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ADSORPTION BEHAVIOUR OF MAGNESIUM FERRITE NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION AND COMBUSTION METHODS

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ABSTRACT

Adsorption of Cr (VI) from aqueous solution by magnesium ferrite ($MgFe_2O_4$) nanoparticles (NPs) synthesized by co-precipitation and combustion methods was studied using batch mode. The factors influencing adsorption viz. solution pH, adsorbent dose, contact time, initial metal ion concentration and temperature were ascertained. Cr (VI) content was estimated spectrophotometrically. The maximum adsorption of Cr (VI) ions was achieved at pH 2.0. Thermodynamic parameters such as change in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were evaluated. NPs synthesized by different methods displayed small variation in the percent removal although BET surface area of NPs showed significant differences. The equilibrium adsorption data were analyzed by the Freundlich, Langmuir and Dubinin-Radushkevich adsorption isotherm models.

Key words: Adsorption, Cr (VI), Magnesium ferrite, Nanoparticles, Thermodynamics

Recently, there has been a surge of interest on the application of nanomaterials as efficient and viable adsorbents for removal of heavy metals from water. Spinel ferrite nanoparticles have general formula AB_2O_4, where tetrahedral-A sites and octahedral-B sites are occupied by metal cations. Owing to their small size and large surface area, they have greater number of active sites for interaction with different chemical species. Stable and non-toxic nature of nanophase spinel ferrites along with their insolubility in water and high surface area can make them potential adsorbents for removing contaminants from water (Khaleel *et al.,* 1999). The properties of ferrite nanoparticles are influenced by the composition and microstructure which is dependent on the preparation methodology (Jacob *et al.,* 2011).

A wide range of novel, wet chemical routes such as sol-gel, precursor, co-precipitation, combustion and hydrothermal methods are used for the synthesis of ferrite nanoparticles (Elahi *et al.,* 2012). In microwave hydrothermal method (MH) both microwave and hydrothermal heating methods are employed for ferrite synthesis (Verma *et al.,* 2004). Sol-gel method is used for producing highly reactive homogeneous powders with various advantages such as good stoichiometric control and formation of active submicron-size particles in a relatively shorter processing time at low temperature (Yang and In, 1996).

Small particle size, low temperature etc. are the major advantages of co-precipitation method. Combustion method leads to the formation of pure and single-phase nano ferrites and it does not suffer from the disadvantage of incomplete precipitation. These techniques involve the formation of ferrites at much lower temperature and in lesser time as compared to conventional ceramic method (Kaur *et al.,* 2012).

The different types of treatment technologies such as phytoremediation, microbial remediation, chemical reduction, physical sorption, membrane filtration, electrokinetic removal etc. have been reported for the removal of Cr (VI) (Owlad *et al.,* 2009). The process of adsorption has received considerable attention as one of the most suitable method for the removal of heavy metals from aqueous solutions. This process is suitable even when the metal ions are present in concentration as low as 1mg/l (Chong and Volesky, 1995). Among several toxic metals discharged into the water bodies, hexavalent chromium has become a serious health concern. We have earlier studied $MgFe_2O_4$ NPs – activated charcoal nanocomposite and bentonite-$MgFe_2O_4$ NPs as adsorbent for Cr (VI) ion (Kaur *et al.,* 2015a, 2015b)

In the present study, magnesium ferrite nanoparticles were synthesized by different wet chemical routes via co-precipitation and combustion method using different fuels – urea, oxalyl dihydrazide (ODH), and polyethylene glycol (PEG). The effect of different synthetic methods on the adsorption of Cr (VI) was studied by batch adsorption experiments. The effect of solution pH, adsorbent dose, contact time, temperature, metal ion concentration, adsorption isotherms and thermodynamic parameters was studied.

MATERIALS AND METHODS

All the chemicals (potassium dichromate, sodium hydroxide, hydrochloric acid, etc.) were purchased from Loba Chemie Pvt. Ltd. (Mumbai) and were of AR grade. All the solutions were prepared in deionized water.

