Remediation of selected heavy metals (Pb, Cd) from fly ash using magnetite nanoparticles

Virendra Kumar Yadav[a]* and M. H. Fulekar[b]

[a]School of Nanosciences, Central University of Gujarat, Gandhinagar-382 030, Gujarat, India

E-mail: yadava94@gmail.com

[b]School of Environment & Sustainable Development, Central University of Gujarat, Gandhinagar-382 030, Gujarat, India

Magnetite nanoparticles has immense potential for the environmental remediation of inorganic contaminants like heavy metals. In the present research work the commercial magnetite nanoparticles were procured, characterized and it's efficiency was analyzed for the removal of Pb and Cd from the aqueous solutions of fly ash using shake flask method in an incubator shaker at room temperature. The morphological analysis was done by microscopic techniques: SEM-EDS and HRTEM which revealed the cuboidal shaped nanoparticles of size 20–45 nm. The crystallinity and microstructure was analyzed by the XRD, Raman and FTIR. The magnetite nanoparticles were segregate, uniform and crystalline in nature. The SEM-EDS revealed the high purity of the sample as the EDS spectra have peaks for Fe and O only. The 20% fly ash solution have higher Pb and Cd heavy metal concentration than others. Magnetite nanoparticles removed Pb upto 95.32% after 18 h and Cr was removed upto 81.52% after 24 h.

Keywords: Magnetite nanoparticles, fly ash, heavy metal, remediation, adsorption.

Introduction

Fly ash is a by-product of thermal power plants which are produced from the pulverized coal during the production of electricity[1]. Fly ash is complex material made up of ferro-alumino-silicate mineral[2]. The most common elements in fly ash includes Si, Al, Fe, Ca, Mg, K and Na, Ti[3]. Besides, this it fly ash have heavy load of heavy metals like Pd, Cd, Cr, Zn, As, Hg, Ni, Cu and Co due to which it is considered as a hazardous pollutant[4]. In the 21st century it has become one of the major solid pollutant produced by industries around the globe. The heavy metals like Hg, Cd, As are volatile at high temperature so they are present in lesser amount in the fly ash while Pb and Cr is present in higher concentration which may challenge a potential threat to the living beings nearby dumping sites[5]. Heavy metals including Pb and Cd may leach out from the fly ash or dumping sites and may contaminate the water bodies. The contamination of the water bodies by Pb and Cr has reported several outbreaks which has caused diseases due to contamination of ground water. Both of these heavy metals have adverse effects on the living beings due to their toxic nature. Both these heavy metals have more concern and pose a serious threat to the environment[6]. Pb may cause numbness, liver diseases, and other chronic diseases while Cr causes cancer as Cr^{6+} form is a mutagenic and carcinogenic in nature. Cr exists in two forms Cr^{4+} and Cr^{6+} and out of which Cr^{6+} is carcinogenic. So, it become very important to convert the hexavalent form of Cr to tetravalent which is non-toxic. The reduction of Cr can be done by co-precipitation, coagulation, absorption, electro-plating and adsorption. Out of all these techniques adsorption is one of the most suitable method for the heavy metal removal whose efficiency can be enhanced by the applications of nanotechnology. Nanotechnology and nanoparticles can play an important role all the fields of sciences[7]. One such particle is magnetite nanoparticles which is magnetic in nature and has drawn the attention of scientists around the globe. It is being used in the magnetic ink printing[8], magnetic storage tape and devices[9], medicine and medical diagnosis[10], gene and drug delivery[11], cancer-hyperthermia[12], biosensors and for bio separation[13] and waste water treatment[14]. For all these applications it is being used as an adsorbent in the nanoscale which makes it very unique and

special due to it's dimension, economical nature, recyclable and recoverable due to the magnetic properties even after many cycles. The magnetite nanoparticles can be used by treating it with 1% NaOH solution which remove all the heavy metals attached to the surface. They can interact specifically with the pollutants due to their unique adsorption sites which is achieved by disordered surface regions and different distribution pattern of reactive surface sites[15]. In the present research work Pb and Cr was removed from the 20% fly ash solution by using commercially procured magnetite nanoparticles. The magnetite nanoparticles were characterized by the PSA, FTIR, HRTEM, SEM-EDS, Raman and XRD for the detailed properties. The remediation of Pb and Cr heavy metals was studied wrt to the contact time, where the contact times varied from 0–24 h while the all other parameters like pH, rpm, temperature, dose of nanoparticles etc. was kept constant. The batch adsorption study was carried out by shake-flask method in an incubator shaker. An aliquot of ~8–10 ml sample was collected after every regular time interval of 1 h, 2 h, 4 h, 8 h, 16 h and 24 h and sample was analyzed by ICP-AES for the concentration of Pb and Cr.

