



Removal of Chromium (VI) cation metal using Poly (N-vinyl-2-pyrrolidone)/Magnetite nanocomposite from aqueous media

Padmalaya G¹, Sreeja BS^{1*}, Radha S¹, Raamdheep G², Saranya J³

Department of Electronics and Communication Engineering, SSN College of Engineering, Kalavakkam-603110, India.

¹padmalayag@ssn.edu.in, ¹sreejabs@ssn.edu.in

Center for Green Technology, Pondicherry University, Kalapet, Pondicherry-605014, India.

²raamdheep@gmail.com

Department of Electronics and Communication Engineering, Rajalakshmi College of Engineering, Thandalam, Chennai-602105, India.

³saranyaj@rajalakshmi.edu.in

ABSTRACT

Groundwater contamination with heavy metals is considered as serious environmental hazard that affect the human society. Nano adsorbents incorporating magnetite nanoparticles provides promising alternative to facilitate removal of heavy metal ions from wastewater. The present work focuses on removal of chromium (VI) cationic metals from aqueous media using Polyvinyl Pyrrolidone (PVP)/Magnetite (Fe₃O₄) Nanocomposite (MNC). Magnetite nanoparticles are synthesized using chemical co-precipitation and grafted using polyvinyl pyrrolidone to form a magnetite nanocomposite. MNC were characterized with X-ray diffraction (XRD) and Infrared absorption spectrum (FT-IR) studies to affirm the formation and presence of polymeric functional groups of PVP/Magnetite nanocomposite. Batch experiments are carried out at exclusive concentration intervals to study about the adsorption efficiency of MNC on chromium (VI) cationic metal using U-Vis spectroscopy. The results obtained through adsorption studies shows the synthesized PVP/Magnetite nanocomposites has a removal efficiency of 94%.

INTRODUCTION

Due to rapid increase in industrialization different contaminants are released into environment and pollute ground water. The presence of toxic trace metals like lead (Pb), chromium (Cr), mercury (Hg), Zinc (Zn) and cadmium (Cd) in the ground water have high toxicity and non-degradable properties which can cause severe health hazards to animals and human society. Chromium is one of the most common trace metal found in ground water particularly in industrialized areas. Chromium exists in +II, +III, and +VI states, among these states +VI state is considered to be most toxic and acts as carcinogens, mutagens, and teratogens due to its strong oxidizing properties [1-5]. Removal of chromium ions is carried out using methods like chemical precipitation, ion-exchange, membrane filtration/ultrafiltration, solvent extraction, sedimentation, reduction, reverse osmosis, dialysis/electrodialysis and adsorption [6-9]. Among these techniques, adsorption is most popular due to its controlled mechanism, increased ion removal rate, higher regeneration capacity and cost effectiveness [10-11]. Activated carbon is the widely used material to remove metal ions. However activated carbon tends to be expensive material and also requires complexing agents to increase removal efficiency. Therefore it is necessary to find alternative adsorbents which are capable of having high metal binding capacities and removal effectiveness at low cost. Compared to traditional adsorbents nanostructured adsorbents exhibited higher efficiency and adsorption capacity at faster rates in ground water treatment. Nano-adsorbents should satisfy few criterions like should be non-toxic, selectivity to low concentration pollutants, easy removal of pollutants and infinitely recycled. Magnetite Nano-adsorbents have attracted researchers due to its multifunctional properties such as super paramagnetic, recyclability, easy processing and low toxicity. Magnetite nanoparticles (MNP) oxidize easily and form aggregates due to dipole-dipole interaction. The stability of the MNP is enhanced by tailoring the surface using natural or synthetic stabilizers like surfactants and polymers with functional groups. The synergistic properties of magnetite nanocomposite containing organic-inorganic materials improve additional properties that cannot be achieved in either single organic or individual inorganic components [17]. Research is being carried out in enhancing the trace metal removal efficiency of magnetite nanocomposite using polymers [12-13]. Polymers like polypyrrole (PPy), polyaniline (PANI), Chitosan, montmorillonite were incorporated with magnetite nanoparticles are found to be high efficient adsorbent in removal of Cr (VI) ions [18, 22-23, 6]. These polymers form environmental friendly and are easy to prepare which provides functionalized media for the enhanced removal of chromium ions. Fe NPs are coated with well-defined SiO₂ shells were used as suitable adsorbent for removal of chromium ions [2]. Magnetite nanoparticles were modified with amorphous FeB alloy and used as efficient adsorbents for chromium removal [19]. Surface modification of magnetite nanoparticles with ionic ligands like trimethoxysilane and hydrophilic compounds PEI were also used as good adsorbents for removal of Cr (VI) ions [20-21]. Herein we report the novel experimental results that interaction of PVP on magnetite nanoparticles provides 94% of efficiency towards the removal of Cr (VI) ions which was not reported before and it has been achieved with different concentration levels of PVP/Magnetite nanocomposite in aqueous media and analyzed using UV-Vis Spectroscopy. As poly (N-vinyl-2-pyrrolidone) is a polar polymer, due to its carbonyl group of double group in the pyrrolidone group. It has the active carbonyl or tertiary nitrogen group. It was reported [24] PVP has three compounds (O, N, and carbonyl) that take part in interaction with magnetite nanoparticles. We made comparative study [Table 1] with other nanocomposites efficiency on removing chromium ions.