Synthesis of magnesium ferrite nanoparticles

Magnesium ferrite ($MgFe_2O_4$) nanoparticles (NPs) were synthesized using co-precipitation (Liu *et al.,* 2007) and solution combustion methods (Randhawa *et al.,* 2005).

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In co-precipitation method, 2.0 mol of $Fe(NO_3)_3.9H_2O$ and 1.0 mol of $Mg(NO_3)_2.6H_2O$ were dissolved in 20 ml distilled water. The pH of the solution was adjusted between 9 and 10 with 0.1 M NaOH resulting in the brown precipitates. The precipitates were filtered and washed repeatedly with distilled water till pH 7 was achieved. Finally, the precipitates were dried at 100°C for 4h and subsequently calcined at 500°C for 3h to get ferrite as end product. In combustion method, three complexing agents/fuels, i.e. poly- ethylene glycol (PEG), urea and oxalyl dihydrazide (ODH), were used. Metal nitrates act as oxidizers (O) and PEG/Urea/ODH act as fuel (F). Equivalence ratio i.e. $\varphi e = (O/F)$ was maintained unity by balancing the oxidizing (O) and reducing valency (F) of the reactants. The end product was characterized employing Fourier Transformation Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), vibrating sample magnetometry (VSM), Brunner Emmet and Teller surface area analyzer (BET), Transmission electron microscopy (TEM) and is discussed in our previous report (Kaur *et al.,* 2014).

Adsorption experiments

A stock solution of Cr (VI) (1000 mg/l) was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ in 1000 ml deionized water. Working solutions of Cr (VI) were prepared by dilution with double distilled water. Adsorption studies were carried out using batch equilibrium process with Cr (VI) concentration ranging from 50-500 mg/l and 100 mg of adsorbent. Samples were mixed and agitated at 150 rpm. Effect of pH and contact time on Cr (VI) removal was studied using 100 mg of adsorbent and Cr (VI) concentration of 100 mg/l. pH was adjusted using 0.1 N HCl and 0.1 N NaOH. The adsorbent was separated using permanent magnet and the filtrate was analyzed spectrophotometrically. The effect of adsorbent dose was studied for initial concentration of Cr (VI) 100 mg/l with adsorbent dose ranging from 10-900 mg. Effect of temperature (10 to 40 ^oC) on Cr (VI) removal was studied using 100 mg of adsorbent with Cr (VI) concentration of 50 mg/l. All the experiments were performed in duplicate and the average values are reported.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Briefly, the lattice constant was in the range of 8.308-8.321 Å. Physical density was found in the range of 1.852-5.431 g/cc and highest for the ferrite synthesized by co-precipitation method *i.e.* 5.431 g/cc. the percentage porosity was highest for $MgFe_2O_4$ synthesized by ODH method. The average particle diameter from XRD was in the range 8.0 to 13.5 nm and 11.0 to 21.0 nm from TEM analysis. Ferrite synthesized by PEG method shows highest saturation magnetization of 13.55 emu/g. BET surface area was in the range 17.09 to 67.178 m^2/g. Some details of the absorbant characterization have been given in our previous study (Kaur and Kaur, 2014).

Effect of pH

The removal of chromium from aqueous solution by adsorption is highly dependent on the pH of solution. The effect of pH on the adsorption capacity was studied over the range 2.0 to 10.0 and the results are shown in Fig 1. The optimum pH was found to be 2.0. Removal efficiency of Cr (VI) decreases at higher pH values which is attributed to the competition between OH^- and chromate ions (CrO_4^{2-}), where the former being the dominant species hinders the adsorption of chromium (Das *et al.*, 2013). The degree of protonation of the surface reduced gradually with increase in the pH from 2.0 to 10.0 and hence decreased adsorption was noticed. Similar trend has been reported for adsorption of Cr (VI) on Illite by (Ajouyed *et al.,* 2011) and on zeolite NaX by (Pandey *et al.,* 2010).

