nanoparticule Zeta-Sizer plot is shown in Figure 7.

Table 1. *Size analysis of nanoparticules.*

Anion	Cu (nm)	Ni (nm)	Co (nm)	Zn (nm)	Mn (nm)	Ave. (nm)
Sulfate	40.49	369.2	1.553	0.8212	0.8907	82.59
Nitrate	281.0	2.171	0.6823	0.7146	770.4	210.99
Chloride	546.9	243.4	307.4	338.8	543.7	457.52
Acetate	0.6393	2.710	364.2	0.6835	0.6696	73.78
Average	294.11	154.37	168.45	85.26	328.92	

When the size analysis of metal salts is examined in the light of the data summarized in table 1, the following order of salts from small to large is formed according to the size of the particles obtained.

$$\mathrm{Cu(CH_3COO)_2 < Mn(CH_3COO)_2 < Co(NO_3)_2 < Zn(CH_3COO)_2 < Zn(NO_3)_2 < ZnSO_4 < MnSO_4 < CoSO_4 < Ni(NO_3)_2 < Ni(CH_3COO)_2 < CuSO_4 < NiCl_2 < Cu(NO_3)_2 < CoCl_2 < ZnCl_2 < Co(CH_3COO)_2 < NiSO_4 < MnCl_2 < CuCl_2 < Mn(NO_3)_2}$$

When anion-based size analysis is examined, the following order is formed from small to large.

$$\mathrm{CH_3COO^- < SO_4^{-2} < NO_3^- < Cl^-}$$

When the cation-based size analysis is examined, the following order is formed from small to large.

$$\mathrm{Zn^{+2} < Ni^{+2} < Co^{+2} < Cu^{+2} < Mn^{+2}}$$

4

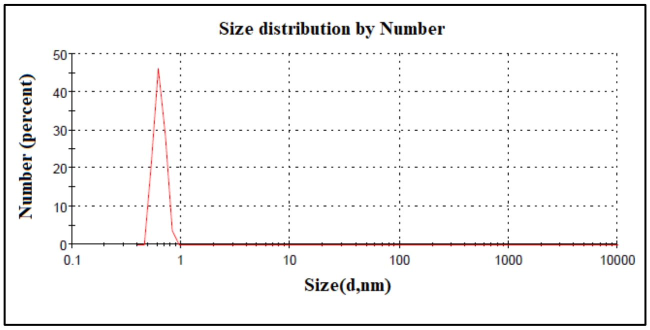


Figure 6. *Smallest size nanoparticule particules Cu(CH$_3$COOH)$_2$*

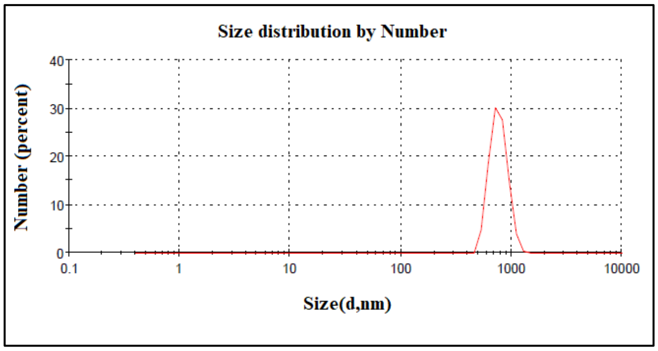


Figure 7. *Largest size nanoparticule particule Mn(NO$_3$)$_2$*

In Table 2 of the metal salts we used in our study, the radius values of the cations with 2+ oxidation steps are given. When these values are examined, it is seen that they change differently from the expected order in the periodic table.