S.No.	Materials used	Initial Concentration used	Adsorbent dose	Removal (%) achieved	References
1.	Polypyrrole magnetic nanocomposite	200mg/L	0.1g/L	100	18
2.	Fe ₃ O ₄ -FeB nanocomposite	32mg/L	-	100	19
3.	Magnetite–Polyethylenimine–Montmorillonite: Hybrid film	12mg/L	4g/L	80	20
4.	Iron core-shell nanocomposite	70mg/L	0.15g/L	100 approx.	2
5.	Montmorillonite supported magnetite nanocomposite	50mg/L	5g/L	99.8	6
6.	Ionically modified magnetite nanocomposite	100mg/L	-	97	21
7.	PPY/maghemite PANI/maghemite nanocomposite	50mg/L	2mg/L	82 49	22
8.	Chitosan-magnetite nanocomposite strip	0.04g/L	0.01g/L	92.3	23
9.	Polyvinyl pyrrolidone/magnetite nanocomposite	40mg/L	0.4g/L	94	This work

Experimental

Materials:

Ferrous sulphate (Fe₂SO₄.7H₂O), ferric chloride (FeCl₃.6H₂O), ammonium hydroxide (NH₄OH), potassium dichromate (K₂Cr₂O₇) and polyvinyl pyrrolidone (C₆H₉NO)_n were purchased from Sigma-Aldrich. All the chemicals purchased for synthesis of magnetite nanocomposite are analytical grade and used without further purification.

Material synthesis:

Magnetite nanoparticles were synthesized using Chemical Co-Precipitation technique. Fig () shows the schematics on preparation of magnetite nanoparticles. In this technique, precursors of ferric chloride and ferrous sulphate were taken in the ratio of (2:1) and stirred well for 20mins. With the continuous stirring, 10% of Ammonium Hydroxide (NH₄OH) was added in drop wise and black precipitate is formed indicating the formation of magnetite nanoparticles. Formed Magnetite nanoparticles were collected using decanted with magnet and washed three times with double distilled water (ddH₂O). In order to form hybrid nanocomposite, 0.5% PVP was added along with magnetite nanoparticles and stirred for 1hour and made into powder form by drying in hot air oven at 80°C. The final product in the powder form was used for further analysis.

Batch Adsorption Experiments

Adsorption of Cr⁶⁺ ions were performed in batch mode with desired concentration of PVP/magnetite nanocomposite. The studies were performed by shaking predetermined adsorbents in 50mL of metal ion solution containing desired concentration of adsorbents (0–1.5g/L) The efficiency in removal of heavy metal using PVP and PVP–magnetite nanocomposites were evaluated using UV–visible spectroscopy. The removal efficiency is calculated using the equ (1).

$$E = (C_0 - C_e / C_0) / 100 \quad \text{----- (1)}$$

Where C₀ is the initial Cr (VI) concentration of the Solution and C_e represents the remaining Cr (VI) existing in solution after the adsorption process.

Results and discussion

X-Ray Diffraction patterns of sample shown in the Fig.1.shows PVP/magnetite nanocomposites denotes the diffraction planes of (220), (311), (400), (422), (511), (440), (553), (444) were matched with standard reference pattern JCPDS 89-2355 reported for inverse spinel structure.

