

Characterization of Magnetic Metal Encapsulated in Multi-Walled Carbon Nanotubes Synthesized from Methyl Ester of *Pongamia pinnata* Oil and Its Application for Removal of Arsenic Ions from Aqueous Solution

P. MAHALINGAM¹, N. SIVAKUMAR², M. KARTHIK³ and S. KARTHIKEYAN^{2*}

¹Department of Chemistry, Arignar Anna Government Arts College, Namakkal-637 002, India

²Department of Chemistry, Chikkanna Government Arts College, Tirupur-641 602, India

³CIC Energigune, Energy Cooperative Research Centre, Parque Tecnológico, 01510 Minano (Alava), Spain

*Corresponding author: E-mail: environkarthi@gmail.com

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Magnetic metals Fe-Co encapsulated in multi-walled carbon nanotubes, were prepared by spray pyrolysis of methyl ester of *Pongamia pinnata* oil, a renewable carbon precursor, over Fe-Co catalyst supported on silica. Carbon nanostructures with different morphologies were obtained over Fe-Co catalyst supported on silica, with 20 mL/h feed rate of precursor at different temperatures (550, 650 and 750 °C). The products were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, thermogravimetry and vibrating sample magnetometer. The Fe-Co encapsulated in multi-walled carbon nanotubes was used as adsorbent for removal of As(V) ions from aqueous solution. Sorption experiments were conducted using batch system. The effect of pH on As(V) ions adsorption on the adsorbent, effect of initial As(V) ions concentration on adsorption by adsorbent and effect of temperature on As(V) ions removal were studied. The kinetics of As(V) ions adsorption on Fe-Co encapsulated in multi-walled carbon nanotubes was discussed.

Keywords: Magnetic metal, *Pongamia pinnata* oil, Multi-walled carbon nanotubes, Spray pyrolysis method, Arsenic removal.

INTRODUCTION

Magnetic nanoparticles are in the focus of research recently because of their attractive properties useful in catalysis¹, biomedicine², magnetic resonance imaging³, magnetic particle imaging⁴, data storage⁵ and environmental remediation⁶. The disadvantages of metallic nanoparticles are its lower stability in various chemical and physical environments such as acid or base media, as well as at high temperature and pressure. To access the much higher magnetic moments of magnetic nanoparticles and more stability, the magnetic core to be protected by surface coating that should be chemically inert towards air, acid and stable at elevated temperatures. The metallic core of magnetic nanoparticles may be passivated by gentle oxidation, surfactants, polymers and precious metals⁷. Nanoparticles with a magnetic core consisting either of Fe or Co with a non reactive shell made of graphene have been synthesized recently⁸. Enclosure of magnetic nanoparticles in graphite is of particular interest since it could prevent their degradation in reaction chemical environments and isolate the particles magnetically from each other to avoid low proximity interactions. In the recent past, various carbon-protected metal nanoparticles have been made by techniques including filling process, template-

based synthesis, chemical vapour deposition, pyrolysis procedure, sol-gel process, self-assembly method *etc.*⁹. Many of these methods still suffer from various drawbacks such as complicated procedure and poor growth control of metal filled carbon nanotubes. Also, most of the encapsulated metals exist as particles or short rods and distribute randomly along the nanotubes¹⁰. Such a low filling efficiency limits the production of large amount of magnetic metal filled multi-walled carbon nanotubes for practical applications. Most of the carbon materials have been synthesized from precursors based on the fossil fuel like petroleum products^{11,12}. Apart from expensiveness, these precursors will deplete at one point of time. It is therefore necessary to look for precursors which are plant based, renewable and environmentally safe. Recently, appreciable attempts were made for preparation of multi-walled carbon nanotubes and carbon encapsulated magnetic metal nanostructures from regenerative precursors¹³⁻¹⁶. Here in we report the results of experiments conducted to study the synthesis of Fe-Co magnetic metals encapsulated in multi-walled carbon nanotubes at different temperatures by spray pyrolysis of methyl ester of *Pongamia pinnata* oil over Fe-Co catalyst supported on silica in nitrogen atmosphere. The results show that ecologically advantageous and regenerative methyl

ester of *Pongamia pinnata* oil may be an effective precursor for preparing magnetic metal encapsulated in MWCNTs by spray pyrolysis technique. Arsenic is considered as one of the most hazardous elements for living organisms and its presence in natural water can result in serious environmental problems. The possible application of Fe-Co encapsulated in MWCNTs as adsorbent for removal of As(V) ions from aqueous solutions were studied.

