Magnetic-Based Coreshell Nanoparticles as Potential Adsorbents for the Removal of Cu$^{2+}$ Under Ultraviolet (UV) Light

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Abstract. The magnetite ($\text{Fe}_3\text{O}_4$) and maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles, magnetite-silica-silver chloride ($\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AgCl}$) and maghemite-silica-silver chloride ($\gamma\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-AgCl}$) coreshell structures have successfully been synthesized by using a simple wet chemistry method. The efficiency of these particles as the adsorbents for the removal of copper ion, Cu$^{2+}$ in aqueous solution under UV light was investigated. Two different parameters were studied, namely the adsorbents contact time (60, 120, 180, 240 and 300s) and the solution-stirring rate (100, 200 and 300 rpm). From the results, the removal percentage of the copper ions from the solution were above 90% after 5 hours of adsorption process at 300 rpm by using $\text{Fe}_3\text{O}_4$ (94%) and $\gamma\text{Fe}_2\text{O}_3$ (92%) nanoparticles. The maximum removal of copper ions was nearly 100% when $\gamma\text{Fe}_2\text{O}_3$$\text{-SiO}_2\text{-AgCl}$ & $\text{Fe}_3\text{O}_4$$\text{-SiO}_2\text{-AgCl}$ coreshell particles were used. The samples that were prepared without magnetic core such as $\text{AgCl-SiO}_2$, $\text{AgCl}$ and $\text{SiO}_2$ particles, showed lower percentage of the copper ions removal (78%, 60% and 20%, respectively). This situation shows that the magnetic nanoparticles plays an important role during the adsorption process due to their large active sites for the adsorption to occur.

1 Introduction

Numerous industries such as paints, mining operations, metal plating, glass production, pigments and battery manufacturing discharged a large quantities of hazardous heavy metals ions such as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb) and zinc (Zn) [1]. These heavy metals ions leads to the serious health problems such as...
kidney failure, cancer, oral ulcer, renal failure and metabolic acidosis in human, animals and plants [2]. Copper (Cu) has been listed as one of the most widespread heavy metal contaminants in industrial wastewater [3]. Cu also is named as one of the toxic metals to human being as excessive Cu could cause harmful lesions in the nervous system, which lead to permanent damage for children [4]. Conventional wastewater treatment methods such as the ion exchange process, electrochemical removal and chemical precipitation have several disadvantages. For example, high energy requirements, production of toxic sludge, incomplete removal and high cost of operations [5]. Recently, an adsorption process is widely used for copper ions removal treatment due to its simplicity and cost-effectiveness. Consequently, the advancement in nanotechnology gave rise to many nanoparticles be used as adsorbents. For instance, the magnetite (Fe₃O₄) nanoparticles. Fe₃O₄ nanoparticles are being extensively used due to its high surface area which favoured adsorption and simple removal from the solution after used with the help of an external magnetic field. There are several methods for the synthesis of Fe₃O₄ nanoparticles. For example, microemulsion, thermal decomposition [6], co-precipitation [7], etc. Many research have been conducted in the synthesis Fe₃O₄ nanoparticles by using a co-precipitation method. Since the pH of the alkaline solution plays an important role in controlling the size and growth of the synthesized magnetic nanoparticles, the reverse co-precipitation method was applied in this work. Therefore, the pH of the solution can be maintained during the precipitation process. In this research, the Fe₃O₄ nanoparticles have been synthesized by using a co-precipitation method. In addition the maghemite (γFe₂O₃) nanoparticles and the core-shell structure consist of Fe₃O₄-SiO₂-AgCl and γFe₂O₃-SiO₂-AgCl core-shell particles also have been prepared. All these synthesized particles were used in the copper ions removal analysis in order to investigate the efficiency and potential of the synthesized particles to be used as the magnetic nanoadsorbents.