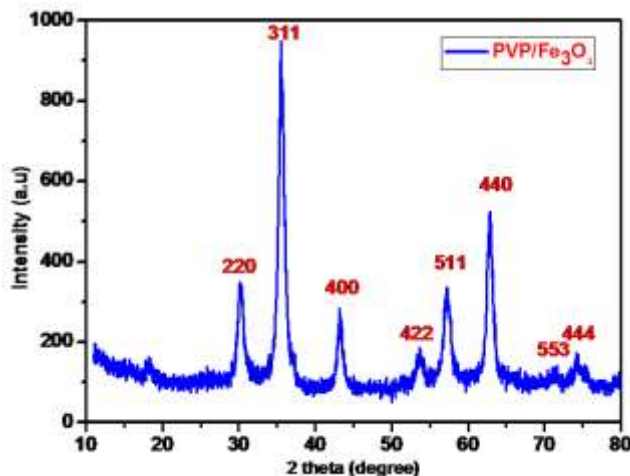


Fig.1. X-Ray diffraction patterns of PVP/Magnetite nanocomposite

Crystallite size of 10.7nm was calculated by using Scherrer formula for preferential orientation plane of (311). Lattice constant values of nanocomposite were calculated (a , $b=8.386$, 8.375) of inverse spinel structure and were in good agreement with literature.

The results of FTIR confirm the functional groups of PVP with Magnetite nanoparticles (fig.2). The most striking evidence from FTIR spectrum of PVP-Magnetite nanocomposite is that the broad peak between 1285cm^{-1} and 1650cm^{-1} confirms the C-N stretching vibration and C=O stretching vibration of PVP, respectively [17]. The narrow absorption peak centered at 1285 and 686cm^{-1} were occurred due to the C-N bonding and Fe-O vibrations [21] of PVP and magnetite nanoparticles attributed to coordinate bond between nitrogen-carbon atoms of PVP and Fe-O ions. As a consequence, the FTIR qualitatively confirms the formation of PVP-Magnetite nanocomposites.

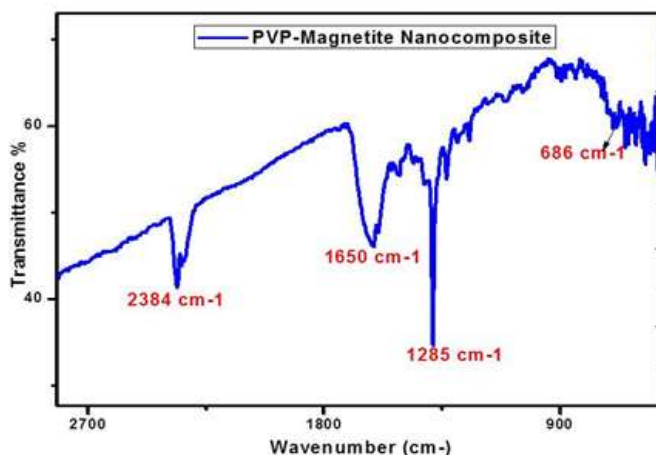


Fig. 2. FTIR study for PVP-Magnetite nanocomposite

Effect of initial concentration and metal removal mechanism:

The PVP/Magnetite nanocomposite is employed for Cr^{6+} removal using the UV-visible absorption spectrophotometer (JASCO V 650) with the 10mg/L in 50mL of Cr^{6+} solution and alternatives after treatment with PVP/Magnetite nanocomposite under ultrasonication for 5min. The evaluation of Cr (VI) removal in the solution was using the colorimetric method with a characteristic peak at 350nm in the U-Vis absorption curve. The higher the Cr (VI) focus in the perfect solution, the better peak intensity was noticed. The solution of Cr^{6+} containing 10mg/L showed greatest absorbance at 2.18, on treating with PVP/Magnetite nanocomposite at different concentrations ($0\text{--}2.5\text{g/L}$) under ultrasonication for 5 min, the peak intensity reduced little by little with increasing the adsorbent concentration indicating the reduced Cr(VI) amount in the solution.

