Preparation of Amino-Modified Iron Oxide Nano Adsorbent and Calcinated Laterite for Chromium (Vi) and Copper (Ii) Removal

M.Suresh Krishna[1], R.K.C.Jeykumar[2]
P.G student, Department of Civil Engineering,Thiagarajar College of Engineering,Madurai,India[1]
Assistant Professor, Department of Civil Engineering,Thiagarajar College of Engineering,Madurai,India[2]

I. INTRODUCTION

Water crisis has become a part of our life. This is not altogether due to shortage of rainfall, but also due to increasing population, growing industrialization, expanding urbanization, agriculture activities etc., demand more and more water. Coping up with these developments requires various tactics to overcome the water shortage and satisfy the need of all. Water pollution is a serious problem in all over the world and particularly more in India as almost 70% of its surface water resources, and groundwater reserves are contaminated by biological, toxic, organic, and inorganic pollutants. The main activity in this direction is to decrease the pollution level of discharged effluents and treatment of contaminated water to acceptable quality. Nanotechnology is quickly developing in various fields. In order to meet diverse requirements, many efforts have been made on the nano-engineering of particle surface to tune the bulk properties, tailor the surface properties (e.g., charge density, functionality, reactivity, biocompatibility, stability, and dispersibility), produce hollow nanostructured materials, and create multi-functional composite nanoparticles. Recent developments are made in a cationic magnetic nano-adsorbent using iron oxide nanoparticles as cores and poly acrylic acid (PAA) as ionic exchange groups. It possessed a high ion-exchange capacity and could recover the positively charged enzymes and basic dyes quite fast and effectively. However, it is less effective for the adsorption of polyvalent metal cations and not valid for the adsorption of anionic species.

II. MATERIALS AND METHODS

In general there were two main parts in this research; where the first part was preparation of mixed adsorbent material and the second part was the chromium and copper removal by adsorption technique. And there were also four steps in this first part (preparation of mixed adsorbent material) roughly. Iron oxide (Fe_3O_4) nanoparticles were synthesized by novel ageing process firstly. Next amino-functionalized the Fe_3O_4 nanoparticles. Then calcination of laterite was carried on to mix with these iron oxide particles. Finally, creating of mixed adsorbent for chromium and copper removal was done by mixing these two adsorbent materials.

A. Synthesis of iron oxide nanoparticles:

The chemical reagents used in this preparation of iron oxide particles were Urea:$(NH_2)2CO$, Ferric chloride: $FeCl_3.6H_2O$, Sodium hydroxide: NaOH, Ferrous Sulphate: $FeSO_4.7H_2O$, and Acetone.A typical approach for this research work was given as follows. 5.41g $FeCl_3.6H_2O$ and 3.6g $(NH_2)2CO$ were dissolved in 200ml distilled water in a container. After that, this solution was placed in a water bath at a constant temperature 90±3˚C. Various heating time parameters tested in this process were 2, 2.5, 3 hr respectively. The solution turned into a kind of khaki slurry gradually and then it was cooled to room temperature. 1.99g $FeCl_2.4H_2O$ was dissolved in the above mixture with mechanical stirring at a speed of 546 rpm for 10 min. Then, NaOH solution (2mol/L) was dropped into the reaction mixture until the pH>10. Greenish precipitate can be observed at that time. The molar ratio of Fe(III) to Fe(II) in the observed system was nearly 2. When the pH reached greater than 10, the mixture was transferred into an ageing can with a cubage of 500 ml. Additional distilled water was added to make the ageing container full and then it was sealed by a capsule to prevent the air from entering. Finally, the container was aged at a room temperature with different ageing times such as 3hr, 4hr, and 5 hr. The black magnetic precipitate was separated by filtration, followed by washing with distilled water of 500 mL and acetone of 100 mL in order. Then, the obtained powders were oven-dried at 50˚C for 7hr.

