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Vanadium Removal from Fuel Oil and Waste Water in Power Plant Using Humic Acid Coated Magnetic Nanoparticles

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Abstract:

A method for treating fuel oil and waste water of power plant is suggested which is including vanadium elimination through contacting with humic acid coated magnetic nano-adsorbent. The nano-adsorbent was modified with humic acid (HA) as a compound having carboxyl, hydroxyl and amin functional groups. HA/Fe3O4 nanoparticles were prepared by a co-precipitation procedure and were characterized using different techniques such as dynamic light scattering (DLS), Transmission electron microscopy (TEM), FTIR spectroscopy, X-ray diffraction spectroscopy. The surface charge of the nano-adsorbents was determined by Zeta potential technique and their magnetic properties were investigated by vibrational sample magnetometer (VSM). It was observed that the synthesized nanoparticles have a mean diameter about 14 nm. The effects of several experimental factors such as pH, adsorbent dosage, contact time and initial vanadium concentration, on the nano-adsorbent ability for vanadium removal were investigated. The best results were obtained using 10 mg/ml of nanoparticles at pH 5 and contact time 30 min. At this condition about 99.5 % of V(IV) could be removed from synthetic samples. Maximum adsorption capacity for vanadium (IV) was 8.97 mg/g which was fitted to Langmuir isotherm model. The ability of HA/Fe3O4 for the vanadium removal from fuel oil and wastewater of power plant was also investigated. It was observed that more than 93% of vanadium content could be removed from waste water and 67% form fuel oil using proposed nano-adsorbent.

Keywords: *Vanadium removal, Magnetic nanoparticle, Humic acid, Adsorption, Waste Water, Fuel Oil.*

1. INTRODUCTION

The environment and all the life forms on earth face a very serious threat from the heavy metal pollution due to their toxicity and strong tendency to concentrate in environment. At recent years heavy metal are classified as toxid and half of these are emitted into the environment in quantities that pose risk to human health [1]. Upgrading of heavy oils is necessary because the world reserves of conventional light oils are dwindling and being replaced by an increasing amount of heavy oils [2]. Most crude oils contain different metals with concentrations varying from a few ppm to 1000 ppm depending on the origin of the crude. Examples of these metals are sodium, potassium, lithium, calcium, strontium, copper, silver, vanadium, manganese, tin, lead, cobalt, titanium, gold, chromium, and nickel [3-5]. The metals are usually in combination with naphthenic acid as soaps and in the form of complex organometallic compounds such as metalloporphyrins. Among these metals the most abundant and undesirable are vanadium and nickel. Depending on the origin of crude oil, the concentration of the vanadium varies from as low as 0.1 ppm to as high as 1200 ppm, while that of nickel commonly varies from trace to 150 ppm [5-8]. Vanadium compounds present in the saleable oil create vanadium pentoxide during combustion raising concerns of toxicity if emitted directly to the environment from a stack, as well as corrosion concerns for turbines when used in power generation [2].

The high concentrations of vanadium in some crude oils have raised the question whether the burning of fossil fuels would change the global chemical cycle of this element. While more reliable data of the concentration of vanadium in natural waters are becoming available, questions remain with respect to the detailed speciation and the kinetics of the principal geochemical reactions of vanadium. In oxic waters the dominant vanadium species are the phosphate-like anions $H_2VO_4^-$, and HVO_4^{2-}. In reducing environments, in shale, and in carbonaceous sediments, the vanadyl ion VO^{2+} has been detected. This cation has a tendency to hydrolyze, and in the pH range of natural waters it is rather insoluble, is strongly adsorbed on particles and forms stable complexes with humic acids and porphyrins [9, 10].

V(V) is the principal stable species of this element in oxidative conditions; however, in anoxic medium V(IV) occurs in significant amounts. Furthermore, V(IV) can be mobilized by soluble soil organic matter under both aerobic and anaerobic conditions. Simple reducing agents, such as oxalates, frequently present in waters, can reduce V(V) to V(IV). They are also capable of dissolving V_2O_5 producing soluble VO^{2+} ions [11, 12].

Vanadium is widely distributed in the earth's crust and has been recognized as a potentially dangerous pollutant in the same class as mercury, lead and arsenic [13]. Vanadium compounds are acutely toxic by most routes of exposure, in most species. In general, the toxicity of vanadium compounds increases with the oxidation state. Vanadium poisoning in humans can be diagnosed on the basis of a history of exposure, the clinical picture, a green tongue (due to the hexa-aqua ion), and measurements of vanadium levels in blood cells, plasma and urine. The value of various tests of the secondary metabolic effects of poisoning is disputed. Dimercaprol and ascorbic acid may have value in the treatment of poisoning in human beings. There are no adequate epidemiological studies of mortality in occupationally exposed populations [14].

Natural occurrence plus anthropogenic emission of vanadium may mean that it must be removed from drinking water, one of the major ways that vanadium enters the human body. Consequently, pollution studies increasingly discuss vanadium removal from wastewater [13].

It is crucial to eliminate the metallic heteroatoms as early as possible during refining and upgrading in order to reduce the environmental impact of oil processing and protect downstream catalysts from poisoning [3].

Several techniques had been utilized for the removal of vanadium from crude oils such as treatment with strong oxidants (hydrofluoric acid, chlorine, sulfuryl chloride, sodium hypochlorite, peroxyacetic acid, organophosphorous reagents); biologicals (chloroperoxidase /H_2O_2, cytochrome c reductase/ NADPH, micro-bial strains isolated from petroleumcontaminated soil); electrolysis; ultrasonic irradiation combined with chromate-graphy; photoirradiation followed by acid extraction; and adsorption. Although hydrodemetallization is the most widely employed process. Among these, electrochemical, microbial, photochemical coupled with liquid−liquid extraction, and oxidative demetallization have shown promising results. These techniques usually require a high investment in the equipment needed for removing vanadium by hydrogenation. Also, the catalysts are difficult to regenerate, which causes problems with the disposal of waste catalysts [3, 15, 16].