Experimental

The magnetite nanoparticles was procured from Sigma Aldrich (Germany).

Sample collection and 20% fly ash solution preparation:

Fly ash was collected from the Gandhinagar Thermal Power Plants in the plastic silos and before preparing solution it was dried in an oven at 110°C for 24 h. The 20% fly ash solution was prepared by method reported by Jerzy *et al.,* (2006) [16].

Results and discussion

The magnetite nanoparticles were characterized by the PSA, FTIR, HRTEM, SEM-EDS, Raman and XRD.

PSA:

The PSA was carried out at 25°C after 10 min of sonication where the average particle size is 1192 nm and PDI is 0.478.

Raman:

The Raman spectra of magnetite nanoparticles reveals peaks at 484, 538 cm^{-1} which are assigned to the vibrations
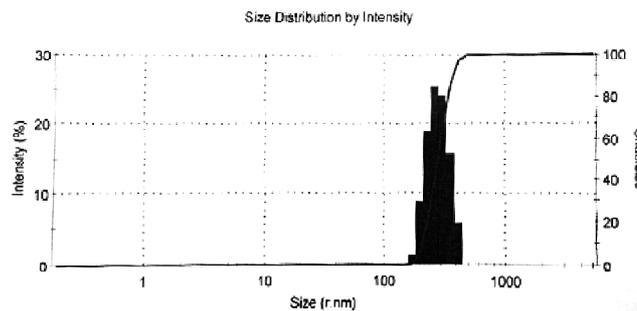

Fig. 1. PSA graph of magnetite nanoparticles.

of magnetite while the other characteristic peaks are around 613 cm^{-1} [17] and at 717 cm^{-1}. The band at 717 cm^{-1} is the strong peak of magnetite. Magnetite phase is easily discernible by its main band centered on 613 cm^{-1} [18].
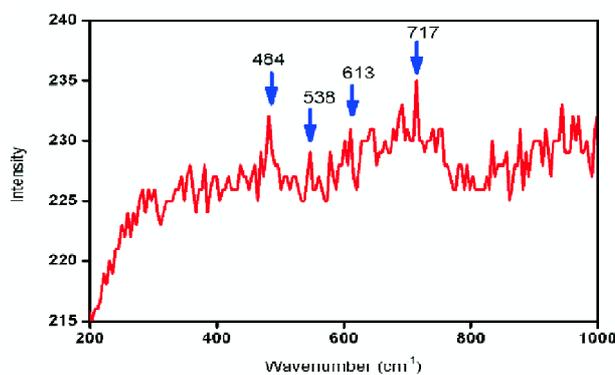

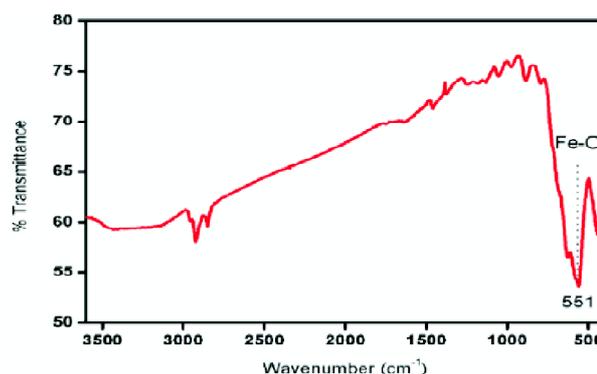**Fig. 2.** Raman spectra of magnetite nanoparticles.

FTIR:

Fig. 3. FTIR spectra of magnetite nanoparticles.

As the magnetite have inverse spinel structure so it shows band at 551 cm^{-1} which is attributed to Fe-O-Fe (corresponding to n(Fe-O) stretching vibration in tetrahedral site) and the

other band around 430 cm^{-1} corresponding to d(Fe-O) torsional vibration mode of Fe in octahedral site[19]. While a peak at 2922 cm^{-1} is due to the absorption of atmospheric CO_2.
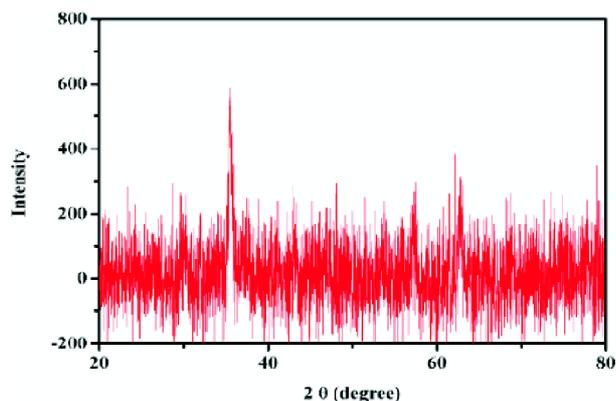
XRD:

Fig. 4. XRD diffractograms of magnetite nanoparticles.