B. Amino-functionalization magnetic nanoparticles

Secondly, for the covalently binding of PAA, 100mg of Fe_3O_4 nanoparticles were mixed with 2mL of buffer A (0.003M phosphate, pH 6, 0.1M NaCl) and 0.5mL of carbodiimide solution (0.025

g/mL in buffer A). After being sonicated for 10min, 2.5mL of PAA solution (60mg/mL in buffer A) was added and the reaction mixture was sonicated for another 30 min. Finally, the PAA-coated Fe_3O_4 nanoparticles were magnetically recovered and washed with water twice. For the amino-functionalization of PAA-coated Fe_3O_4 nanoparticles, the above PAA-coated Fe_3O_4 nanoparticles were first mixed with 4.32mL of buffer A (0.003M phosphate, pH 6, 0.1M NaCl) solution and 0.5mL of carbodiimide solution (0.025 g/mL in buffer A).After being sonicated for 10min, the reaction mixture was mixed with 0.18mL of diethylenetriamine (9.1M) and sonicated for another 60 min. By varying the amount of diethylenetriamine and the volume of buffer A, the concentration of diethylenetriamine was tuned in the range of 0.016–1.62M and the volume of reaction mixture was fixed at 5mL. Finally, the magnetic nanoparticles were magnetically recovered and washed with 0.2M NaOH solution and ethanol, and then dried in a vacuum oven. NaOH was used for the flocculation of magnetic nanoparticles.

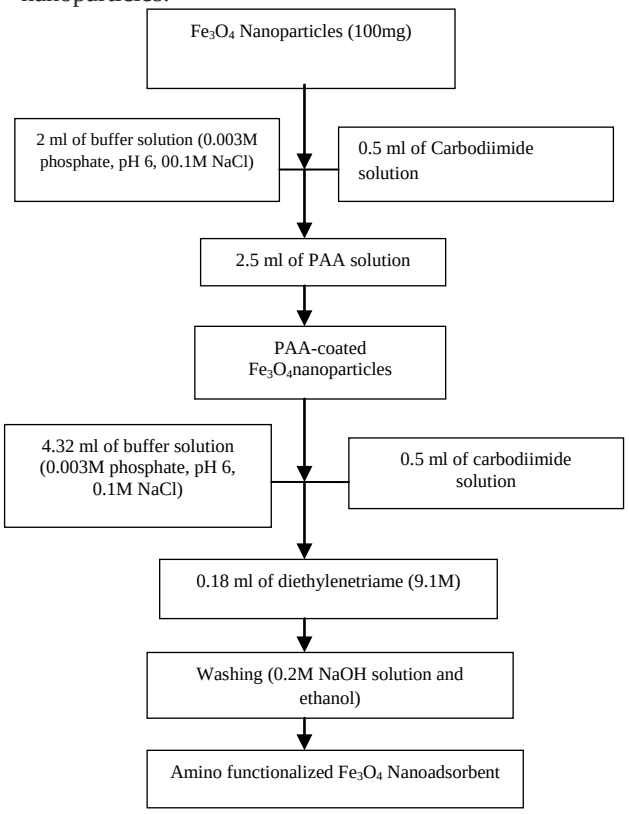

Fig.1Chemical preparation route of amino-functionalization of Fe_3O_4 nanoparticles

C. Laterite calcinations

After synthesized these nanoparticles, laterite calcinations step was carried on. The collected iron rich raw laterite (collected from Mon State) was then calcinated at 400˚C for 4 hours.After calcination, the laterite was crashed and sieved to obtain powder laterite with a particle size less than 75µm. These laterite powders were washed with deionized water at least three times. If not washing like this it can not remove the laterite dust, as well as other undesired particle. It was dried at 110˚C for 12 hr; then it was stored in a desiccator for use in the next step of mixing experiments.

III.RESULTS AND DISCUSSIONS

The study were conducted to findout the removal of copper and chromium with calcinated laterite adsorbent in the prepared synthetic water. The removal of copper and chromium is studied varying time from 20 to 80 minutes and the adsorbent concentration from 30 mg/l to 70mg/l results are tabulated as below.