Literature describing the removal of vanadium from contaminated aquatic systems is rather limited. Several methods have been developed for the removal of vanadium from aqueous solutions, for example chemical precipitation, ion exchange, activated carbon, biological and chemical treatments, membrane filtration, waste metal sludge, sodium carbonate softening, calcium hydroxyapatite (CAP) adsorption, combination of adsorption/co-precipitation with FeO(OH), modified chitosan, aluminum-pillared bentonite, and Fe(III)/Cr(III) hydroxide waste [11, 17-20].

Amid of these efficient techniques, adsorption is one of the fascinating methods due to its feasible operation. It is not only the ease of operation and insensitivity to toxic substances and simplicity of design, but the application of adsorption technique is limited due to its high cost. Application of wastewater treatment using nanoparticles is driven by many factors such as reduction of cost, durability at high temperature, large surface area, high reactivity, high specificity, and ability to penetrate through porous media to remove the contaminants selectively [21].

Recently, it was reported that using superparamagnetic monodispersed iron oxide (Fe_3O_4) nanoparticles as an effective adsorbent for heavy metals removal from water, may result in development of a new and efficient technology in industrial wastewater treatment [1]. Application of iron oxide based nanomaterial is more attractive for removal of heavy metals contamination, because of their important features like small size, high surface area, low toxicity, chemical stability and magnetic property. Magnetic property of iron oxide nanoparticles enables easy separation of the adsorbents system and could be reused for further application. Reusability of iron oxide based nanomaterial leads to a decrease in the economic burden [22-26]. These particles are superparamagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, suspended are superparamagnetic particles adhered to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal of the field [27].

Bare magnetite nanoparticles are very much susceptible to air oxidation and are easily aggregated in aqueous systems.

Organic matters such as humic acid which are found in sediments and surface soils, have natural and powerful adsorbent properties. Researches indicated that humic acid has high affinity to Fe_3O_4 nanoparticles, and sorption of HA on the Fe_3O_4 nanoparticles enhanced the stability of nano dispersions by preventing their aggregation. Abundant in natural aqueous systems, HA has a skeleton of alkyl and aromatic units that attach with carboxylic acid, phenolic hydroxyl, and quinone functional groups. The carboxyl (COOH) group reactsreadily with metals, and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO−) group. The phenolichydroxyl (OH) group is more abundant in the early stages of decomposition, isderived from lignin in woody plants, reacts less with metals, and dissociates between pH 8 and 13.5. The COOH and phenolic OH groups account for the total acidity of HA while the alcoholic OH group is only weakly acidic and reacts minimally with metals. As these functional groups have high complex capacity with heavy metal ions, HA was applied to remove heavy metal ions from water. Binding of HA to metal oxides influences the sorption behavior of both HA and metal oxides. This is because the adsorption of HA results in a poly anionic organic coating on metal oxides and thus essentially altering the surface properties of the particles [28, 29].

The main purpose of the present work is to explore the use of HA/Fe_3O_4 nanoparticles as nano-adsorbent in treatment of power plant fuels and also industrial effluents to evaluate their abilityfor the removal of vanadium from oil environment and aqueous solutions. HA/Fe_3O_4 nanoparticles were synthesized according to co-precipitation method and then characterized using different methods such as, dynamic light scattering (DLS), transmission electron microscopy (TEM), zeta potential measurement, vibrating sample magnetometer (VSM), X-ray diffraction (XRD) and FTIR spectroscopy. After that, the adsorption ability of the proposed nano-adsorbent was evaluated in different experimental conditions. In all experiments vanadium content determination were carried out using inductively coupled plasma (ICP) method. The results showed that this nano-adsorbent can remove vanadium content from fuel oil andindustrial aqueous sample sefficiently. To the best of our knowledge, there is no similar report on using this kind of nano-adsorbent for treatment of vanadium polluted industrial samples, especially oily samples.

2. EXPERIMENTAL

2.1. Materials

Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH, 25%), humic acid sodium salt and vanadyl soulfate ($VOSO_4$) were purchased from Merck company. All water used for synthesis of HA/Fe_3O_4 magnetic nanoparticles was deionized double distilled water (Millipore, FNR8-UV 0.22). All chemicals were the guaranteed or analytic grade reagents commercially available and used without further purification. The pH of the solutions was adjusted using a pHmeter (Metrohm, 827).

2.2. Apparatus

The size and size distribution of nanoparticles were investigated by particle size analyzer based dynamic light scattering (L-550, HORIBA) and TEM images (Zeiss - EM10C - 80 KV). Humic acid's grafting onto the surface of magnetic nanoparticles (MNPs) was monitored by Fourier transform infrared (FTIR) spectroscopy (RX1, Perkin-Elmer). The crystalline structure of Fe_3O_4 nanoparticles was characterized by X-ray diffraction technique (D8 Advance, Bruker). Zeta potential analysis (ZEN 3600, Malvern) was performed to investigate the surface net charge of nanoparticles. The magnetic properties of the Fe_3O_4 nanoparticles coated with humic acid were measured using a vibrating sample magnetometer (Megnatis Daghigh Kavir, Iran) and the concentrations of vanadium were measured using the inductively coupled plasma (ICP– Varian, vista– pro).

2.3. Preparation of Humic Acid-Bound Fe_3O_4 Nanoparticles

5.2 g of $FeCl_3.6H_2O$ and 2 g of $FeCl_2.4H_2O$ were dissolved in 100 mldeoxygenated water and heated up to 90°C under N_2 protection. Then two solutions, 10 ml of ammonium hydroxide (25%) and 2 mg/ml of humic acid sodium salt dissolved in 50 ml of water, were added rapidly and sequentially to above solution. The mixture was stirred at 90°C for 30 min and then cooled to room temperature. The black precipitate was collected by filtrating and washed to neutral with water. The obtained black precipitate was HA/Fe_3O_4 nanoparticles and was ready for use [30].

