RESEARCH SEPARATE OF SOME HEAVY METAL IONS FROM PLATING METAL WASTEWATER BY FERROMAGNETISM NANO-OXIDE AND FERROMAGNETISM NANO-OH MATERIALS

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ARTICLE INFO

Article history: *Received Nov. 6.2018, Accepted Jan. 6.2019.*

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Abstract

The study evaluated the effect of artificial plating wastewater treatment with the survey parameters: when using ferromagnetic nano ($CoFe_2O_4$) and ferromagnetic Nano-OH material, pH = 5; Ni^{2+} = 25 (mg/l), Cu^{2+} = 25 (mg/), Zn^{2+} = 25 (mg/l). Results of the study on the plating wastewater, the efficiency of removing ion Ni^{2+}, Cu^{2+}, Zn^{2+} when using ferromagnetism nano materials, the results are as follows: Ni^{2+} reached 62.53%; Cu^{2+} reached 69.32% and $\overline{Zn}^{2+}$ reached 61.47%. While, using ferromagnetism nano -OH materials, the results are as follows: Ni^{2+} reached 65.45%; Cu^{2+} reached 67.85% and Zn^{2+} reached 84.20%. In sum, the results of the study indicated the potential of new materials for improving and treating wastewater.

Keywords: *chemical flocculants, Nano-OH material, plating wastewater, perromagnetism*

INTRODUCE

Heavy metal pollution is one of the most serious environmental problems (Dushenkov et al., 1995). Most of heavy metal ions such as copper, nickel, zinc, chromium, etc are present in wastewater of many industries (alloys, battery manufacturing, plating, mining operations,…(Kadirvelu, Thamaraiselvi, & Namasivayam, 2001)). These heavy metal ions are highly soluble in water and are not biodegradable as other organic wastes, so they can easily accumulate in living tissue causing serious health effects for organisms on the earth (Baath, 1989; Barakat, 2011; Ngah & Hanafiah, 2008).

Many methods have been used to remove heavy metal ions before they were released into the environment such as precipitaion, ion exchange, electrolytic filtration and membrane separation (Akbal & Camci, 2011). Adsorption is one of the physical and chemical treatment methods that is found to be effective in removing heavy metals from aqueous solutions without giving rise to any harmful products after treatment (Ngah & Hanafiah, 2008; Hu, Lo & Chen, 2007). At present, the adsorption process combined with magnetic materials was widely used in many applications such as biochemistry, biomolecules, analytical chemistry, mining and recently they were applied in water treatment and environmental applications. Pollutants can be readily removed from magnetic particles by a simple magnetic field and through research reports such as Guo et al., (2014); Zhang et al., (2014); Mittal et al., (2016) showed that magnetic particles are capable of removing heavy metals in wastewater.

This study used $CoFe_2O_4$ magnetic materials synthesized with nano size by co-precipitation method and investigated Ni^{2+}, Cu^{2+}, Zn^{2+} heavy metal ions adsorption in plating wastewater.

MATERIALS AND METHOD

Research subjects: Plating wastewater (Ni^{2+}, Cu^{2+}, Zn^{2+}) with concentration of 25mg/L.

Research Chemitry: H_2SO_4 1N (China), $CuSO_4.5H_2O$ (China, 99%), $CoCl_2.6H_2O$ (China, 99%); $FeCl_2.4H_2O$ (China, 98%); NaOH (China, 96%), SDS (India, 85%); n – hexan (China, 97%); C_2H_5OH (China, 99.7%); NH_4OH (China 25 – 28%); $(CH_3)_2CO$ (China, 95%).

Research Materials: Magnetic nano particles ($CoFe_2O_4$) and nano – OH at dosage of 12,5g/L.

Research Methods: Determinination of pH measured directly with Mettler Toledo pH Meter (2017). Determinination of heavy metal concentration on Atomic Absorption Spectrometer (AAS) (2016).

Materials Preparation: Based on research report of Pui et al., 2011, ferromagnetic nano oxide ($CoFe_2O_4$) were synthesized by co-precipitation method with SDS as the surfactant. The mixture contained 250mL of 0,02M $CoCl_2.6H_2O$ and 0,04M $FeCl_2.4H_2O$ solution and they was stirred with 250m of 111M SDS solution for 30 min, heating to 70±5°C. According to the study results of Vijayaraghavan et al., (2011) explainted that SDS was added as a agent to control particle size and evenly distributed during synthesis. After 5 hours, the nano particles were separated from the solution using an external magnet. The nano was washed with water, ethanol and n-hexan to remove impurities on the particle surface.