The XRD graphs shows a single peak at 35° and a small peak at 64° confirms the crystalline and spinel nature of the magnetite nanoparticles.
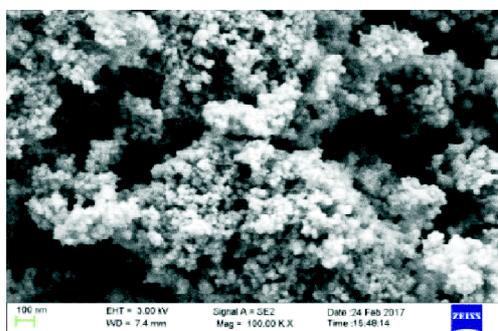
SEM-EDS:

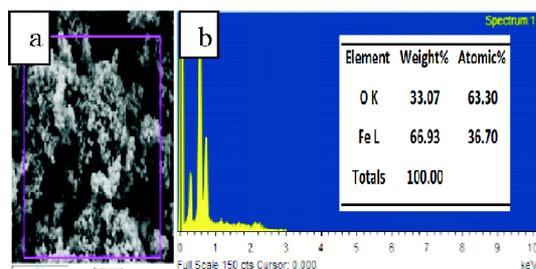**Fig. 5.** FESEM images of magnetite nanoparticles.

Fig. 6. EDS of magnetite nanoparticles.

The SEM images reveals spherical shape of the magnetite nanoparticles whose size varies from 10 nm to 50 nm and average size of the particles is 35–40 nm. The particles are individual and non-aggregated. The SEM-EDS spectra show major peaks for Fe and O which indicates the high purity of the magnetite.
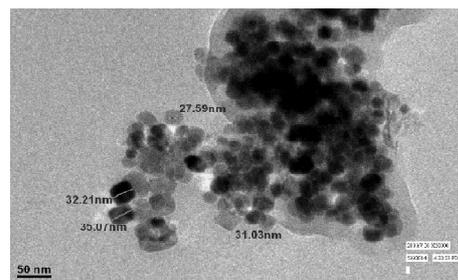
TEM:

Fig. 7. TEM micrographs of magnetite nanoparticles.

TEM revealed both spherical and cuboidal shaped particles where the cuboidal shaped particles of size 30–35 nm more dominant then the spherical shaped particle of size 22–27 nm. The cuboidal shaped particles were not visible by SEM.
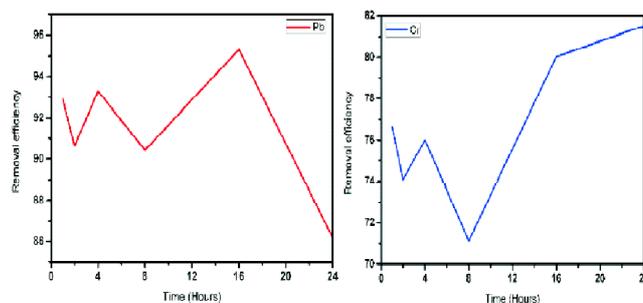
Adsorption study:

Fig. 8. Pb and Cr removal by magnetite nanoparticles.

The initial concentration of Pb and Cr was almost same in the 20% fly ash solution. After one hour 92.88% Pb was removed, but slight decrease at 2 h i.e. 90.65%. Again an increase was seen 93.29% with a decrease 90.44%. But maximum removal efficiency attained about 95.32% after 16 h and a then a decrease with final value 86.17%. The decrease in the efficiency of Pb removal after one hour is due to the non-availability of free adsorption sites on the magne-

tite. The desorption starts after reaching to the equilibrium which was seen 8 and final 24 h 90.44% and 86.17% respectively. Cr removal efficiency reached to 76.64%, at one hour after that a slight decrease in the efficiency at 2 h and 8 h i.e. 74.09% and 71.12% respectively. This desorption is due to the non-availability of free cationic binding sites on the surface of magnetite nanoparticles. But increase was seen at 4 h, 16 h and maximum at 24 h i.e. 76%, 80.04% and 81.52% respectively. As the fly ash is a source of multicomponent system, i.e. having different heavy metals, which competes for the limited adsorption sites along with Pb and Cr. Initially as all the adsorption sites present on the nanoparticles might be unoccupied, so there was adsorption and after reaching equilibrium desorption started. After that adsorption sites were not vacant for the Pb and Cr, once reaching to equilibrium, desorption starts to occur[20]. The Pb has more adsorption capacity than the Cr in a multi-element system at neutral pH.