2.4. Fuel Sample Preparation

In order to determination of trace elements in crude petroleumand petroleum products, a digestion process should be carried out on the samples. A method for the microwave decomposition of the residual fuel oil in closed-pressurized vessels was developed using a mixture of HNO_3 and H_2O_2 as reagents of digestion. A certain amount of sample was weighed and then 9.5 ml HNO_3 and 2.5 ml H_2O_2 were added into the digestion vessel. The mixture was shaken carefully and the glass tube is placed inside the micro wave chamber. The system was equipped with an automatic pressure and temperature controller. The proper microwave power could be set for the digestion of our samples according to the tabulated values. Finally, a clear solution was obtained [30].

3. RESULT AND DISCUSSION

3.1. Characterizations of Humic Acid-Bound Fe3O4 Nanoparticles

One of the most important steps in magnetic nanoparticle preparation is their characterization. It means the investigation of their size, shape and size distributions and also, their magnetic properties. For this purpose different methods were used and the results were shown flowingly.

3.1.1. Dynamic Light Scattering (DLS)

The particle size analysis were carried out using DLS experiment which was conducted at a fixed scattering angle of 90° and at a constant temperature of 25°C. Fig. 1 shows the size distribution graphs for the humic acid coated Fe_3O_4 nanoparticles obtained by DLS method. These reveal a relatively narrow range of distribution for the resultant nanoparticles and the average size of the nanoparticles was about 37 nm.

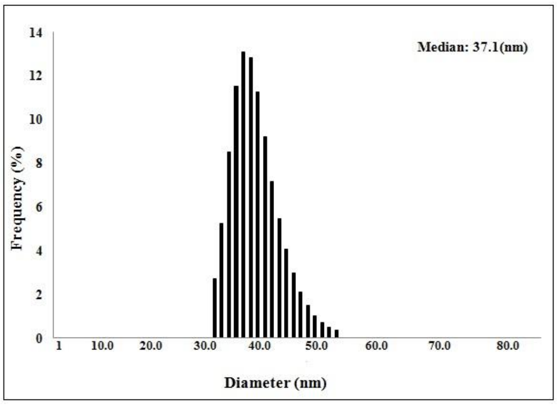


Figure 1. *DLS plot of humic acid modified HA/Fe_3O_4 nanoparticles.*

3.1.2. Transmission Electronmicroscopy (TEM)

Transmission electron microscope images were collected to investigate the size and morphology of the prepared nanoparticles. Fig. 2 shows TEM image of humic acid coated magnetic nanoparticles. As can be seen the spherical nanoparticles with mean diameter about 14 nm were synthesized using proposed method.

It should be noticed that the TEM method, which is a microscopic method, shows the size of the dry particle, and in DLS analysis, because of the size of the particles in the solution have been reported, can be a criterion for agglomerating particles.

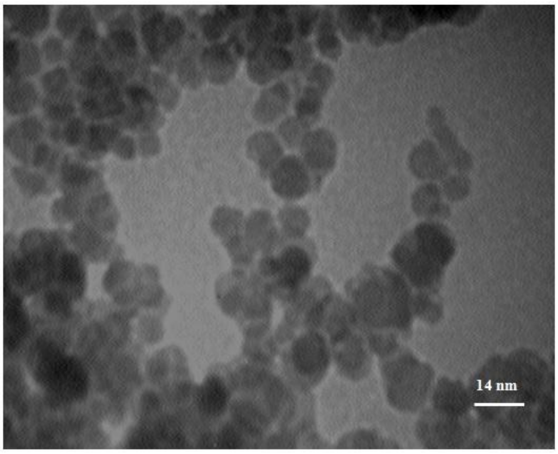


Figure 2. *TEM image of HA/Fe_3O_4 nanoparticles.*

3.1.3. FT-IR Spectroscopy

FTIR spectrophotometric analysis was carried out to prove the successful coating of HA on the Fe_3O_4 nanoparticle surface. FTIR spectra (Fig. 3) showed the C=O stretches of HA/Fe_3O_4 at~1541 cm^{-1}, indicating the carboxylate anion interacting with FeO surface, as the C=O stretches in free carboxylic acid was above 1700 cm^{-1}. The band at ~ 1392 cm^{-1} was most likely due to the CH_2 scissoring. Forthe bare Fe_3O_4 materials a peak at 590 cm^{-1} observed which is due to Fe—O bond stretching vibration. However, no C=O stretches were observed for bare particles and suggest that carboxylate groups indeed play an important role in the bonding of the HA to the magnetite surface. It is generally believed the binding of HA to Fe_3O_4 surface is mainly through ligand exchange [28, 31, 32].

3.1.4. Zeta-Potential Analysis

Zeta potential analysis was performed to investigate the surface net charge of nanoparticles. Zeta potential values of

HA/Fe_3O_4 nanoparticles dispersed about neutral solution (pH~6) were measured.

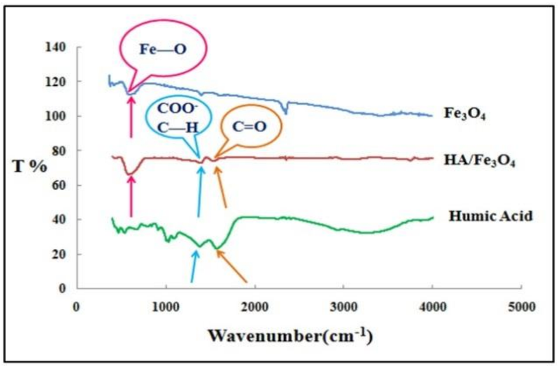


***Figure** 3. FTIR spectra of (a) naked and (b) HA/Fe_3O_4 nanoparticles and(c) pure humic acid.*

As can be seen in Fig. 4 surface charge of HA/Fe_3O_4 nanoparticles is negative. The low pH_{PZC} indicates that the HA/Fe_3O_4 are negatively charged at the entire environmentally relevant acidity (pH 3-9), which prohibits the aggregation of HA/Fe_3O_4 and benefits the sorption of positively charged metal ions (VO^{2+} here).