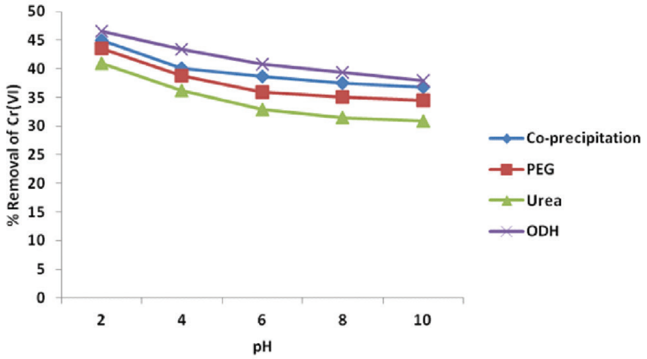

Fig.1. Effect of pH on percent removal of Cr (VI)

Removal efficiency of $MgFe_2O_4$ nanoparticles

Removal efficiency of the synthesized ferrite nanoparticles was studied and compared (Fig. 2). Ferrite synthesized by ODH method displayed best percentage removal of Cr (VI) (46.5 percent) and those synthesized by co-precipitation, PEG and urea displayed percentage removal of 45.0, 43.5 and 41.0 percent respectively for Cr (VI) ions. As it is clear from the results that there is small difference in the percentage removal of ferrite nanoparticles synthesized by different chemical methods. Although BET surface area of NPs is different, but removal efficiency showed no correlation with particle surface area as particles show agglomeration in the solution due to their high surface energy.

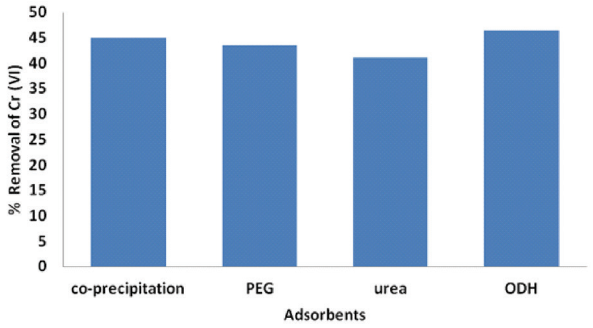

Fig. 2. Removal efficiency of $MgFe_2O_4$ synthesized by different chemical methods for Cr (VI)

Effect of contact time and adsorbent dose

Fig. 3 shows the influence of contact time on adsorption of Cr (VI) onto $MgFe_2O_4$ NPs. The uptake of Cr (VI) from the solution by ferrite NPs had no significant difference, indicating a strong interaction between the adsorbent and adsorbate. The adsorption rate was considerably fast as upto 50 percent removal of Cr (VI) ions took place in first two minutes. Since the adsorbent was nanosized, it provided high surface area for interaction between Cr (VI) and active site.

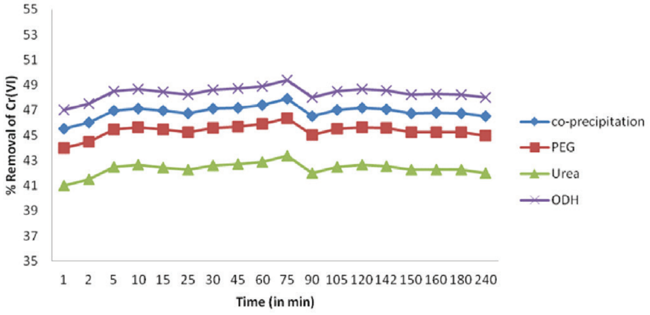

Fig. 3. Effect of contact time on percentage removal of Cr (VI)