$\mathrm{Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}}$ expected order in the periodic table

$\mathrm{Co^{2+} < Cu^{2+} < Mn^{2+} < Ni^{2+} < Zn^{+2}}$ actual size order of metal cations with +2 charge valence

Table 2. *Cation radius values [21]*

Cation	Radius(pm)
Co^{+2}	65(ls), 74,5(hs)
Cu^{+2}	73
Mn^{+2}	81(ls), 97(hs)
Ni^{+2}	83
Zn^{+2}	88

ls: low spin, hs: high spin

The behavior they show differently from what is expected in the periodic table can be attributed to the change in electronic configurations of the metal cations when they turn into the +2 oxidation step form. The Mn^{2+} cation, which is expected to have the smallest radius, becomes stable by distributing all the electrons it has in the form of d^5 semi-full stability to the *3d* orbitals one by one, which causes its radius to increase. The fact that the Ni^{2+} cation is smaller than the Cu^{2+} cation can also be attributed to the difference in the expected +2 metal cation electronic configuration compared to the lean electronic configurations of the metal [22], [23].

When the radius values of the anions given in Table 3 are compared, it has been determined that SO_4^{2-} anion has the largest radius value and CH_3COO^- anion has the smallest value according to the expected conventions.

Table 3. *The radius values of anions [24]*

Anion	Radius (nm)
CH_3COO^-	162
NO_3^-	179
Cl^-	184
SO_4^{2-}	258

As the cation / anion ratio of the ionic salts formed by the hard acid - hard base and soft acid - soft base binary compounds approaches 1, the solubility properties are expected to decrease due to the increasing covalent character. When the solubility values of the metal salts given in g / ml in an aqueous medium at 20 °C in Table 4 are examined, they show the expected changes (due to the periodic table exceptions), including small deviations.

Table 4. *The solubility values of the metal salts [16]*

Metal Salt	Solubility (g/100mL, 20°C)
$Zn(CH_3COO)_2.2H_2O$	43.0
$Zn(NO_3)_2.6H_2O$	184.0
$ZnSO_4.7H_2O$	96.0
$ZnCl_2$	395.0
$Cu(CH_3COO)_2.H_2O$	7.2
$Cu(NO_3)_2.3H_2O$	125.0
$CuSO_4.5H_2O$	32.0
$CuCl_2.2H_2O$	73.0
$Co(CH_3COO)_2.4H_2O$	38.0
$Co(NO_3)_2.6H_2O$	134.0
$CoSO_4.7H_2O$	36.2
$CoCl_2.6H_2O$	52.9
$Ni(CH_3COO)_2.4H_2O$	182.0
$Ni(NO_3)_2.6H_2O$	238.5
$NiSO_4.7H_2O$	75.6
$NiCl_2.6H_2O$	254.0
$Mn(CH_3COO)_2.4H_2O$	23.3
$Mn(NO_3)_2.4H_2O$	380.0
$MnSO_4.4H_2O$	70.0
$MnCl_2.4H_2O$	198.0

Comparisons of metal salts based on +2 metal cations are as follows, but the anion salts with the highest solubility are salts with Ni^{2+} metal cations, and the anion salt group with the lowest solubility is salted with Cu^{2+} metal cation.

$Cu(NO_3)_2 > CuCl_2 > CuSO_4 > Cu(CH_3COO)_2$	59,30
$Co(NO_3)_2 > CoCl_2 > Co(CH_3COO)_2 > CoSO_4$	65,28
$Mn(NO_3)_2 > MnCl_2 > MnSO_4 > Mn(CH_3COO)_2$	167,82
$ZnCl_2 > Zn(NO_3)_2 > ZnSO_4 > Zn(CH_3COO)_2$	179,50
$NiCl_2 > Ni(NO_3)_2 > Ni(CH_3COO)_2 > NiSO_4$	187,53

Unlike NO_3^-, Cl^- and CH_3COO^- anions with 1- oxidation step, SO_4^{2-} anion with -2 oxidation step will create a desire to give stronger electrons than other anions in order to reduce the electronic stress caused by the -2 charge in its structure. For this reason, compared to the radius ratios of other anions, it will perform a stronger ionic interaction with metal cations, and consequently, the solubility of the salt compounds it creates will be higher than expected.