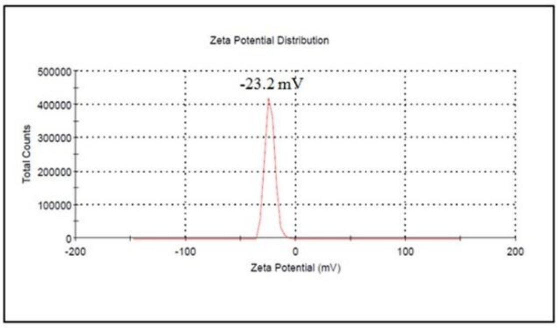


***Figure** 4. Zeta Potential analysis of HA/Fe_3O_4 nanoparticles.*

3.1.5. X-Ray Diffraction (XRD)

Fig. 5 shows the XRD pattern of the humic acid modified Fe_3O_4 nanoparticles. There are six characteristic reflection for Fe_3O_4 at 2θ values of 30.1˚, 35.6˚, 43.3˚, 53.6˚, 57.4˚, and 63˚ marked by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0), respectively. These observations confirm the presence of inverse cubic spinel structure of the resultant nanoparticles [28]. It is also clear that the coating did not lead any phase change of Fe_3O_4 particles. Although the results of the X-ray diffraction analysis prove the presence of a rich magnetite phase (Fe_3O_4), the obtained reflection in 2θ=34 (by the Miller indices (1 0 4)) could indicate a small percentage of the hematite phase (α-Fe_2O_3) [33].

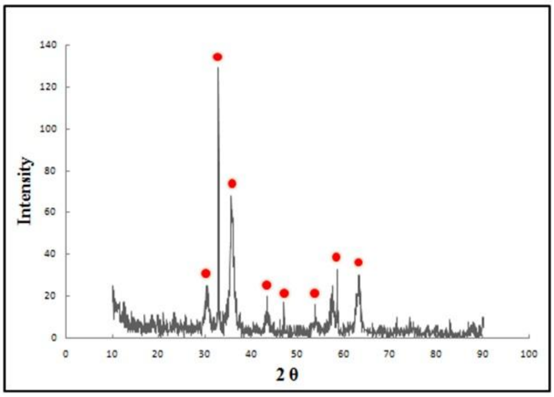


***Figure** 5. XRD patterns of HA/Fe_3O_4 nanoparticles.*

The average size of the crystals can be calculated from Scherrer equation:

$d=0.9\lambda/\beta cos\theta$ (3-1)

Where d is crystal diameter, λ is X-ray wavelength, β is the peak width of half maximum, and θ is Bragg's diffraction angle in degree. The obtained size of the crystals using strongest peak (3 1 1) at 2θ=35.6˚ and λ=1.54 A˚ was about 11.9 nm.

3.1.6. Vibration Sample Magnetometer (VSM)

The magnetic properties of both uncoated and coated Fe_3O_4 nanoparticles were measured with a vibrating sample magnetometer at room temperature. Fig. 6 shows a typical magnetization curve of naked Fe_3O_4 nanoparticles and HA/Fe_3O_4 nanoparticles. As could be seen, the hysteresis loop shows super paramagnetic property indicating that the single-domain magnetic nanoparticles remained in these HA-coated nanoparticles. The saturation magnetization of the naked Fe_3O_4 nanoparticles was about 60emu/g, while for HA/Fe_3O_4 nanoparticles was about 43 emu/g in this experiment. The decrease in saturation magnetization is due to the presence of humic acid coated on the nanoparticles surface. Therefore, our HA/Fe_3O_4 nanoparticles can still be separated easily and fast by applying the external magnetic field.

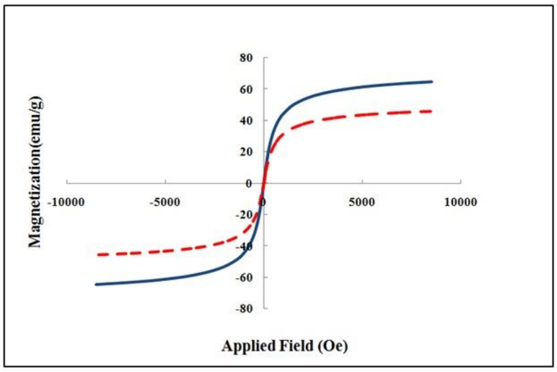


Figure 6. *Magnetic hysteresis curves of naked (solid line) and HA/Fe_3O_4 nanoparticles (dot line).*

3.2. Investigation of the Removal Ability of the Humic Acid Coated MNPs in Aqueous Media

The removal ability of the designed nano-adsorbent was evaluated in aqueous media because of simplicity. Investigation of the effect of some experimental factors such as pH, contact time, temperature, adsorbent dosage and initial concentration of vanadium on the removal efficiency can be studied well. The vortex shaker by the agitation speed of 1000rpm used in all experiments of the adsorption process.

3.2.1. The Effect of pH on the Removal Efficiency

In solutions, the pH can influence the metal chemistry or the protonation/ deprotonation of the nano-adsorbent, relative to its pK_a values. V(IV) at various pH appearsas threedifferentspecies. At pH range of 0-4, VO^{2+} is dominant species, while at pH range of 4-14, 90% of vanadium is in the form of $VO(OH)^+$ and 10% is $VO_2(OH)_2^{2+}$. Humic acid molecules include several aromatic rings consist of different functional groups such as phenolic and carboxylic species which can lead to different interactions with surrounding environment. Humic acid molecules have two pK_a values. One of them is around 4 related to the protonation of carboxylic groups and the other is around 8 for protonation of phenolic groups [34].