EXPERIMENTAL

A silica supported Fe-Co catalyst (Fe:Co:SiO₂ = 1:0.6:4) was prepared by wet impregnation method.¹⁷ Appropriate quantities of metal salts (Merck) *i.e.* Fe(NO₃)₃·6H₂O and Co(NO₃)₃·3H₂O were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 h, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 h at 450 °C and then re-ground before loading into the reactor. The prepared catalyst was directly placed in a quartz boat and kept at the centre of a quartz tube which was placed inside a tubular furnace. The carrier gas nitrogen was introduced at the rate of 100 mL/min into the quartz tube to remove the presence of any oxygen inside the quartz tube. The temperature was raised from room temperature to the desired growing temperature. Subsequently, methyl ester of *Pongamia pinnata* oil was introduced into the quartz tube through spray nozzle and the flow was maintained at the rate of 0.5 mL/min. Spray pyrolysis was carried out for 45 min and thereafter furnace was cooled to room temperature. Nitrogen atmosphere was maintained throughout the experiment. The morphology and degree of graphitization of the as-grown nanostructures were characterized by scanning electron microscopy (Hitachi SU6600), high resolution transmission electron microscopy (JEOL-3010), Raman spectroscopy (JASCO NRS-1500W, green laser with excitation wavelength 532 nm) and thermogravimetric analysis (TGA). Magnetic properties of the sample at room temperature were studied using vibrating sample magnetometer. The as-grown products were subjected to purification process as follows¹⁸. The sample material was added to 5 % HF solution to form acidic slurry. This slurry was heated to 60 °C and stirred at 600 rpm. The sample was filtered and washed with distilled water. The collected sample was dried at 120 °C in air for 2 h. The stock solution of As(V) was prepared by dissolving Na₂HAsO₄·7H₂O in distilled water. The residual As(V) concentration in solution after adsorption was analyzed using flame atomic adsorption spectrometer (AAS). The solution pH was adjusted with HCl and NaOH.

RESULTS AND DISCUSSION

The yield, morphology and magnetic properties of as-grown products obtained from spray pyrolysis of methyl ester of *Pongamia pinnata* oil were studied. The carbon nanostructure yield at different temperatures *viz.*, 550, 650 and 750 °C under constant precursor feed rate of 20 mL/h over Fe-Co catalyst supported on silica were shown in Fig. 1. A typical SEM and HRTEM image of samples synthesized at different reaction temperatures (550, 650 and 750 °C) under constant

precursor feed rate of 20 mL/h were shown in Fig. 2. The I_G/I_D values obtained from Raman spectral studies and the TGA result of carbon samples synthesized under constant precursor feed rate of 20 mL/h for different temperatures were given in Table-1. The magnetic properties of purified sample of Fe-Co encapsulated in MWCNTs synthesized using methyl ester of *Pongamia pinnata* oil with a flow rate of 20 mL/h at 650 °C was characterized by EDX and vibrating sample magnetometer (Fig. 3). Fe-Co encapsulated in MWCNTs as adsorbent for removal of As(V) ions from aqueous solutions were studied (Fig. 4).

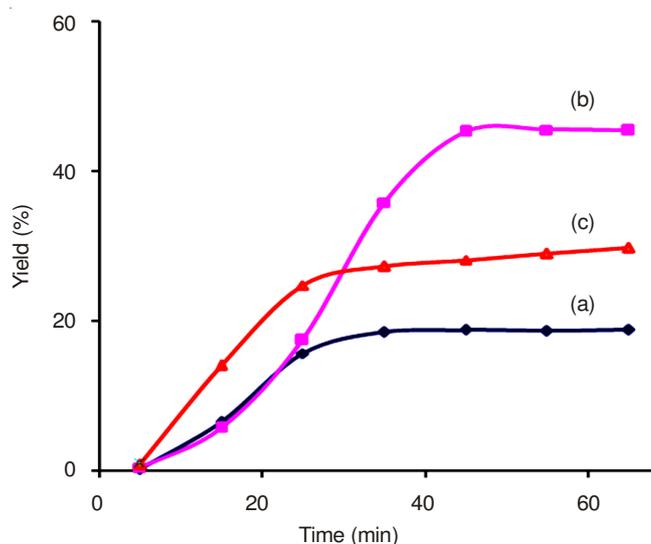


Fig. 1. Reaction time dependence of carbon yield under constant precursor feed rate of 20 mL/h for different reaction temperatures (a) 550 °C (b) 650 °C (c) 750 °C