2 Experimental

2.1 Materials and Chemicals

The reagents that were applied consist of iron (II) sulfate heptahydrate, FeSO₄•7H₂O (97%, Sigma-Aldrich), ammonium hydroxide, NH₄OH (25%, J.T Baker), tetraethylorthosilicate, TEOS (98%, Acros), ethanol (96%, Altia), silver nitrate, AgNO₃ (Sigma-Aldrich), sodium chloride, NaCl (37%, Sigma-Aldrich), polyvinylpyrrolidone, PVP (m.w. 10 000, Sigma-Aldrich), copper (II) sulphate, CuSO₄ (60 %, Sigma-Aldrich) and deionized water. All the materials were used without prior purifications.

2.2 Synthesis of magnetite (Fe₃O₄) and maghemite (γFe₂O₃) nanoparticles.

For the preparation of magnetite (Fe₃O₄) nanoparticles, a base solution was made by mixing 50 ml of NH₄OH with 50 ml of deionized water. The iron precursor, Fe²⁺ was prepared separately. In a different beaker, an amount of 0.7 g of FeSO₄•7H₂O was dispersed in deionized water, under ultrasonic agitation for 15 minutes to ensure that all the ferrous salt was dissolved. Then, the Fe²⁺ was added drop-wise into the magnetically stirred base solution under constant stirring for 1 hour. The dark solution was washed with deionized water by centrifugation. The obtained particles were dried overnight at 333 K in the oven and ground. The maghemite (γFe₂O₃) nanoparticles were prepared from the same method as described above, except the ground sample was heat treated at 473 K for 3 hours. The obtained magnetite was labelled as A and maghemite was labelled as B.
2.3 Synthesis of (Fe$_3$O$_4$ & $\gamma$Fe$_2$O$_3$)-SiO$_2$-AgCl coreshell particles

For the synthesis of Fe$_3$O$_4$-SiO$_2$-AgCl coreshell particles, an amount of 200 ml ethanol and 2 ml of tetraethyl orthosilicate (TEOS) was mechanically mixed in 500 ml beaker for 5 minutes, followed by the addition of 14 ml of ammonium hydroxide (NH$_4$OH) drop-wise. After 15 minutes, 0.5 g magnetic nanoparticles dispersed in 10 ml of ethanol solution was added. The solution was stirred for 3 hours to ensure a complete formation of the silica-shell. For AgCl deposition onto the surface of silica, a 10 ml of 0.05 M AgNO$_3$ solution was added into the magnetite-silica coreshell solution. The mixture was stirred for 1 hour in order to ensure the adsorption of Ag$^+$ ion onto the silica surfaces. Then, a 10 ml of 0.05 M of polyvinylpyrrolidone (PVP) and 2 ml of 0.3 M of NaCl solution was added. The mixture was stirred continuously for 2 hours then washed with deionized water for the removal of the excess PVP by a centrifuge, dried in oven at 323 K and ground into fine powder. This sample was labelled as C. Same method was applied for the synthesis of $\gamma$Fe$_2$O$_3$-SiO$_2$-AgCl coreshell nanoparticle and was labeled as D.

2.4 Synthesis of AgCl, SiO$_2$ and AgCl-SiO$_2$ coreshell particles

For AgCl particles, an amount 0.05 M of PVP, 5 ml of 0.3 M of NaCl solution and 100 ml of ethanol was mechanically stirred for 1 hour. This mixture was then poured into the Ag$^+$ solution. Then, the solution was stirred by ultrasonic bath for 3 hours and aged overnight. The obtained sample was washed by using a centrifuge, dried at 80 °C in the oven for 3 hours and grounded into a fine powder. This sample was labelled as F. For synthesis of SiO$_2$ particles, An amount of 100 ml ethanol and 1 ml of TEOS were mechanically stirred in 500 ml beaker for 5 minutes, followed by the addition of 7 ml of NH$_4$OH. The mixture was stirred for 3 hours, then washed by using a centrifuge, dried at 80 °C in the oven for 3 hours and grounded into fine powder. This sample was labelled as G. The synthesis AgCl-SiO$_2$ coreshell particles used the similar method as used for the preparation of (Fe$_3$O$_4$ & $\gamma$Fe$_2$O$_3$)-SiO$_2$-AgCl coreshell particles, except the Fe$_3$O$_4$ and $\gamma$Fe$_2$O$_3$ nanoparticles were excluded. This sample was labelled as E.