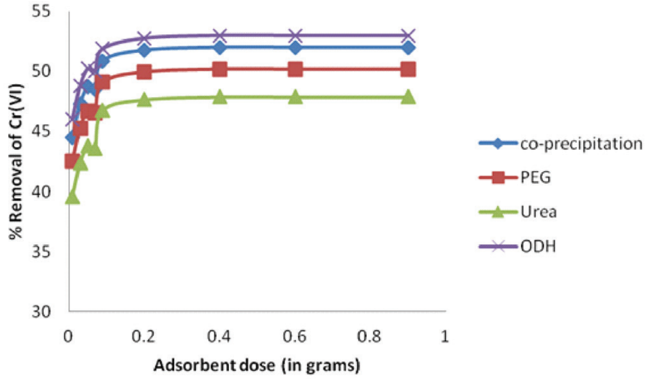

Fig. 4. Effect of adsorbent dose on percentage removal of Cr (VI)

The rate of uptake of Cr (VI) by magnesium ferrite NPs is shown in Fig. 4. As adsorbent dose was increased from 0.01 to 0.05 g, the removal efficiency of Cr (VI) increased from 46 to 50%. However, the removal efficiency of Cr (VI) remained unchanged thereafter. Similar trend was reported by Li *et al.* (2011) in his study on Cr (VI) adsorption onto polyaniline/humic acid composite.

Effect of temperature

With the increase in temperature at the interval of 10°C from 20 to 40°C it was observed that adsorption capacity of the adsorbent for Cr (VI) (50 mg/l) was suppressed (Fig. 5). This can be attributed to the fact that magnitude of adsorption increases with fall in temperature as adsorption is invariably accompanied by evolution of heat (Gregg and Sing, 1967). These results suggested the exothermic nature of adsorption process which was further confirmed by negative ΔH values. In the case of physical adsorption, the amount adsorbed increases as the temperature decreases (Kawasaki *et al.,* 2006). The maximum percentage removal of Cr (VI) was attained at temperature of 10°C i.e. 59.87, 58.37, 55.87 and 61.37 percent respectively using co-precipitation, PEG, Urea and ODH as adsorbent. On the other hand, when the temperature is 40°C the maximum percentage removal of Cr (VI) reaches 57.57, 56.07, 53.57 and 59.07 percent, respectively.

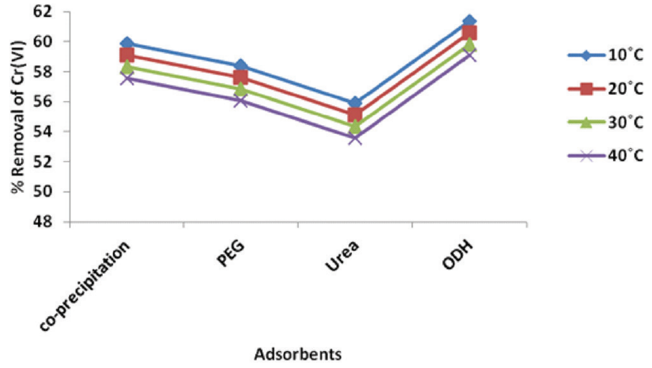

Fig. 5. Effect of temperature on percentage removal of Cr (VI)

The adsorption data obtained at four different temperatures was used to measure the thermodynamic properties of the adsorption process (Table 1). The negative ΔG° values for the experimental range of temperatures, confirmed that the adsorption process was favorable and spontaneous. The values of ΔH and ΔS were calculated from the slope and intercept of the plot of lnK vs 1/T. The calculated value of ΔH was in the range -2.234 to -2.368 $kJmol^{-1}$, indicate exothermic nature of the adsorption process. The negative ΔS values in the range -0.004 to -0.005 $kJmol^{-1}K^{-1}$ suggested the decrease in the degree of freedom of the adsorbed species. The value of ΔG° decreases with rise in temperature from 10°C to 40°C for all adsorbents which indicated that the process is more favorable at low temperature and is exothermic in nature.