TABLE-1
CHARACTERIZATION PARAMETERS: I_G/I_D RATIO DETERMINED BY RAMAN STUDIES AND % WEIGHT OF RESIDUE OBTAINED IN TGA FOR THE SAMPLES SYNTHESIZED AT DIFFERENT TEMPERATURES FOR THE PRECURSOR FLOW RATE OF 20 mL/h

| Temperature (°C) | I _G /I _D ratio (Raman) | % Weight of residue in TGA for the purified sample |
|------------------|--|--|
| 550 | 0.53 | 8.6 |
| 650 | 0.94 | 21.9 |
| 750 | 1.42 | 5.7 |

The influence of temperature on carbon yield shows low yield at 550 °C (Fig. 1a). This may be due to low catalytic activity of catalyst at this temperature. At reaction temperature 650 °C, the increased yield of MWCNTs at early stage of reaction is due to the high catalytic activity of the catalyst (Fig. 1b). However, the low yield of MWCNTs obtained, as shown in Fig. 1c, at high temperature range (750 °C) compare to yield of MWCNTs at 650 °C may be due to deactivation of catalyst particles by the encapsulation of graphitic carbon. The fact can be referred to the report by Kang *et al.*¹⁹ that at high synthesis temperature, the rate of carbon nucleation was too fast compared to that of precipitation resulting in a rapid encapsulation of the catalyst particles by graphitic carbon.

The SEM observations of the sample synthesized at reaction temperature 550 °C show less densely populated and large diameter carbon nanotubes (Fig. 2a). The poor crystallization

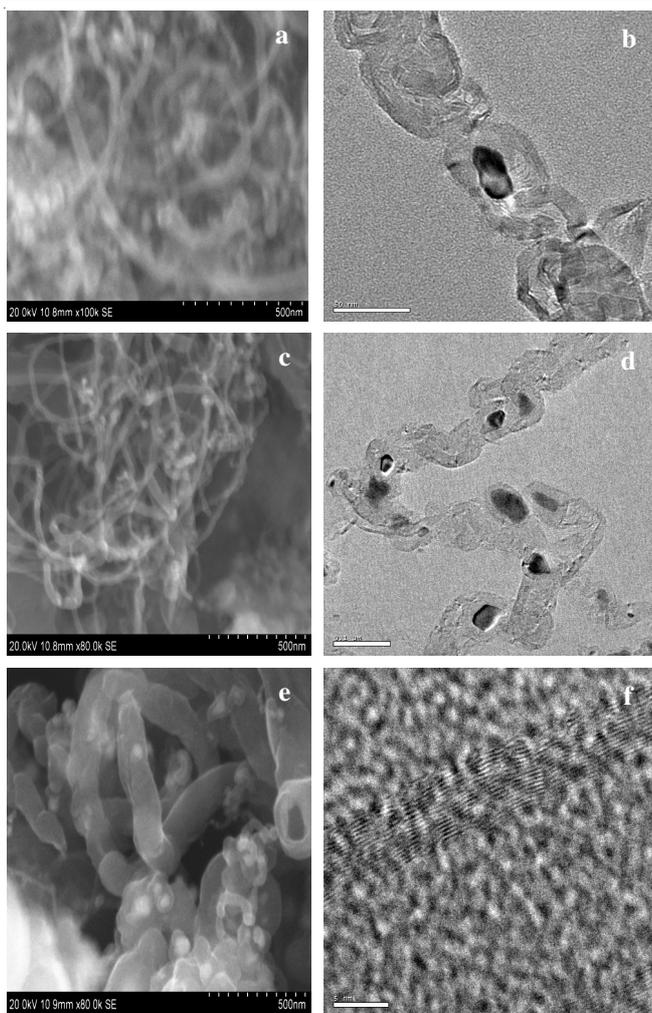


Fig. 2. A typical SEM and HRTEM image of samples synthesized at different reaction temperatures under constant precursor feed rate of 20 mL/h SEM: (a) 550 °C (c) 650 °C (e) 750 °C and HRTEM: (b) 550 °C (d) 650 °C (f) 750 °C