In this experiment, the adsorption of V(IV) ions (50 ppm) on HA/Fe_3O_4 nanoparticles (as a magnetic nano-adsorbent) surface was investigated in aqueous solutions in different pH values in the range of 3–11 (Fig. 7). It is notable that 8 mg/ml of nano-adsorbent were used in all experiments. As can be seen, the removal efficiency of vanadium increased with increasing pH solution up to 5 and then remained almost constant at pH 5-11. According to the mentioned pk_a values of humic acid, it can be concluded that the most interaction of V(IV) is related to its interaction with carboxylic groups. At higher pH values deprotonation of phenolic groups was occurred which it seems that has no significant influence on the adsorption process. So pH 5 was chosen as the optimum pH value.

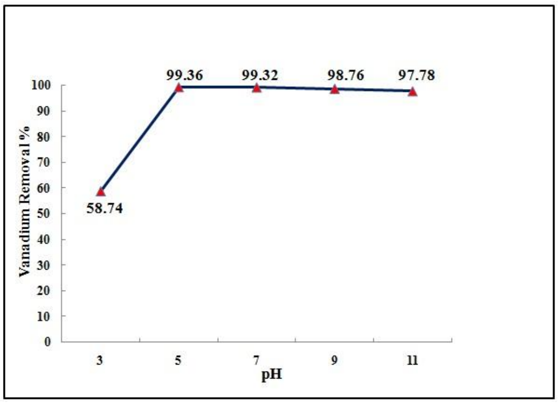


Figure 7. *The effect of pH on the vanadium removal efficiency by the HA/Fe_3O_4 nanoparticles.*

3.2.2. The Effect of Nano-Adsorbent Dosage on the Removal Efficiency

Adsorbent dosage is an important parameter in the determination of removal ability. As the adsorbent dosage increases, the available adsorbent sites for V(IV) ions increase, so itleads to more efficient adsorption. The amounts of 2, 5, 8, 10, 15, and 20 mg/ml of nano-adsorbent were used for the removal of 50 ppm vanadium solutions (at pH 5), respectively. The results were shown in Fig. 8. It reveals that the removal efficiency of vanadium increased as increasing the adsorbent dosage. By increasing the amount of nano-adsorbent to 10 mg/ml, 99.33 %of vanadium ions were removed. No significant improving in removal efficiency was observed at higher amounts of nano-adsorbent. So, 10 mg/ml was chosen as the optimum dosage for the nano-adsorbent which is economically more acceptable.

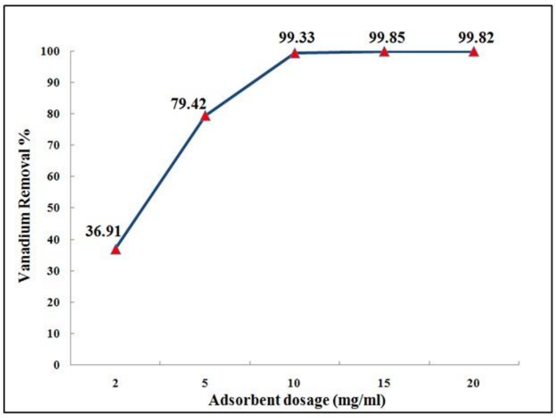


Figure 8. *The effect of HA/Fe$_3$O$_4$ nanoparticle adsorbent dosage on adsorption of vanadium ions.*

3.2.3. The Effect of Contact Time on the Removal Efficiency

The effect of contact time of vanadium containing solutions with nano-adsorbent was investigated in range 5–120 minutes at pH 5 and adsorbent dosage 10 mg/ml. According to Fig. 9, it can be seen that the adsorbed amount of V(IV) increased with increasing the contact time. Clearly, HA/Fe$_3$O$_4$ nanoparticles had a good performance in adsorption during the first 30 min.

3.2.4. The Effect of Temperature on the Removal Efficiency

Temperature variation effect was also investigated in range 25–85 °C at pH 5 and adsorbent dosage 10 mg/ml during 30 min (Fig. 10).

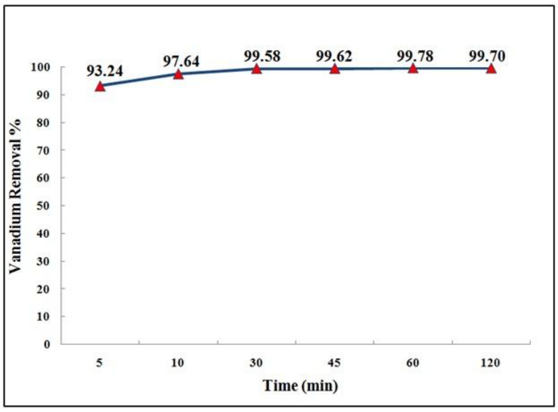


Figure 9. *The effect of contact time on the V(IV) removal by the HA/Fe$_3$O$_4$ nanoparticle.*

Since, at room temperature (25°C) the removal efficiency reached up to 99%, increasing the temperature did not show any significant improvement on the adsorption process. Since, all experiments were carried out at room temperature.

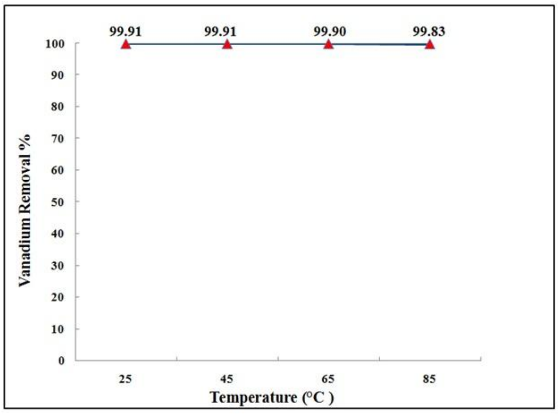


Figure 10. *The effect of temperature on the V (IV) removal by the HA/Fe$_3$O$_4$ nanoparticle.*

Generally, Humic substances, as naturally occurring organic matter with different functional groups, can exert a major influence on the fate of metal in a number of ways such as through reduction and complexation. Although vanadium has been found to be naturally associated with humic substances [35]. This metal ions may act as effective cross-links between the several humic components. From this point of view, oligomeric complexes formed by vanadium ions acting as bridges between phenolic carboxylic ligands may be reliably considered as simple humic-like compounds or as building blocks of the complicated humic matter [36].