Conclusion

The study revealed that the commercial magnetite nanoparticles of spherical shaped, highly ordered, crystalline particles efficiently remove the fly ash Pb and Cd heavy metals from a 20% solution. The removal efficiency of up to 92.32% was achieved for Pb after 18 h and 81.52% for Cr after 24 h. Pure magnetite nanoparticles have potential to detoxify the Cr from the hexavalent to tetravalent form. Magnetite nanoparticles of size 20–50 nm can efficiently acts as an economical in a fly ash like solution of multi-component system/quaternary system.

Acknowledgements

References

1. K. Styszko-Grochowiak, a J Go, H. Jankowski and S. Kozi ski, *Fuel*, 2004, **83**, 1847.

2. M. Nyale Sammy, O. Babajide Omotola, D. Birch Grant, Böke Nuran and F. Petrik Leslie, *Procedia Environmental Sciences*, 2013, **18**, 722.

3. S. A. Akinyemi, A. Akinlua, W. M. Gitari, S. M. Nyale, R. O. Akinyeye and L. F. Petrik, *Energy Science and Technology*, 2012, **3**, 28.

4. Virendra Kumar Yadav and M. H. Fulekar, *IJERD*, 2018, **5(4)**, 768.

5. A. Singh and S. M. Prasad, *Int. J. Environ. Sci. Technol.*, 2015, **12**, 353.

6. S. Khan, Q. Cao, Y. M. Zheng, Y. Z. Huang and Y. G. Zhu, *China. Environ. Pollut.*, 2008, **152(3)**, 686.

7. Ibrahim Khan, Khalid Saeed and Idrees Khan, *Arabian Journal of Chemistry*, 2017.

8. Briza Pérez-López and Arben Merkoçi, *Advanced Functional Materials*, 2011, **21(2)**, 255.

9. J. H. Jang and H. B. Lim, *Microchemical Journal*, 2010, **94(2)**, 148.

10. Won Gu Leea, Yun-Gon Kima, Bong Geun Chunga, Utkan Demircia and Ali Khademhosseini, *Advanced Drug Delivery Reviews*, 2010, **62(4-5)**, 449.

11. Conroy Suna, Jerry S. H. Leeb and Miqin Zhang, *Advanced Drug Delivery Reviews*, 2008, **60(11)**, 1252.

12. Donglu Shi, Nicholas M. Bedford and Hoon-Sung Cho, *Small*, 2011, **7(18)**, 2549.

13. Jianlong Wang, Zanzan Zhu, Ahsan Munir and H. Susan Zhou, "Magnetic nanoparticle (MNP) enhanced biosensing by surface plasmon resonance (SPR) for portable devices", Proc. SPIE 7647, Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems, March 31, 2010, 76470T.

14. Mini Namdeo, *Adv Recycling Waste Manag*, 2017, **2**, 3.

15. Dhermendra K. Tiwari, J. Behari and Prasenjit Sen, *World Applied Sciences Journal*, 2008, **3(3)**, 417.

16. Jerzy Jankowski, R. Colin, D. F. Ward and G. Sarah, *Fuel*, 2006, **185**, 243.

17. L. Slavov, M. V. Abrashev, T. Merodiiska, Ch. Gelev, R. E. Vandenberghe, I. Markova-Deneva and I. Nedkov, *Journal of Magnetism and Magnetic Materials*, 2010, **322**, 1904.

18. D. S. Dunn, M. B. Bogart, C. S. Brossia and G. A. Cragnolino, *Corrosion*, 2000, **56**, 470.

19. R. Balasubramaniam, A. V. Ramesh Kumar and P. Dillmann, *Curr. Sci.*, 2003, **85**, 1546.

20. M. R. Lasheen, Iman Y. El-Sherif, Shaimaa T. El-Wakeel, Dina Y. Sabry and M. F. El-Shahat, *JMES*, 2017, **8(2)**, 503.