of carbon layers were evident from the HRTEM image of the sample synthesized at 550 °C (Fig. 2b). The SEM image of the sample synthesized at 650 °C shows densely formed carbon nanotubes (Fig. 2c). The HRTEM of the sample synthesized at 650 °C (Fig. 2d) indicate the metal particles, seen as a dark spot, were tightly covered by carbon layers with a thickness of a few nanometers and graphitic layers surrounding the

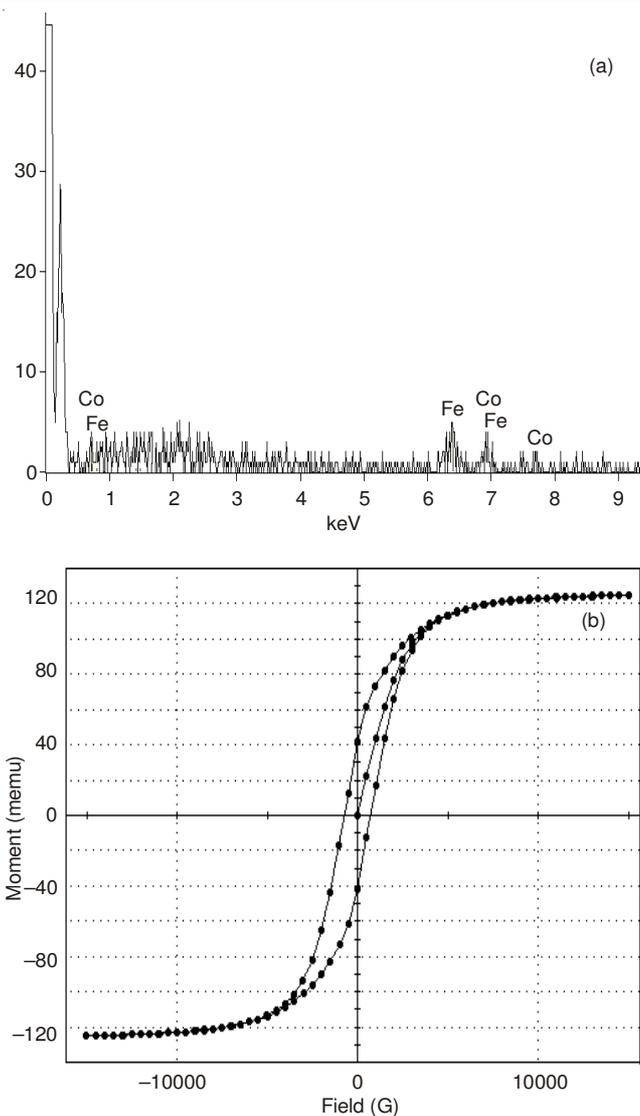


Fig. 3. Fe-Co encapsulated in MWNTs sample synthesized at 650 °C (a) EDX result; (b) Hysteresis loops (M vs. H) recorded

catalyst particles were with good crystallinity. The SEM image (Fig. 2e) of the sample synthesized at 750 °C indicates that the carbon nanotubes formed were thick in size. The sample contains less densely populated MWCNTs along with amorphous carbon. However, The HRTEM image (Fig. 2f) of