The VO(IV) ion is strongly complexed with the soil organic fractions. Mono and di-carboxylates, salicylate as well as dihydroxybenzoate coordinating through the (COO-, O-) donor set were proposed as good models for the binding sites of humic acids. It seems that the components predominant at low pH values are similar to those of ligands with pure carboxylate coordination. As the pH is raised, sites with parameters in the range of the mono-salicylate type of coordination become increasingly filled [36].

3.2.5. Effect of Initial Concentration on the Removal Efficiency

As mentioned above, HA/Fe_3O_4 nanoparticles provided good adsorption capacity for V(IV) at pH 5 and 10 mg/ml adsorbent amount by applying 30 minutes contact time. The adsorption isotherm of vanadium was obtained by changing the initial concentration of V(IV) at values ranging from 25 to 100 ppm. At lower concentration, high removal efficiency was observed but it decreased by increasing vanadium content up to 100 ppm (Fig.11). This behavior was due to the fact that the adsorption sites are limited and the most available positions were occupied after increasing the concentration more than 50 ppm.

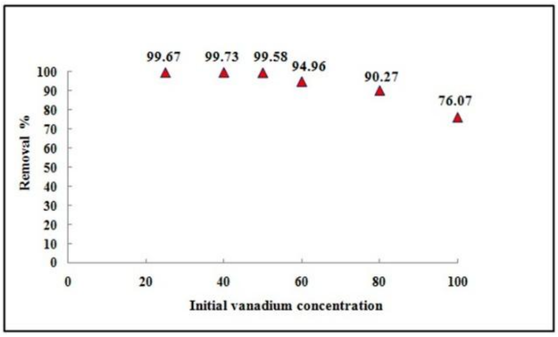


Figure 11. *Effects of initial concentration on adsorption of V(IV) ions on removal efficiency by HA/Fe_3O_4 magnetic nanoparticles.*

3.2.6. Regeneration and Reuse

One of the most important steps in an adsorption study is the regeneration of adsorbent for further uses to keep the process cost down. Commonly, different organic and inorganic eluents such as acids or bases can be selected in order to desorption of analyte from the nano-adsorbent surface. In this study HCl and acetic acid were examined as eluents and the results were shown in Table 1. Evidence shows that 0.1 M HCl solution can cause releasing about 99% of the vanadium ions from nano-adsorbent. So it can be introduced as the best eluent for regenerating HA/Fe_3O_4 nanoparticles for further uses.

Table 1. *Results of desorption and recovery of HA/Fe_3O_4 nanoparticles.*

	Time	% Adsorption	% Desorption	% Recovery
HCl	30 min	99.58	99.63	97.01
CH_3COOH	30 min	99.58	1.68	—

To investigate the removal ability of regenerated nano-adsorbent a fresh solution of V(IV), 50 ppm, was used and the experiment repeated for four times. Fig. 12 shows that regenerated nano-adsorbent in the fourth stage can remove vanadium content of sample up to 50%. Therefore, it is possible to reuses the eluted nano-adsorbent for multiple cycles of adsorption.

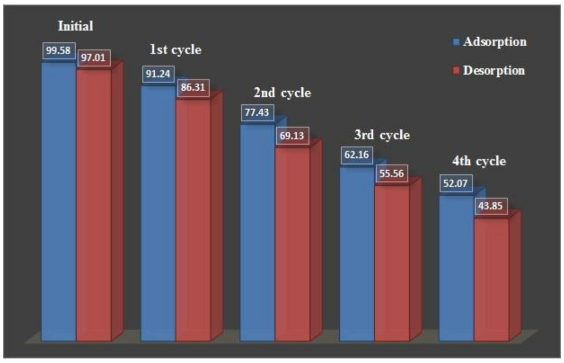


Figure 12. *Effect of the adsorption and desorption time on the recovery of vanadium ions on synthesized sorbent.*

3.2.7. Physical Adsorption

In general, adsorption of vanadium by nano-adsorbent may be done through two different mechanisms including physisorption or chemisorption. Physisorption is a type of adsorption in which the adsorbate adheres to the surface only through *Van der Waals* interaction; otherwise in chemisorption the adsorbate can form a chemical bond on the adsorbent surface. In order to investigate the adsorption mechanism in this study, exact amounts of nano-adsorbent has been used in a removal process was dispersed again in warm water (80^{o}C) and shaken for 30 min. The results showed that, only 0.05 % of adsorbed vanadium has been released in this condition. So it can be concluded that the chemisorptions is dominant mechanism.

3.2.8. Adsorption Kinetics

As mentioned above, the contact time of polluted solution with nano-adsorbent can efficiently influence on the vanadium removal. So, the kinetic behavior of the system should be studied here. In order to investigate adsorption kinetics mechanism, pseudo-first order and pseudo-second order models were considered as possible models which may be fitted to the experimental data [37].

The equation used at pseudo-first order kinetic model is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3-2}$$

The equation of pseudo-second order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3-3}$$

where q_e and q_t are the amounts of vanadium adsorbed by each unit of HA/Fe_3O_4 nanoparticles at equilibrium state and time *t*, respectively (mg/g).

$k_1$and k_2 are the pseudo-first order and pseudo-second order rate constants for the adsorption process, respectively. The value of k_2 can be calculated from the intercept of plot of t/q_t against *t* (Fig. 13).

By comparing the correlation coefficient values, it can be concluded that pseudo-second order model can better fit the experimental data.

Calculated value for the equilibrium adsorption capacity ($q_{e,cal}$) according to pseudo-second order model was 5.51 mg/g, which is consistent with the experimental value ($q_{e,exp}$= 4.97 mg/g). So, it was found that the rate of the vanadium adsorption to be controlled by the chemisorption process [38].

