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THE EFFICIENCY OF IRON OXIDE NANOPARTICLES (Fe₃O₄ MNPS) LOADED ON ZEOLITE AS ADSORBENT FOR ADVANCED TREATMENT OF SECONDARY EFFLUENT: AN INSIGHT OF ADSORPTION ISOTHERM AND KINETIC

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Abstract

Increasing levels of organic compounds (COD, BOD₅)¹ NO₃⁻ and PO₄³⁻ in sewage of wastewater treatment plant, today, impose a great challenge to the existing wastewater treatment process. This work presents treatment of secondary effluent by Fe₃O₄MNPs loaded on zeolite adsorbent (zeolite /Fe₃O₄MNPs). The synthesized material was characterized for the phase composition, quantitative description, surface morphology, and surface area, pore volume and pore diameter. The x-ray diffraction (XRD) used to find the crystal structure and to estimate size. The volume and surface area were 0.06 cm³g⁻¹ and 20.74 m²g⁻¹ for zeolite which were calculated by N₂ vapor adsorption experiments and Brunauer-Emmett-Teller (BET) plot. The x-ray fluorescence (XRF) analysis showed SiO₂ and Al₂O₃ as main components of natural zeolite.

The scanning electron micrograph (SEM) and XRD proved loading of zeolite with magnetite successfully. The influence of parameters such as pH, initial concentration, contact time and adsorbent dosage were surveyed and described in details. The equilibrium data fitted for isotherm and kinetic studies. The results observed that the adsorption followed Langmuir and pseudo second-order models. The equilibrium time was obtained between 60-80 min. According to Langmuir model, the maximum adsorption capacity was 3.7, 0.83, 0, 0.3 mg/g at pH = 3 and 10 g/L dose, for COD, BOD₅, NO₃⁻ and PO₄³⁻ respectively.

Keywords:

Isotherm, Kinetic, Secondary effluent, Zeolite /Fe₃O₄MNPs,

Introduction

Increase in factories, industrial and population growth, cause adverse effects on the environment due to production of contaminated and fatal wastewater. Effluent of municipal wastewater treatment plant is one of the main sources which contaminate surface and underground water sources (1-4). Pollutants of the secondary effluent included heavy load COD, BOD₅, PO₄³⁻ and NO₃⁻, which have adverse effects on health and ecosystems (5). In many cities of Iran (Mashhad, Rasht, Sari, Hamedan, Arak and...) excessive nitrate concentrations have been observed (6, 7). The Energy Department has reported that discharge of the municipal wastewater treatment plant effluent to the river and surface water resources lead to an increase in amount of organic matter, Phosphorus and nitrate in them. Pollution of agricultural lands and crops irrigated with wastewater effluent has been reported by other researchers (8). Increasing of this compounds raise the ecosystem consumption rate, and the problem of excess nitrogen and phosphorus compounds and organic matter concentration appear (4,9). The smaller the water body is, the higher effect of these problems is. In this way, the condition becomes more critical. Therefore the purification of contaminated waters is essential due to pollution of surface and ground waters by effluent, available water restrictions, dehydration crisis and drought of country and also the problems mentioned above. So reducing the amount of pollution of wastewater before discharge into the natural environment, both in terms of health researchers and legally is a priority and must implement. The removal and recovery conventional processes of phosphorus, nitrate and organic matter such as oxidation with ozone, adsorption with activated carbon, clays and other adsorbent (3). biodegradation, coagulation and flocculation (9) and ion exchanger that are used in the wastewater treatment facilities has several strong deficiencies. The complete removal of this material with some of this process is problem and with some impossible. these processes are not able to remove all impurities that require treatment and produce a large volume of sludge that requires more treatment and disposal (10). The removal of phosphorous from sludge of coagulation and sludge Flocculation processes than other biological advanced treatment methods is more difficult. Determining the correct dose of chemicals is not possible because conditions such as pH, alkalinity and competitive reactions are different. Operator safety, large installations for the transport and storage of chemicals, as well as the high price of consumer polymers are the other disadvantages of these methods. The restrictions of biological process include reliability, stability and low performance, the possibility of stopping the process during operation due to lack of nutrients, heavy rainfall, excessive nitrate in anaerobic zone and other external disturbances. There is microbial competition for uptake phosphorus and glycogen, which reduces the efficiency of phosphorus removal with this approach. Membrane