Fig.3. Shows the kinetics of adsorbent that describes the Cr (VI) uptake rate is one of the important characteristics which controls the property of absorbate moments uptake at the solid-solution interface. Hence, in our study, the kinetics of Cr (VI) removing was accomplished to understand the adsorption behavior of the prepared PVP/Magnetite nanocomposite. On the basis of above experimental results, it is believed that PVP-Magnetite nanocomposite shows high adsorption towards the Cr (VI) ions. Chromium (VI) exists in aqueous solutions as $\text{Cr}_2\text{O}_7^{2-}$,

HCrO_4^- , CrO_4^{2-} and HCr_2O_7^- [23, 46]. So, here high adsorption of 94% of PVP-Magnetite nanocomposite was believed to come from strong interaction between functional groups (eg. C=O and C-N) of PVP [24] and metal ions which provides lots of adsorption sites for removal of Cr (VI) ions. Moreover, it is clear that chromium uptake by PVP- Fe_3O_4 nanocomposite is a physicochemical process, which carries electrostatic interaction.

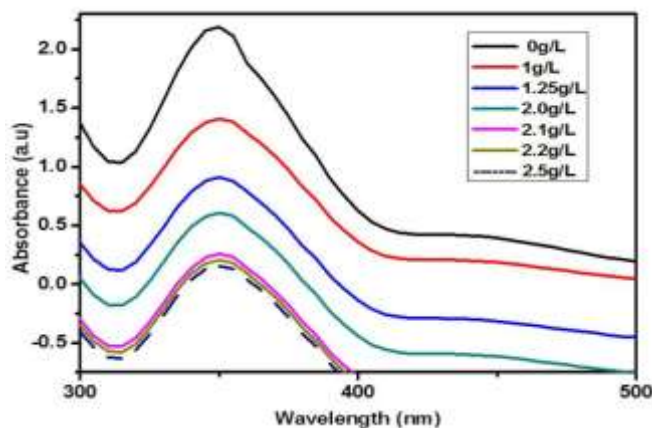


Fig.3. UV-Absorption with different concentration using PVP-Magnetite nanocomposite

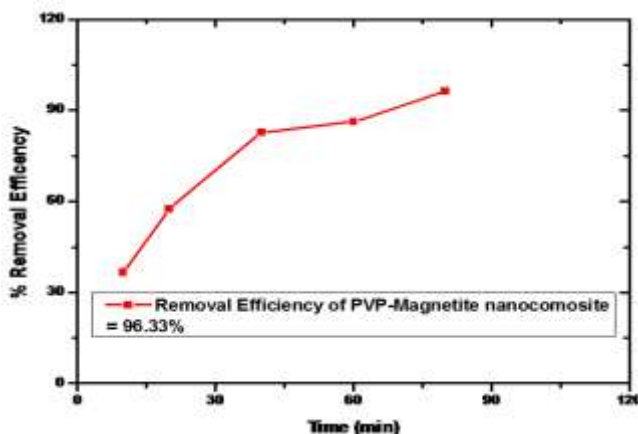


Fig.4. Removal efficiency of PVP-Magnetite nanocomposite

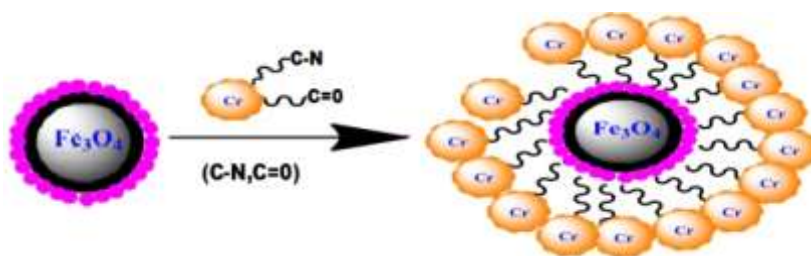


Fig.5. Schematics on representation of PVP-Magnetite nanocomposite mechanism

Conclusion

Magnetite nanoparticles were prepared by coprecipitation of Fe^{2+} and Fe^{3+} with NH_4OH , and then surface is grafted with polyvinyl pyrrolidone polymer. Powder X-ray diffraction shows the spinel structure for these nanoparticles. FT-IR spectra indicate that C-N and C=O molecules have been bound onto the surface of the magnetite nanoparticles through Fe-O. Then they could be used successfully as a magnetic cation exchanger with the possibility of removal of chromium (VI) cationic metal from water solution through grafted polymerization with polyvinyl pyrrolidone. The effect of concentration on cation separation was investigated too. From the results, it is obvious that the grafted nanocomposite shows high removal efficiency about 94%. Subsequently, the removal of chromium (VI) cationic metals using PVP-magnetite nanocomposite is highly efficient.



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