Effect of initial metal ion concentration

The percentage removal of Cr (VI) ions at 35 ± 2°C and 25 ± 2°C from the solutions containing different concentrations of Cr (VI) ion with NPs synthesized by different chemical methods was calculated (Fig. 6a and b). With 0.1g of adsorbent prepared by co precipitation, PEG, urea and ODH method in 100 mg/l of Cr solution 36.38, 34.81, 31.80 and 38.54 percent removal of Cr (VI) ions from the solution was achieved at 35°C respectively for $MgFe_2O_4$ synthesized by co-precipitation, PEG, Urea and ODH method. As the concentration was increased from 100 to 500 mg/l, removal efficiency decreased to 23, 21.26, 19 & 26.8 percent respectively. These results correspond to increase in the number of ions competing for the available binding sites and also lack of active sites on the adsorbent at higher concentration. On decreasing the temperature to

Table 1. Thermodynamic parameters for adsorption of Cr (VI)

Adsorbent T(K)	Co-precipitation		PEG		Urea		ODH	
	lnK (Lmg^{-1})	ΔG ($kJmol^{-1}$)	lnK (Lmg^{-1})	ΔG ($kJmol^{-1}$)	lnK (Lmg^{-1})	ΔG ($kJmol^{-1}$)	lnK (Lmg^{-1})	ΔG ($kJmol^{-1}$)
283	0.462	-1.086	0.429	-1.010	0.366	-0.860	0.494	-1.162
293	0.429	-1.046	0.397	-0.968	0.334	-0.814	0.462	-1.124
303	0.404	-1.017	0.366	-0.921	0.303	-0.762	0.429	-1.081
313	0.369	-0.959	0.334	-0.869	0.271	-0.706	0.397	-1.034

25°C, removal efficiency of $MgFe_2O_4$ increased from 36.38 to 45.00 percent, 34.81 to 43.24 percent, 31.80 to 40 percent and 38.54 to 46.5 percent respectively for 100 mg/l Cr (VI) solution.

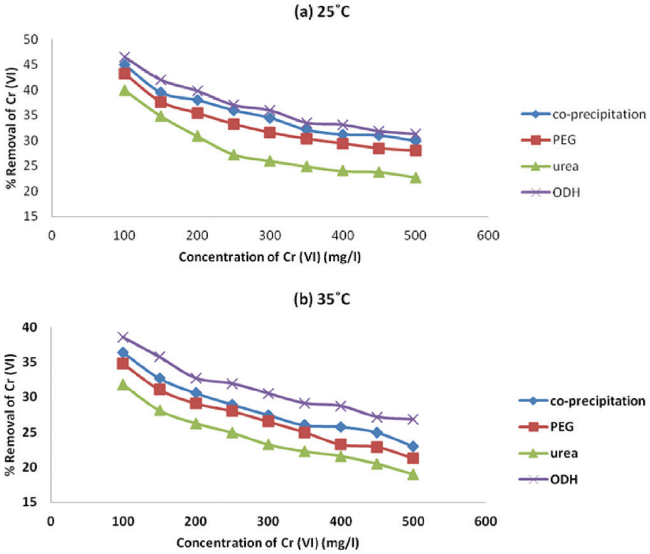

Fig. 6. Effect of initial metal ion concentration at (a) 25˚C and (b) 35˚C for Cr (VI) ion

Adsorption isotherms

In order to model the adsorption behavior and to calculate the adsorption capacity of $MgFe_2O_4$ NPs, adsorption isotherms were studied (Table 2 a-c). Langmuir, Freundlich and Dubinin Radushkevitch (D-R) isotherms were employed for Cr (VI) adsorption. Adsorption followed both Langmuir and Freundlich isotherms but D-R model was not followed in best way.

The adsorption capacity Q_{max} was calculated from the slope of the Langmuir plot and found to be in the range of 250.0 to 333.33 mg/g at 25°C and 35°C; energy of adsorption (b) comes out to be 2.09 to 4.41 mg/g respectively at 25°C and 2.14 to 4.06 at 35°C for $MgFe_2O_4$ NPs synthesized employing various chemical methods.