Table 1: Physicochemical characteristics of simulated synthesis solution before and after treatment using laterite adsorbent

Sl. No	Parameter	Adsorption Time (min)	Adsorbent dosage (g)	Before treatment (mg/L)	After treatment (mg/L)
1	Cr	20	0.03	0.3	0
2	Cr	20	0.05	0.3	0
3	Cr	20	0.07	0.3	0
4	Cr	40	0.03	0.3	0
5	Cr	40	0.05	0.3	0
6	Cr	40	0.07	0.3	0
7	Cr	60	0.03	0.3	0
8	Cr	60	0.05	0.3	0
9	Cr	60	0.07	0.3	0
10	Cr	80	0.03	0.3	0
11	Cr	80	0.05	0.3	0
12	Cr	80	0.07	0.3	0
13	Cu	20	0.03	0.3	0
14	Cu	20	0.05	0.3	0

15	Cu	20	0.07	0.3	0
16	Cu	40	0.03	0.3	0
17	Cu	40	0.05	0.3	0
18	Cu	40	0.07	0.3	0
19	Cu	60	0.03	0.3	0
20	Cu	60	0.05	0.3	0
21	Cu	60	0.07	0.3	0
22	Cu	80	0.03	0.3	0
23	Cu	80	0.05	0.3	0
24	Cu	80	0.07	0.3	0

The results of the study shows that the calcinated laterite is efficient in removal of the copper and chromium concentration of 0.3mg/l. A further study is to be done by varying the concentration of these heavy metal and with the mixture of calcinated laterite and nano modified iron oxide. The iron oxide adsorbent and calcination of laterite have been done in this project and modification process of iron oxide is to be carried out.

IV. CONCLUSION

Calcinated laterite adsorbent and nine different types of Fe_3O_4 nano particles were prepared. The iron oxide (Fe_3O_4) nanoparticles are prepared by novel ageing process with various parameters for examining which process can produce the smaller particle size.The iron oxide (Fe_3O_4) nanoparticles are prepared by novel ageing process with various parameters for examining which process can produce the smaller particle size. The adsorption treatments have been conducted on a laboratory scale in batch reactors which gives accurate result. Thus the experiment was successfully done by removing the chromium and copper ions from the synthesis solution using calcinated laterite adsorbent with 100% The removal of copper and chromium is studied varying time from 20 to 80 minutes and the adsorbent concentration from 30 mg/l to 70mg/l results.In next phase, the Fe_3O_4 nano particles will be aminofunctionalized. Then, to find the removal efficiency of aminofunctionalized Fe_3O_4 nano particles in the synthesis solution. Finally, to find the removal efficiency in the synthesis solution with the help of mixed calcinated laterite adsorbent and aminofunctionalized Fe_3O_4 nano particles and to workout the cost economics of the treatment.

V. SUMMARY

A detailed literature review was carried out to study the adsorption technology. It is also considered to be potentially an effective tool for treatment of chromium and copper from synthesis solution with high removal efficiency. The removal efficiency was found to be dependent on the adsorbent dosage, adsorption time and pH in batch mode. The synthetically prepared chromium and copper effluent would be subjected to batch adsorption process by changing the operational parameters.

REFERENCES

[1] Piao Xu, Guang Ming Zeng, Dan Lian Huang, Chong Ling Feng, Shuang Hu, Mei Hua Zhao, Cui Lai, Zhen Wei, Chao Huang, Geng Xin Xie, Zhi Feng Liu(2012): Use of iron oxide nanomaterials in wastewater treatment: A review.

[2] B.M. Sunil and Saifiya Faziludeen(2015): Removal of hexavalent chromium Cr(VI) by adsorption in blended lateritic soil.

[3] I.J. Syama, Arun KumarThallaand D.S. Manu(2015):Performance of Laterite Soil Grains as Adsorbent in the Removal of Chromium.

[4] Wint Myat Shwe, Dr. Mya Mya Oo, Dr. Su Su Hlaing(2015): Preparation of Iron Oxide Nanoparticles Mixed with Calcinated Laterite for Arsenic Removal.

[5] Shih-Hung Huang, Dong-Hwang Chen(2008): Rapid removal of heavy metal cations and anions from aqueous solutions by anamino-functionalized magnetic nano-adsorbent.