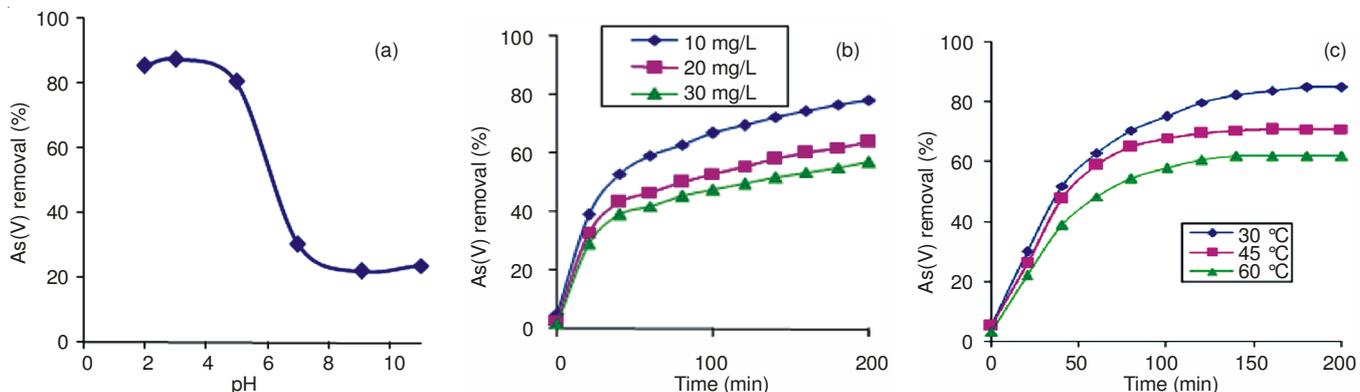


Fig. 4. (a) Effect of pH on As(V) ion adsorption on Fe-Co encapsulated in MWNTs; (b) Effect of initial As(V) ion concentration on adsorption by Fe-Co encapsulated in MWNTs; (c) Effect of temperature on As(V) ion removal

the MWCNTs formed at a reaction temperature 750 °C evidenced good crystalline graphitic layers of MWCNTs.

The crystallinity of MWCNTs was characterized by Raman scattering studies. The G band at 1578 cm⁻¹ is attributed to crystalline carbon layers. The D band at 1343 cm⁻¹ is associated with the defects, vacancies and impurities that destroy the graphitic layer symmetry^{20,21}. The intensity ratio of G-band and D-band (I_G/I_D) obtained from Raman scattering spectral values for the MWCNTs synthesized at different temperatures were shown in Table-1. The poor quality of carbon layer formed for the sample synthesized at 550 °C was evident from the I_G/I_D value of 0.53 and the fact was supported by HRTEM images (Fig. 2b). The I_G/I_D value of 0.94 (Table-1) for samples prepared at 650 °C with flow rate of 20 mL/h indicates that magnetic nanoparticles encapsulated in carbon nanotubes structure had defects and moderate crystallization of graphene planes. The I_G/I_D (Table-1) value 1.42 for the samples synthesized at 750 °C indicate the formation of MWCNTs with good crystalline graphitic layers.

The as-grown samples consists of support material silica, the metals Fe and Co used as catalyst, Fe-Co encapsulated in MWCNTs, amorphous carbon and carbon nanostructures. The process of purification removes the support material silica and un-encapsulated Fe and Co. The TGA results of purified samples were shown in Table-1. The weight of residue was 8.6, 21.9 and 5.7 % mass fraction for the purified samples synthesized at 550, 650 and 750 °C respectively. The low percentage weight of residue observed for the products synthesized at 550 °C and 750 °C were attributed to acid leaching of support and catalyst particles that were not encapsulated by carbon. The carbon sample synthesized at 650 °C with a precursor feed rate of 20 mL/h after purification process shows 21.9 % weight of residue in TGA studies. The high value of residue obtained in TGA for the purified sample is attributed to the fact that carbon layers covering the metal particles prevent the dissolution of metal during purification. This indicates effective formation of Fe-Co nanoparticles encapsulated in MWCNTs at 650 °C for 20 mL/h precursor flow rate compared to other experimental conditions employed in this study.

The magnetic hysteresis loops (Fig. 3b), for the purified sample synthesized using methyl ester of *Pongamia pinnata* oil with a flow rate of 20 mL/h at 650 °C, shows the ferromagnetic behaviour of Fe-Co encapsulated in MWCNTs. The saturation magnetization for the sample was 6 emu/g. The coercivity of the sample was 721.45 G. The results confirmed the successful encapsulation of Fe-Co in MWCNTs. The encapsulation of Fe-Co in MWCNTs was also evidenced by EDX (Fig. 3a) for the sample. The hysteresis loops for the sample are the typical loops of soft magnet. The saturation magnetization value of Fe-Co encapsulated in MWCNTs is comparable with the reported values²².