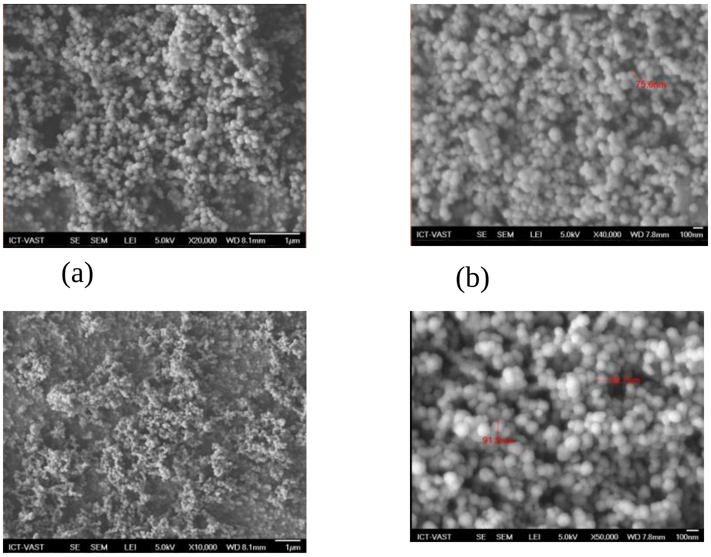
Preparation of ferromagnetic nano –OH oxide particles: the nano particles obtained after synthesising process were dispersed by ultrasound in a mixture of water and ethanol (350mL, 1:1) for 30 min. After that, 35mL of Ammonia was added and stirred at 60±5°C for 24 hours. The resulting mixture was washed with water, ethanol and n-hexan to remove impurities.

RESULTS AND DISCUSSION

Material preparation results

Analysis of SEM

The results of SEM in Fig 3.1 (a) and (B) showed that ferromagnetic nano particles have a high porosity with relatively dense interconnected particles and they are relatively homogenerous in size with a particle diameter of 70 – 95nm. For nano – OH particles, the SEM in Fig 1 (c) and (d) showed that when the –OH groups were added, the size and shape of nano particles are changed negligible.



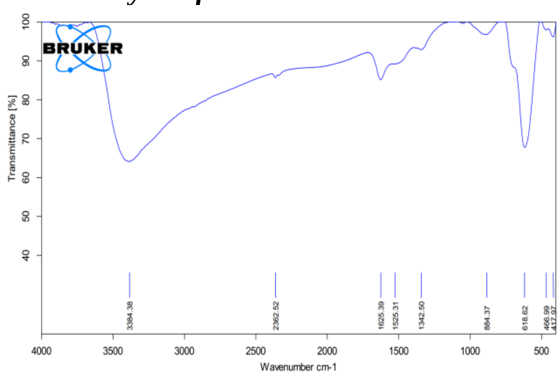
(a) (b)

(c) (d)

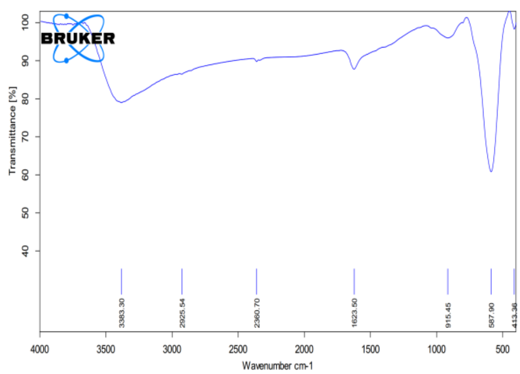
Fig 1. *SEM images of materials* (a), (b): magnetic nano particles (c), (d): nano – OH particles

Comparison to the results of Sadr et al., (2014) suggested that these two sudies have a similarity in particle size. However, the results of particle size in this study are better than those of Pramanik et al., (2005), in results of study of Pramanik et al., (2005) the materials reached the size of 400 – 500nm. Based on the results of several studies, size of ferromagnetic oxide nano particles depended on many factors such as pH, salt concentration, density, stirring speed and SDS concentration (Kim et al., 2003).