2.5 Characterization

The phases of the synthesized particles were determined by using an X-ray diffraction (XRD, D8 Advance Bruker AXS diffractometer) over a 2θ range 20°-90° using Cu-Kα radiation (λ = 0.15406 nm) with acceleration voltage of 30 kV and emission current of 10 mA.

2.6 Adsorption Testing

The adsorption test was conducted in batch experiments using 100 ppm copper solution. An amount of 0.1 g of each synthesized particles was dissolved in different conical flask containing 100 ml of 100 ppm copper solution. The solution was corked and agitated with rotary shaker at 100, 200 and 300 rpm for duration of 5 hours under UV light. The experiments were conducted at room temperature (~25 °C) and at constant pH 6. There were two parameters studied, which is the effect of contact time on the adsorption of copper ions and the effect of shaking speed. The effect of contact time was evaluated for the duration ranging from 60 min to 300 min. The supernatant was taken for every one hour of time interval (60, 120, 180, 240 and 300 min) and filtered with filter paper. This filtrate was analyzed by using a DR HACH 2010 spectrometer and an atomic absorption spectrometry (AAS) spectrometer Shimadzu (ASC-7000) in order to check the concentration of the copper ions.
ions left after the absorption process [8]. Adsorption at each time interval was determined by a mass-balance calculation, where the equilibrium adsorption capacities of all adsorbents were calculated using Equation (1) [9]. Adsorption efficiency or the percentage of copper ions removed were expressed as a percentage using Equation (2) [10-11].

\[
q = \frac{(C_0 - C_f)V}{W}
\]

(1)

where,

- \(C_0\) = initial concentration of copper ions before adsorption
- \(C_f\) = final concentration of copper ions after adsorption
- \(V\) = volume of copper ions solution in L
- \(W\) = Mass of the adsorbent used in g

\[
R(\%) = \left(\frac{C_0 - C_f}{C_0}\right) \times 100\%
\]

(2)

where,

- \(R(\%)\) = ratio of difference in copper ions concentration before and after adsorption.

For the effect of shaking speed, the supernatant was taken at every 100, 200 and 300 of rotation speed per minute (rpm). The supernatant then was filtered and further characterized by DR HACH 2010 and AAS spectrometer.

3 Results and Discussion

Fig. 1 shows the XRD pattern for all the synthesized samples. Sample A shows reflection of magnetite at 30˚ (220), 35˚ (311), 43˚ (400), 53˚ (422) 56˚ (511), 62˚ (440) and 75˚ (622) while Sample B shows the reflection of maghemite at 30˚ (220), 35˚ (311), 43˚ (400), 53˚ (422), 57˚ (511), 62˚ (440) and 75˚ (622), respectively. Both phase have quite similar XRD pattern except the unit cell length of \(\gamma\)Fe\(_2\)O\(_3\) nanoparticles is smaller (\(a=0.8351\) nm) compare to Fe\(_3\)O\(_4\) nanoparticle (\(a=0.8396\) nm). For Samples C (Fe\(_3\)O\(_4\)-SiO\(_2\)-AgCl), D (\(\gamma\)Fe\(_2\)O\(_3\)-SiO\(_2\)-AgCl) and E (SiO\(_2\)-AgCl) a clear reflection of AgCl peaks can be observed at 27˚ (111), 32˚ (200), 46˚ (220), 54˚ (311), 57˚ (222), 66˚ (400), 74˚ (331) and 76˚ (420). No silica peaks can be observed from Samples C, D, and E since the Stöber silica is an amorphous structure.