As a result of the interaction of the aqueous solutions of the metal salts with the strong reducing sodium borohydride ($NaBH_4$), the order of the particule size of the metal oxide nanoparticules obtained from the reduction of the metals from the M^{2+} oxidation step to the M^0 plain metal form is as follows:

$$Cu(CH_3COO)_2 < Mn(CH_3COO)_2 < Co(NO_3)_2 < Zn(CH_3COO)_2 < Zn(NO_3)_2 < ZnSO_4 < MnSO_4 < CoSO_4 < Ni(NO_3)_2 < Ni(CH_3COO)_2 < CuSO_4 < NiCl_2 < Cu(NO_3)_2 < CoCl_2 < ZnCl_2 < Co(CH_3COO)_2 < NiSO_4 < MnCl_2 < CuCl_2 < Mn(NO_3)_2$$

When the anion radius order of the salts from which the metal nanopowder is obtained was examined, it was determined that the salts with acetate anion formed the smallest particules, while the radius average of the metal nanopowder from the chloride anion-containing salts was the largest.

The anion-based particule size order of nanopowders obtained from metal cation salts by reduction with $NaBH_4$ is as follows.

$$CH_3COO)_2^- < SO_4^{2-} < NO_3^- < Cl^-$$

The cation-based particule size order of nanopowders obtained from metal cation salts by reduction with $NaBH_4$ is as follows.

$$Zn^{2+} < Ni^{2+} < Co^{2+} < Cu^{2+} < Mn^{2+}$$

The smallest particule size among the cations was obtained in Zn(II). Among the anions, the smallest size is reached in the acetate anion. Accordingly, it can be said that the higher solubility of zinc acetate in aqueous media compared to other salts caused the nanoparticules to be smaller in size. Based on the same idea, copper(II) chloride salt, which dissolves relatively slowly in aqueous media, was also identified as the largest particule.

The smallest metal oxide nanoparticules were formed as a result of the reduction of the salt compounds containing the lowest solubility of CH_3COO^- anion according to the radius ratios of the cations and anions given above accordingly increasing or decreasing solubility values. In particular, the nanoparticule obtained from the $Cu(CH_3COO)_2$ salt has the smallest radius. Metal oxide nanoparticules with the largest radius were obtained by reducing the Cl^- ion salts in contrast to those obtained from the NO_3^- ion salts with the highest solubility. The reason is that the average solubility values of the salts formed by chloride and nitrate anions are very close to each other.

5 Conclusion

As a result of the study, metal oxide nanoparticules of the smallest size were obtained from metal salts formed by metal cations and acetate anions. Although the solubility of the metal salts formed by the acetate anions is less than that of the others, the controlled reduction of the metal cations in the solution may have caused this result. We think, metal oxide nanoparticules obtained by reducing metal salts that have a higher solubility in an aqueous medium with $NaBH_4$ are grown as a result of agglomeration.

When the cation radius of the salts from which metal nanopowders are obtained is examined, it is expected that the particule size of the nanopowders obtained from the Zn^{2+} cations with a radius greater than the other cations is the smallest, and the radiuses of the nanometal powders obtained from the Co^{2+} cation salts with the smallest radius are expected to have the largest average. However, nanoparticules obtained from Cu^{2+} and Mn^{2+} metal cations were found to be smaller in size. This behavior, which develops differently than expected, can be attributed to the behavior of the Co^{2+} metal cation with high spin and radii of Co^{2+} (with high spin), Cu^{2+}, and Mn^{2+} metal cations very close to each other. According to the anion / cation radius ratio, the particule sizes of the nanopowders obtained from the $Ni(CH_3COO)_2$ and $Mn(CH_3COO)_2$ salts with the lowest solubility are the smallest, and the particule size of the nanopowder obtained from the $Mn(NO_3)_2$ salt with the highest solubility is found to be the highest. The particule sizes of the other metal oxide nanoparticules were also found to be changing (including the exceptions) in parallel with the change in the solubility of the ionic salts.

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