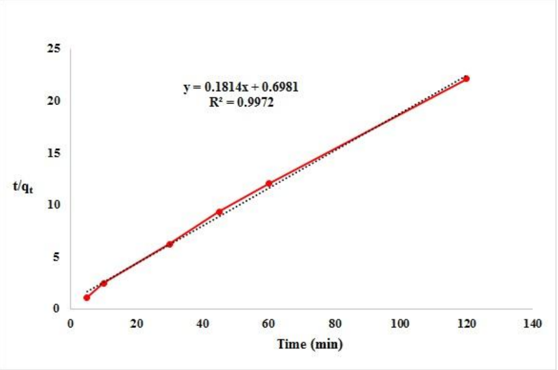


Figure 13. *Plot of t/qt against t that can show pseudo second-order kinetics for adsorption of V(IV).*

Table 2. *Adsorption kinetic parameters of V(IV) on to HA/Fe_3O_4 nanoparticles.*

R^2	K_2(mg/g. min)	$q_{e\ cal}$ (mg/g)	$q_{e\ exp}$ (mg/g)
0.99	0.047	5.51	4.97

3.2.9. Adsorption Isotherms

In order to investigate the adsorption mechanism, Langmuir and Freundlich adsorption isotherm models were used to describe the equilibrium data at a constant temperature. The adsorption isotherms can be used to express the surface properties of adsorbent and its affinity to the adsorbate [38-40].

Generally, Langmuir model assumes that adsorption takes place at specific homogeneous sites within the adsorbent and is applied to monolayer adsorption processes. The linear form of the Langmuir isotherm can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_l} \tag{3-4}$$

Otherwise, the Freundlich model is based on a multilayer adsorption. In this model the adsorption energy decreases with the surface coverage. It is an empirical equation used to describe heterogeneous adsorption systems which can be represented as follow:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \tag{3-5}$$

where q_e is the equilibrium adsorbate loading on the adsorbent in mg/g, C_e is the solute equilibrium concentration in mg/L, q_m the maximum capacity of adsorbent (mg/g). k_l and K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively.

The equilibrium isotherms for the adsorption of vanadium ions by HA/Fe_3O_4 nanoparticles at pH 5 and room temperature were shown in Fig. 14.

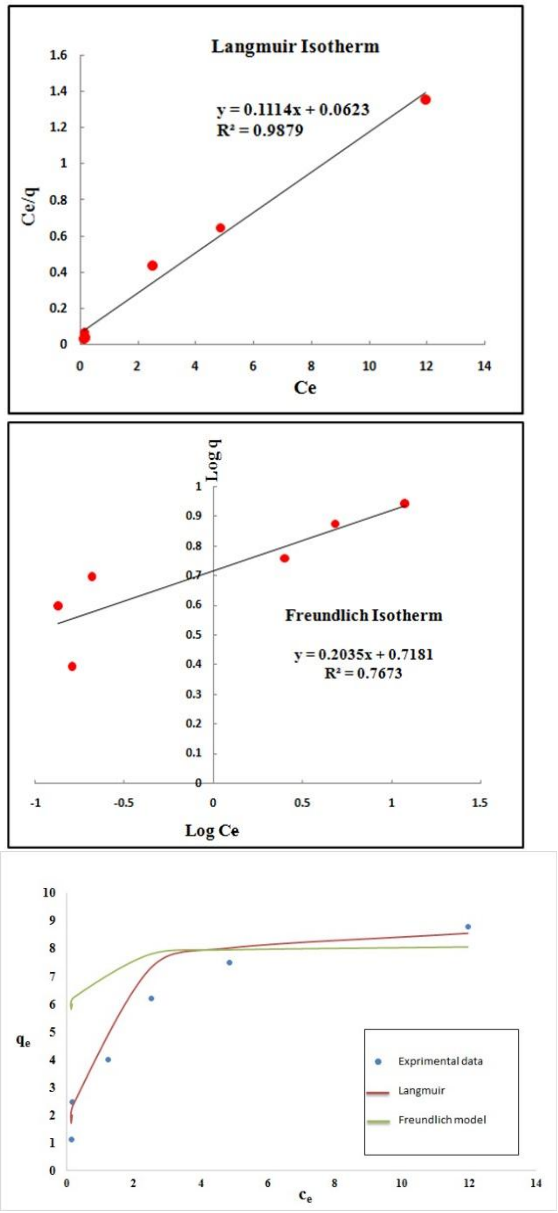


***Figure 13**. The (a) Langmuir, (b) Freundlich and (c) Comparison of the experimental data and predicted adsorption isotherm models plots for V(IV) adsorption by HA/Fe_3O_4 nanoparticles at pH 5.*

For Langmuir model the values of q_m and k_l were determined from the slope and intercept of the linear plots of C_e/q_e versus C_e (Fig. 14,a). For Freundlich model the values of K_F and $1/n$ were determined from the slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$ (Fig. 14,b). The isotherm parameters are shown in Table 3. The higher correlation coefficient calculated according to Langmuir model indicated that this model is preferred. Also, the non-linear plot of q_e versus C_e shown in Fig. 14.c, based on experimental data and absorption isotherms, is evidence of the truth of this claim. The maximum adsorption capacity obtained from the Langmuir isotherm was 8.97 mg/g.

***Table 3.** Adsorption isotherm parameters of V(IV) adsorption on HA/Fe_3O_4 nanoparticles at pH 5.*

Isotherm models					
Langmuir			Freundlich		
R^2	k	q_m (mg/g)	R^2	n	K_F
0.98	1.78	8.97	0.76	—	—

3.3. Real Samples

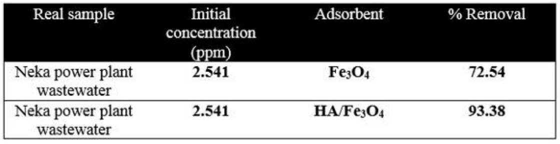
In power plants that use heavy fuel oils with a high sulfur content, combustion chamber of the boiler have been covered by sediments due to direct contact of the combustion products of various compositions. Due to the quality of fuel, carbon compounds, vanadium, nickel and sulfur compounds can be often deposited on different kinds of chamber. During the combustion of vanadium containing fuels the formation of vanadyl salts may be occurred. At high temperature (500-600°C) the molten salts were precipitated on the combustion boiler chambers. This precipitate accompany with other materials such as catalyst particles remaining from oil refinery, black sticky layers were formed on the chamber surfaces. This phenomenon can also cause the corrosion of boiler tubes which may cause lowering the heat transfer rate of the boiler. In this research HA coated magnetic nanoparticles were used for vanadium removal from fuel oil and waste water of Neka power plant at the north of Iran.