Analysis of FT-IR



(a) Ferromagnetic nano oxide



(b) Ferromagnetic nano –OH oxide

Fig 2. *FT-IR schema of materials*

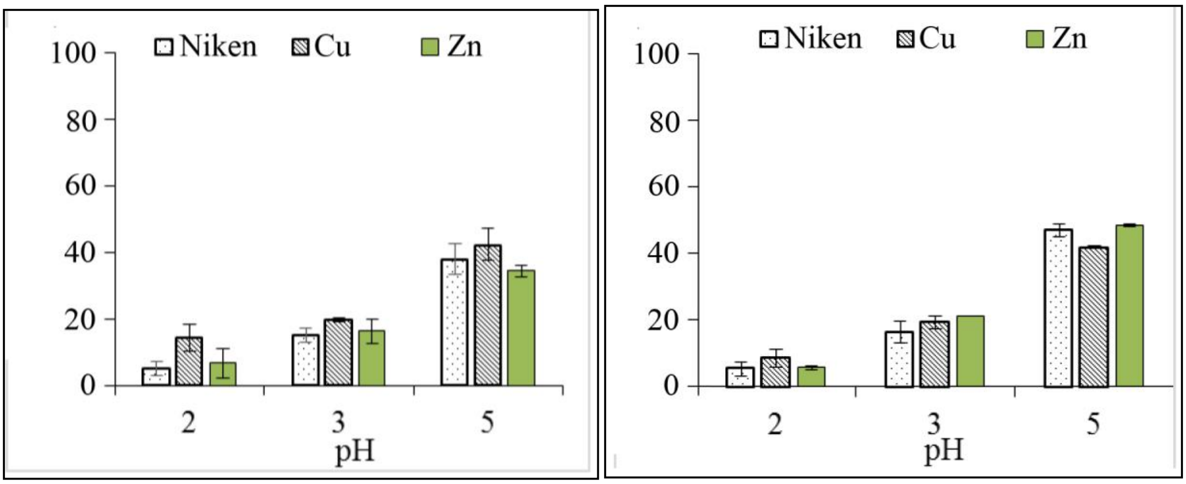
The results of analysis in Fig 2 (a) showed that fluctuating peaks featured functional groups mounted on the surface of $CoFe_2O_4$ material. The –OH group is present at different wavelengths such as 3384 cm^{-1}, which is the oscillating peak of the free water bond and ther are absorbed on the surface of nano particles and at 1625,39 cm^{-1} wavelength may be due to the adsorption of H_2O on the surface of particle (Pui et al., 2011). There are also strong fluctuations at 618,62 cm^{-1}, 446,99 cm^{-1} and 417,97 cm^{-1-} wavelengths corresponding to network fluctuations within the tetrahedral structure of the spinel structure can be thought of as the bonding length of oxygen to metal ions (O-Me) in octahedral holes shorter than the O-Me bond length in the tetrahedral hole (Pui et al., 2011).

When attaching –OH function groups to the surface of nano particles, the fluctuating peak of –OH group at 3383,3 cm^{-1} (Pui et al., 2011) were wider than Nano material. This could prove that the nano particles attached the –OH fuctional group by intermolecular hydrogen bonding. There are also strong oscillations at 587,9 cm^{-1} and 413,36 cm^{-1} wavelengths corresponding to the internal oscillation of the tetrahedral structure coordinates with the octahedron in the spinel structure. It is thought that the bonding length of oxygen to metal ions (O-Me) in the octahedral holes is shorter than the O-Me bond length in the tetrahedral holes (Pui et al., 2011). At the 1623,5 cm^{-1} wavelength, that is also due to the oscillation of the –OH group, this may be due to the adsorption of H_2O onto the surface of the particle (Pui et al., 2011).

The results of preparation of nano particles were similar to those of Pui et al., (2011); Maensiri et al., (2007).

Determination of optimum operating parameter of materials on plating wastewater

Determination of optimum pH



a) Magnetic Nano *b) Nano – OH*

***Fig 3.** The results of determination of optimum pH*

The results of Fig 3 (a) showed that at three differrent pH levels as in the graph, the heavy metal ions removal efficiency of magnetic nano material was the best at pH = 5. The Ni^{2+}, Cu^{2+}, Zn^{2+} ions removal efficiency was 38,11%; 42,40% and 34,53%.

Fig 3 (b) showed that the heavy metal ions removal at many pH levels. It also showed that pH = 5 was the optimum pH for Nano – OH material. The Ni^{2+}, Cu^{2+}, Zn^{2+} ions removal efficiency was 45,03%; 40,12% and 46,53%.