Fig. 2(a) and (b) showed the FESEM image of both synthesized Samples C (Fe\(_3\)O\(_4\)-SiO\(_2\)-AgCl) and D (\(\gamma\)Fe\(_2\)O\(_3\)-SiO\(_2\)-AgCl) nanoparticles. The spheres refers to the magnetic-silica particles with white cubical structures of AgCl particles doped onto the silica surfaces. The elemental composition is supported by FESEM-EDS (not shown). Based on TEM characterization in Figs. 3(a) and (b), the particle size and morphology of Samples C and D can be observed. The diameter of SiO\(_2\) particle for C (Fe\(_3\)O\(_4\)-SiO\(_2\)-AgCl) is about 88 nm and the AgCl is about 18 nm. Meanwhile, for Sample D (\(\gamma\)Fe\(_2\)O\(_3\)-SiO\(_2\)-AgCl), the diameter of is SiO\(_2\) about 83 nm while the AgCl is about 10 nm. An irregular and agglomerated AgCl nanoparticles were observed from TEM images. This is due to the exposure of AgCl under the high electron beam that led to the agglomeration of AgCl (due to the reduction of AgCl to Ag) nanoparticles during TEM imaging.
Fig. 1. The XRD patterns of A, B, C, D and E.

Fig. 2. (a) The FESEM images of the synthesized C (Fe₃O₄-SiO₂-AgCl) and (b) D (γFe₂O₃-SiO₂-AgCl) coreshell particles.

The adsorption testing proved that the removal of copper ions was rapid and the reactions were increased as a function of time. The amount of Cu²⁺ (mg/g) that was adsorbed by all of the adsorbents (Samples A-G) increase as contact time increased (Fig. 4). Besides that, the concentration of copper ions left in every samples were inversely proportional to the contact time of adsorption process as can be observed in Table 1.
Fig. 3. TEM image of (a) C (Fe$_3$O$_4$-SiO$_2$-AgCl) and (b) D (Fe$_2$O$_3$-SiO$_2$-AgCl).

Fig. 4. The effect of contact time on the amount of copper ions adsorbed by Samples A-G.

Table 1. The concentration of Cu$^{2+}$ after every 1 hour of time interval at 300 rpm.

| Contact Time (Hours) | A   | B   | C   | D   | E   | F   | G   |
|----------------------|-----|-----|-----|-----|-----|-----|-----|
| 0                    | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 1                    | 2.58| 3.19| 0.60| 0.70| 9.33| 10.20| 16.50|
| 2                    | 2.21| 3.45| 0.70| 0.50| 9.93| 10.42| 15.10|
| 3                    | 2.20| 2.66| 0.50| 0.40| 10.46| 11.15| 14.35|
| 4                    | 1.67| 2.45| 0.20| 0.34| 10.32| 10.17| 14.25|
| 5                    | 1.52| 1.26| 0.10| 0.21| 11.30| 12.05| 14.60|

From Table 1, the amount of Cu$^{2+}$ that were adsorbed by Samples A, B, C and D increased gradually where only 1.52, 1.26, 0.20 and 0.21 mg/L of the Cu$^{2+}$ concentration left after 5 hours of the adsorption process. Meanwhile, Samples E, F and G that showed quite high concentration of Cu$^{2+}$ left at the end of the adsorption process, which are 11.30, 12.05 and
14.60 mg/L, respectively. Based on Fig. 5, the optimum removal of Cu\(^{2+}\) by Samples A, B, C and D were practically achieved after 4 hours of the adsorption process. This observation demonstrates that the used magnetic nanoparticles materials are more efficient because they can remove the copper metal much faster due to their large active sites for the adsorption of copper metal ions [12]. Besides that, Samples C, D and E which consisted of AgCl dopant showed a good adsorption of copper ions as the contact time increased. AgCl is a great help in accelerating the adsorption of Cu\(^{2+}\) under the UV region. Upon photoexcitation, AgCl reacted with the solvent to form highly reactive radicals, which are able to break the chemical bonds of the heavy metals. Consequently, the charge carriers will be directly transferred to the Cu\(^{2+}\) adsorbed on the surface of the AgCl catalyst to induce photochemical transformations. In either way, the Cu\(^{2+}\) are photocatalytically degraded into short chain molecules [13]. For instance, the adsorption of Cu\(^{2+}\) on F (AgCl) is much more better compared to G (SiO\(_2\)).