The Freundlich isotherm was also used to explain observed phenomena. K_f was in the range 1.389 to 2.541 mg/l at 25°C and 1.011 to 3.637 at 35°C (Table 2b). The value of 'n' was in the range 1 .248 to 1.420 at 25°C and 1.176 to 1.562 at 35°C, respectively. Dubinin Radushkevitch (D-R) isotherm model gives information regarding adsorption mechanism. From the plot of $\ln Q_e$ against ε^2, the value of D-R constant β and Q_m were computed. β was found to be 0.001 mol^2/kJ^2 at 25°C and range from 0.001 to 3×10^6 mol^2/kJ^2 at 35°C Q_m ranges from 7.964 to 8.052 mg/g at 25°C and from

Table 2 (a). Estimated Langmuir parameters for adsorption of Cr (VI)

Method	25°C			35°C		
	Q_m(mg/g)	b(L/mg) × 10^{-3}	R^2	Q_m (mg/g)	b(L/mg) × 10^{-3}	R^2
Co-precipitation	250.00	4.02	0.951	250.00	4.06	0.947
PEG	333.33	2.51	0.980	333.33	2.14	0.978
Urea	333.33	2.09	0.989	250.00	3.06	0.985
ODH	250.00	4.41	0.951	250.00	3.22	0.975

Table 2 (b). Estimated Freundlich parameters for adsorption of Cr (VI)

Method	25°C			35°C		
	n	K_f(mg/L)	R^2	n	K_f(mg/L)	R^2
Co-precipitation	1.414	2.541	0.980	1.562	3.637	0.957
PEG	1.364	2.070	0.995	1.264	1.445	0.986
Urea	1.248	1.389	0.997	1.340	1.754	0.983
ODH	1.420	2.529	0.982	1.176	1.011	0.999

Table 2 (c). Estimated D-R parameters for adsorption of Cr (VI)

Method	25°C				35°C			
	Q_m (mg/g)	β (mol^2/kJ^2)	E (KJ/mol)	R^2	Q_m (mg/g)	β (mol^2/kJ^2)	E (KJ/mol)	R^2
Co-precipitation	8.052	0.001	0.022	0.687	8.465	0.002	0.016	0.749
PEG	7.972	0.001	0.022	0.750	7.893	0.001	0.022	0.744
Urea	7.964	0.001	0.022	0.772	7.744	0.001	0.022	0.762
ODH	7.988	0.001	0.022	0.702	7.932	0.002	0.016	0.810

7.744 to 8.465 mg/g at 35°C respectively (Table 2c). From the constant k, magnitude of E was computed which was used to estimate the type of adsorption. If the value of E is in the range of 8-16 kJ/mol then the adsorption type can be ion exchange and if the E value is less than 8 kJ/mol then the adsorption is physisorption (Maji *et al.,* 2007). From the D-R plots, the value of E was 0.022 kJ/mol at 25°C and ranged from 0.016 to 0.408 kJ/mol at 35°C, which indicated that the adsorption was purely physical in nature. But correlation coefficient (R^2) was having values in the range of 0.687 to 0.810 indicating that D-R model was not followed in the perfect way.

Magnesium ferrite NPs are used as an adsorbent for removal of Cr (VI) from aqueous solution. Effect of processing methodology on the adsorption capacity of nano ferrites is studied. NPs synthesized by different methods showed small difference in the percentage removal of Cr (VI), although BET surface area for $MgFe_2O_4$ NPs displayed large variation. These results confirmed that the percentage removal depends not only upon surface area but also on the agglomeration behavior of the NPs in aqueous solution. Langmuir and Freundlich isotherms fit the data better than D-R isotherm.

LITERATURE CITED

Ajouyed O, Hurel C and Marmier N 2011. Evaluation of the adsorption of hexavalent chromium on kaolinite and illite. *J Environ Prot* **2**: 1347-52.

Chong K H and Volesky B 1995. Description of two-metal biosorption equilibria by Langmuir-type models. *Biotech Bio Eng* **47**: 451-60.