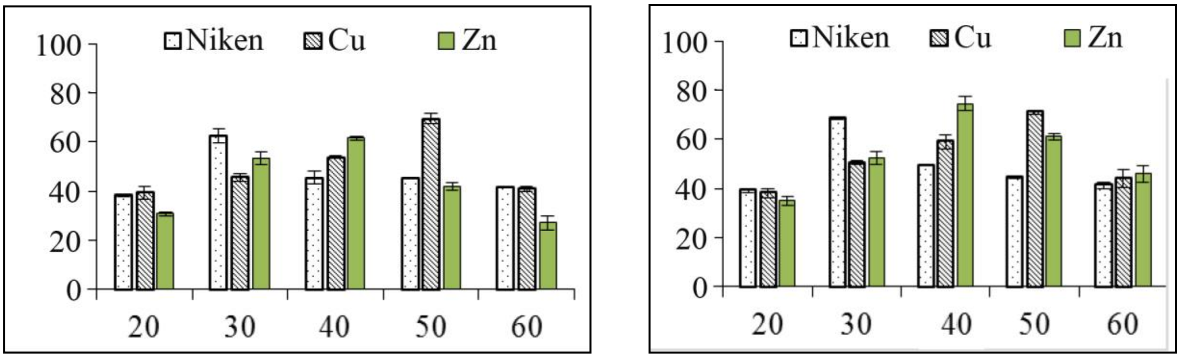
In order to explain for the effect of pH on the removal capable of metal ions, the study showed that metal ion removal capable at the initial pH was the best of the effluent is due to the acidic environment of the H + Nano-iron oxide competition with metal ions, with the smallest size of ions, easily enters and occupies gaps in the ferromagnetic nanoparticle molecules, locating in the molecule Filled and ferromagnetic Nanofibers are no longer capable of capturing metal ions, resulting in reduced treatment efficiency. In addition, the protonation of the -OH groups also reduces the complexity and reduces the metal removal efficiency of the Nano material.

This results showed that the same optimum pH condition, however, the heavy metal ions removal efficiency of Nano – OH and magnetic nano materials were significantly different. Nano materials were added –OH group for better removal capable. They proved that the addition of –OH group allowed material to easily convalently bond with many other metal ions in the solution, resulting in better initial treatment efficiency (Ayhan Demirbas, 2008).

According to research results of Warner et al., (2012), they reported on the use of activated carbon to adsorb Ni^{2+}, Zn^{2+} ions with 37% and 11%. Comparation with the research results of using Nano and Nano - OH materials, they were able to treatment better than the research results of Warner et al., (2012).

The research results of Cu^{2+} ions removal efficiency of using Nano and Nano – OH materials showed that they have a similarity with the study results of Önnby et al., (2010), $HN(CH_2CO_2H)_2$ iminodiacetic acid could be removed 38% Cu^{2+}.

Determination of optimum dosage



a) Magnetic Nano *b) Nano – OH material*

Fig 4. *The results of determination of optimum dosage*

The study results from Fig 4 (a) showed that the optimum pH = 5 and nano particles concentration at 50mL had the highest heavy metal ions removal efficiency in assumed plating wastewater. The results reached 61,47% Zn^{2+}; 62,53% Ni^{2+} and 69,32% Cu^{2+}.

In Fig 4 (b), this study showed that dosage of material were surveyed from 20 to 60mL and optimum pH at 5, the removal efficiency was the best at Nano -OH material concentration of 40mL. The ressearch results reached 84,20% Zn^{2+}; 65,45% Ni^{2+} and 67,85% Cu^{2+}.

When changing the dosage of Nano and Nano –OH materials, the performance of Nano – OH material was better the efficiency of Nano material with significantly higher Zn^{2+} treatment efficiency.

For Cu^{2+} ion removal results, this study was a similarity with the study results of Önnby et al., (2010) when using TBA adsorption gel to treatment Cu^{2+} and reach 63% removal efficiency. The other reported results of Warner et al., (2012), the use of ferromagnetic oxide mixed with 4,5%Mn material treatmented 61% Cu^{2+}. In addition, this materials had Ni^{2+} removal capability better than UF membrane of Akita et al., (1999). According to the study of Akita et al., (1999), the results showed that Ni^{2+} removal efficiency reached 60%.

When comparring the results of Zn^{2+} removal in the effluent solution, it was found that the removal capable of two research materials in this study was more favorable than activated carbon of Önnby et al., (2010), the study showed that activated carbon only reached 11% of the heavy metal ions treatment efficiency.

CONCLUSION

The research results showed that there is a difference between plating wastewater treatment application of Nano and Nano – OH materials. The treatment efficiency of Nano material was quite high with treatment concentration Zn^{2+} < Ni^{2+} < Cu^{2+} corresponding 61,47%; 62,53% and 69,32% at optimum pH = 5 and dose range at 50mL. For Nano – OH material, the removal efficiency of $Zn^{2+}$was 84.20%, while treatment efficiency of Ni^{2+} was 65.45% and Cu^{2+} was 67.85% at pH = 5 and Nano -OH concentration was 40 mL.

The results of the study are the basis for scientific studies to improve the quality of waste water containing other metal components in the future. In addition, the creation of recovered and environmentally-friendly bio-materials can be a research direction in the future.

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