For different shaking speed (rpm) used during the adsorption process, an almost similar trends can be observed from Fig. 5 for all the synthesized samples. It was found that the amount of Cu\(^{2+}\) that were adsorbed on the surface of all the particles increased as the shaking speed increased from 100 to 300 rpm after 5 hours of the adsorption process. For example, based on Table 2 the removal percentage of Cu\(^{2+}\) by A (Fe\(_3\)O\(_4\)) and B (γFe\(_2\)O\(_3\)) were increased from 40% and 39% to 89% and 85% as shaking speed increased from 100 to 200 rpm. Consequently, the amount of Cu\(^{2+}\) ions adsorbed on both samples continued to increase as shaking speed increased to 300 rpm.

![Fig. 5. The effect of shaking speed on the removal percentage of copper ions by A-G.](image)

Apparently, the highest removal percentage of Cu\(^{2+}\) after 5 hours of adsorption testing at 300 rpm was recorded by Sample C. About 99% of Cu\(^{2+}\) was removed, meanwhile Sample D which is consisted of γFe\(_2\)O\(_3\)-SiO\(_2\)-AgCl showed about 97% removal of the copper ions, followed by Samples E (AgCl), F (AgCl-SiO\(_2\)) and G (SiO\(_2\)) recorded about 78%, 60% and 28% respectively. Thus, from the obtained results, it is showed that the composite coreshell structure of iron oxide, silica and silver chloride played an essential part in the removing of copper ions from the aqueous solution. The presence of SiO\(_2\) interlayer in between magnetite and maghemite cores can optimize the function of the synthesized adsorbent by providing the specific functionalities that can be selective for copper ions uptake. The presence of AgCl as the photocatalyst was important to maximize the amount of copper ions adsorbed on the synthesized adsorbent. Eventually, it promotes slow release of Ag\(^{+}\) ions under UV light and created electrostatic force or surface charge interaction occurred between copper ions and...
chloride ions. Therefore, more spaces were present for copper ions attachment at the hole on the surface of adsorbents [14-15].

Table 2. The removal percentage of copper ions at different shaking speed (rpm)

| Shaking Speed (rpm) | A  | B  | C  | D  | E  | F  | G  |
|---------------------|----|----|----|----|----|----|----|
| 100                 | 40 | 37 | 53 | 53 | 25 | 20 | 10 |
| 200                 | 89 | 85 | 93 | 93 | 55 | 45 | 23 |
| 300                 | 94 | 92 | 99 | 97 | 78 | 60 | 28 |

4 Conclusion

The magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), magnetite-silica-silver chloride Fe₃O₄-SiO₂-AgCl, maghemite-silica-silver chloride (γFe₂O₃-SiO₂-AgCl), silver chloride (AgCl) and silica (SiO₂) has successfully been synthesized and applied as nanoadsorbents for the removal of the copper ions from the solution. It was found that both of the magnetic nanoparticles (Fe₃O₄ & γFe₂O₃) have a good potential to be used as an adsorbent where about 94% and 92% of the copper ions can be removed from the solution. When this magnetic nanoparticles were constructed into the coreshell structures (Fe₃O₄-SiO₂-AgCl & γFe₂O₃-SiO₂-AgCl), the removal efficiency increased nearly 100% where almost all the copper ions can be removed from the solution, which the Cu²⁺ concentration left about 0.10 and 0.21 mg/L, respectively. The samples that were prepared without magnetic core (AgCl-SiO₂, AgCl and SiO₂ particles), showed lower percentage of the copper ions removal (78%, 60% and 20%, respectively). This situation shows that the magnetic nanoparticles plays an important role during the adsorption process due to their large active sites for the adsorption to occur.

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