Das B, Mondal N K, Roy P and Chattaraj S 2013. Equilibrium, kinetic and thermodynamic study on chromium(VI) removal from aqueous solution using *Pistia stratiotes* biomass. *Chem Sci Trans* **2**(1): 85-104.

Elahi I, Zahira R, Mehmood K, Jamil A and Amin N 2012. Co-precipitation synthesis, physical and magnetic properties of manganese ferrite powder. *African J Pure Appl Chem* **6**:1-6.

Gregg S J and Sing K S W 1967. *Adsorption, Surface Area and Porosity*. Pp. 1-27, 35- 49.Academic Press, London and New York.

Jacob B P, Kumar A, Pant R P, Singh S and Mohammed E M 2011. Influence of preparation method on structural and magnetic properties of nickel ferrite nanoparticles. *Bull Mat Sci* **34**:1345-50.

Kaur M, Kaur N, Jeet K and Kaur P 2015a. $MgFe_2O_4$ nanoparticles loaded on activated charcoal for effective removal of Cr (VI) - A novel approach. *Ceram Int* **41**: 13739-50

Kaur M, Rana S and Tarsikka P S 2012. Comparative analysis of cadmium doped magnesium ferrite $Mg_{(1-x)}Cd_{(x)}Fe_2O_4$ (x=0.0, 0.2, 0.4, 0.6) nanoparticles. *Ceram Int* **38**: 4319-23.

Kaur M, Singh M, Mukhopadhyay S S, Singh D and Gupta M 2015b. Structural, magnetic and adsorptive properties of clay ferrite nanocomposite and its use for effective removal of Cr (VI) from water. *J Alloy Comp* **653**: 202-11.

Kaur N and Kaur M 2014. Comparative studies on impact of synthesis methods on structural and magnetic properties of magnesium ferrite nanoparticles. *Process Appl Ceram* **8(3)**: 137–143.

Kawasaki N, Bunei R, Ogata F, Tanei S and Tanada S 2006. Water treatment technology using carbonaceous materials produced from vegetable biomass. *J Water Environ Technol* **4**: 73-82.

Khaleel A, Kapoor P N and Klabunde K J 1999. Nanocrystalline metal oxides as new adsorbent for air purification. *Nanostruct Mater* **11**:459-68.

Li Q, Sun L, Zhang Y, Qian Y and Zhai J 2011. Characteristics of equilibrium, kinetics studies for adsorption of Hg(II) and Cr (VI) by polyaniline/humic acid composite. *Desalination* **266**: 188-94.

Liu C P, Li M W, Cui Z, Huang J R, Tian Y L, Lin T and Mi W B 2007. Comparative study of magnesium ferrite nanocrystallites prepared by sol-gel and coprecipitation methods. *J Mater Sci* **42**: 6133-38.

Maji S K, Pal A, Pal T and Adak A 2007. Adsorption thermodynamics of arsenic on laterite soil. *J Surface Sci Tech* **22**: 161-76.

Owlad M, Khireddine D, Daud W A W and Baroutian S 2009. Removal of hexavalent chromium contaminated water and wastewater: A review. *Water Air Soil Pollut* **200**: 59-77.

Pandey P K, Sharma S K and Sambi S S 2010. Kinetics and equilibrium study of chromium adsorption on zeolite NaX. *Int J Environ Sci Tech* **7**: 395-404.

Randhawa B S, Dosanjh H S and Kaur M 2005. Preparation of ferrites from the combustion of metal nitrate-oxalyl dihydrazide solutions. *Ind J Eng Mater Sci* **12**: 151-54.

Verma S, Joy P A, Khollam Y B, Potdar H S and Deshpande S B 2004. Synthesis of nanosized $MgFe_2O_4$ powders by hydrothermal method. *Mat Letters* **58**: 1092-95.

Yang K S and In H O 1996. Preparation of ultrafine$YBa_2Cu_3O_{7-x}$ superconductor powders by the poly(vinyl alcohol)-assisted sol-gel method. *Ind Eng Chem Res* **35**: 4296-300.