The perspectives of Fe-Co encapsulated in MWCNTs in environmental treatment are outlined with study of adsorption of arsenate [As(V)] ions on the purified Fe-Co encapsulated in MWCNTs. The adsorption of arsenic from aqueous solution using MWCNTs was found to be highly pH dependent process. The effect of pH on the adsorption process is mainly influenced by the two factors: (i) distribution of arsenate ion species [As(V)] in the solution phase and (ii) the surface charge of the adsorbent. Therefore, the interaction between As(V) ion and MWCNTs is basically a combined result of charges on the As(V) ion and MWCNTs. The effect of pH for the adsorption of As(V) ion on MWCNTs over a pH range of 2 to 11 is presented in Fig. 4a. It is evident from the Fig. 4a that high percentage As(V) ion adsorption on MWCNTs occurs at pH value of 2. The percentage adsorption of As(V) ion decreases rapidly to a low value at pH 7 and remain almost constant for increase of pH up to 11. In an aqueous solution, in the pH range of 2 to 11, the As(V) ion exist as H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻ ions²³. The isoelectric point value of 5.8 for MWCNTs indicate that the surface of MWCNTs is positively charged under acidic conditions and these positive charges facilitate the removal of As(V) ions. At higher pH value the adsorption of As(V) ion on MWCNTs decreases due to the electrostatic repulsion between the ionized MWCNTs and the As(V) ion. However, small amount of adsorption observed may be attributed to physicochemical adsorption of As(V) ion over the surface of MWCNTs. The effect of initial As(V) ions concentration and contact time for the removal of As(V) ions by MWCNTs were shown in Fig. 4b. In this study 10, 20 and 30 mg/L As(V) ion concentrated solutions were used. Fig. 4b shows that As(V) ions adsorption depends on initial concentration of As(V) ion. Rapid removal of As(V) ions were noticed during the initial 0.5 h of contact time and reaches the equilibrium around 2 h for all range of concentrations studied. Decrease in adsorption percentage at higher concentrations might be due to the relatively smaller number of active sites available at higher As(V) ions concentration. The kinetics of As(V) ions adsorption on MWCNTs were determined for initial As(V) ions concentration 20 mg/L, pH value of 4, MWCNTs dose 1 g/L at different temperatures *viz.* 30, 45 and 60 °C. The analyses of results are shown in Table-2. Pseudo second order equation provided a best fit description for the adsorption of As(V) ions on to chosen MWCNTs relative to Elovich and pseudo first order equations²⁴⁻²⁶.

Conclusion

A green synthesis of magnetic metal encapsulated in multi-walled carbon nanotubes by spray pyrolysis of methyl ester of *Pongamia pinnata* oil, an eco-friendly natural precursor using Fe-Co catalyst supported on silica was demonstrated.

TABLE-2
ADSORPTION KINETIC MODEL RATE CONSTANTS FOR MWCNTs AT DIFFERENT TEMPERATURE

| Adsorbent | Initial temperature (°C) | Pseudo first order | | Pseudo second order | | | Elovich model | | |
|------------------------------|--------------------------|---------------------------------------|----------------|--|---|----------------|--------------------------|---|----------------|
| | | k ₁ (L min ⁻¹) | r ² | k ₂ (g mg ⁻¹ min ⁻¹) | H (mg g ⁻¹ min ⁻¹) | r ² | β (g min ⁻¹) | α (mg g ⁻¹ min ⁻¹) | r ² |
| Fe-Co encapsulated in MWCNTs | 30 | 0.131 | 0.974 | 0.120 | 22.615 | 0.988 | 203.709 | 0.211 | 0.977 |
| | 45 | 0.135 | 0.980 | 0.011 | 15.210 | 0.992 | 74.150 | 0.139 | 0.967 |
| | 60 | 0.168 | 0.971 | 0.128 | 11.229 | 0.988 | 121.554 | 0.358 | 0.977 |

The optimum reaction conditions for synthesis of magnetic metal encapsulated in multi-walled carbon nanotubes were 650 °C and the precursor flow rate of 20 mL/h. The removal of As(V) ions from aqueous solution was possible using Fe-Co encapsulated in MWCNTs. The adsorption of As(V) ions was found to be dependent on pH, temperature and concentration of adsorbent. The percentage saturation was found to be almost 75 %. The kinetics of As(V) ions adsorption on Fe-Co encapsulated in MWCNTs adsorbent was found to follow a pseudo second-order rate equation.

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