On the other hand, the power plant waste water that usually enter to the environment includes some extent of vanadium ions can cause many problems for human and animals health. That is why finding a way to remove vanadium from oil samples of the oil industry, petrochemical and power generation are the most important issues.

3.3.1. Investigation of the Removal Ability of Humic Acid Coated MNPs in Waste Water

Industrial waste sample containing vanadium ions was examined to evaluate the removal ability of as-prepared nanoparticles at optimum conditions. The optimum conditions which were examined for synthetic samples were used in waste water treatment. To determine vanadium concentration, inductively coupled plasma-mass spectrometry (ICP-Ms) was utilized. Table 4 lists the initial concentration and the removal efficiencies of vanadium after treatment with HA/Fe_3O_4 nanoparticles. Also, to evaluate the role of humic acid in selective adsorption of vanadium, both coated and uncoated Fe_3O_4 nanoparticles were carried out to remove this ions from Neka*[a] power plant wastewater (Table 4).

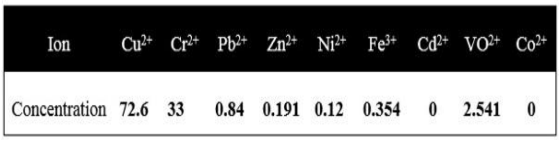
Table 4. *Removal efficiency of V(IV) in real sample by magnetic nan-adsorbent.*



Real sample	Initial concentration (ppm)	Adsorbent	% Removal
Neka power plant wastewater	**2.541**	**Fe_3O_4**	**72.54**
Neka power plant wastewater	**2.541**	**HA/Fe_3O_4**	**93.38**

More than 93% of vanadium contents of these samples could be removed using proposed nano-adsorbent. It can be concluded that the HA/Fe_3O_4 nano-adsorbents were rarely affected by the commonly coexisted ions in waste water samples with complex matrix and can preserve their activity. (Table. 5)

Table 5. *Results of measuring heavy metals in Neka power plant wastewater. (The concentration of Cu, Cr and Pb ions are in ppb and the other ions in ppm)*



Ion	Cu^{2+}	Cr^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}	Cd^{2+}	VO^{2+}	Co^{2+}
Concentration	**72.6**	**33**	**0.84**	**0.191**	**0.12**	**0.354**	**0**	**2.541**	**0**

3.3.2. Investigation of the Removal Ability of Humic Acid Coated MNPs in Fuel Oil

Fuel oil treatment was carried out by collecting some heavy fuel oil samples from Neka power plant. Practically, pH adjusting did not carry out in the oily samples and also temperature was adjusted to 70 °C in order to lubricating fuel oil samples. Because of the differences between oil and aqueous matrices we preferred to examine the different amounts of the nano-adsorbent dosage and contact time in the fuel samples. Nano-adsorbent dosage of 5, 25 and 50 mg/ml was taken, respectively. The contact time of vanadium containing fuel samples with nano-adsorbent was adjusted in 5, 20 and 45 minutes. The results were shown in Fig. 15. It is revealed that the removal efficiency of vanadium increased by increasing the adsorbent dosage and contact time and reached up to 67% by using 50 mg/ml during 45 minute.

4. CONCLUSION

In summary, HA/Fe_3O_4 nanoparticles were prepared by co-precipitation procedure with iron salts and HA, and its properties for removal of V(IV) from aqueous solution was investigated.

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[a] A region in North of Iran.

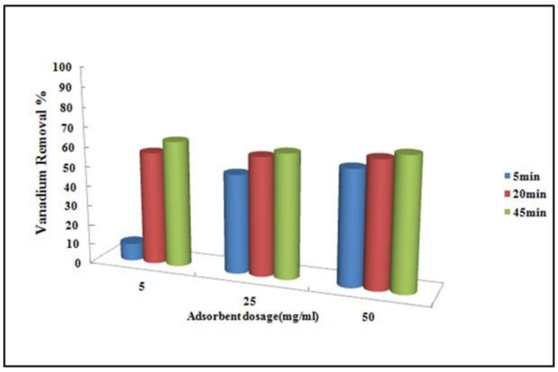

***Figure 15**. The effect of HA/Fe$_3$O$_4$ nanoparticles adsorbent dosage and contact time on adsorption of vanadium in fuel oil.*

The characterizations of prepared nanoparticles using different methods prove the synthesis of spherical nanoparticles with mean diameters about 14 nm. HA/Fe$_3$O$_4$ nanoparticles could be simply collected from water with magnetic separations at low magnetic field gradients within a few minutes. Some experimental effective factors on the removal ability of nano-adsorbent were examined and the best condition was obtained at pH 5, adsorbent dosage of 10 mg/ml and at contact time of 30 minutes at room temperature. Adsorption of V(IV) on to HA/Fe$_3$O$_4$ nanoparticles reached 99.58 % at optimum conditions and agreed well to the Langmuir adsorption model with maximum adsorption capacities of 8.97 mg/g. Also Adsorption of vanadium on to HA/Fe$_3$O$_4$ nanoparticles in fuel oil reached 67% at 45 minutes by using 50 mg/ml of nano-asorbent. HA/Fe$_3$O$_4$ nanoparticles can be used as efficient nanomaterials for vanadium removal from fuel oil and wastewater in power plant.

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