processes require a complete initial study. High consumption of energy, produce a large amount of sludge and high cost of operation and maintenance are the disadvantages of this system (3, 11, and 12). With the advancement of nanotechnology, attempts have been made in the use of MNPs for removal of organic pollutants and heavy metals from water and wastewater. The use of MNPs is highly desirable due to, high specific surface (surface to volume ratio) and high absorption efficiency, lack of penetration resistance due to the elimination of the interior absorption surfaces in porous adsorbent, the possibility to modify and adjust the surface properties of MNPs, easy to disperse the particles in isolation and ability to recovery after the absorption of pollutants using MNPs. The magnetite nanoparticles have a low price and provide a low toxicity (11, 13). Nowadays because of the low cost, simplicity and high performance, adsorbents such as ion exchange resins, zeolites, activated carbon fibers and polymeric adsorbents are used for the removal of phosphate, nitrate and organic substances. But the fundamental problem is related to the separation of the adsorbents from aqueous solutions. One of the simple techniques to eliminate this problem is using MNPs loaded onto the adsorbents. The presence of MNPs on the surface of the zeolite lead to chemical stability, reduce of toxicity and excellent recyclability. This feature can extend the application of this method for the removal of ions and organic compounds from water and wastewater. The purpose of this study was to making Fe₃O₄ MNPs loaded on zeolite (zeolite /Fe₃O₄ MNPs) as an adsorbent, for polishing of secondary effluent. In this regard, Ramnath Lakshmanan et al (2011) surveyed the efficiency of organic carbon removal with functionalized magnetite nanoparticles. Also I.de Vicente et al (2011) showed that nanoparticles of magnetite have a high ability to remove phosphorus. Caterina Borghi et al. (2011) used iron oxide nanoparticles to removal of surfactants. The result showed high performance of iron oxide nanoparticles. In the research of Asya Drenkova et al (2013), the removal of phosphate from wastewater using modified super magnetic particles is studied. The result showed the high removal of this compound by modified super magnetic particles.

Abbreviations

BOD	→	Biological oxygen demand
COD	→	Chemical oxygen demand
SEM	→	scanning electron micrograph
XRD	→	x-ray diffraction
BET	→	Brunauer-Emmett-Teller
XRF	→	x-ray fluorescence

Materials and methods

Chemicals and instruments

The starting materials included Hydrochloric acid solution, 85% phosphoric acid, N-(1-naphthyl)-ethylenediamine dihydrochloride, sulfanilamide, conc. H_2SO_4 , Ferrous ammonium sulfate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), Ag_2SO_4 , 1,10-phenanthroline monohydrate, Mercuric sulfate HgSO_4 , ammonium molybdate, ammonium met vanadate, anhydrous KH_2PO_4 , Potassium hydrogen phthalate, ferrous-ferric salts, FeSO_4 and FeCl_3 , that were purchased from Merck. Zeolite Powder was purchased from Afrazan .co of Iran.

Analyses

Distilled deionized water was used in all of experiments. pH meter (Corning Model-En) was used for control pH of solution (± 0.01) and residual and initial concentrations of COD, BOD_5 , NO_3^- , NO_2^- , PO_4^{3-} were determined by methods of number 5220 A (Open Reflux Method), 5210B (Respirometric methods), 4500- NO_3^- -A, 4500 - NO_2^- , 4500 - P C. (Vanadomolybdo phosphoric Acid Colorimetric Method) of Standard Methods for the Examination of Water and Wastewater, 20th edition. Spectrophotometer DR 5000 was used as Colorimetric equipment. The MWW treatment effluent, before disinfection, was obtained from a wastewater treatment plant of Ecbatana minacity (Tehran). Table (1) shows COD, BOD_5 , NO_3^- , NO_2^- and PO_4^{3-} initial concentrations of the secondary effluent of MWW plant. Samples were filtrated with paper and fiberglass filter (45μ) before test for rough colloidal separation. The zeolite / Fe_3O_4 MNPs adsorbent was synthesized and characterized by XRD (Quanta chrome, NOVA2000), XRF and SEM (AIS2300C, W.d=8.).

Table-1: Basic characteristics of the secondary effluent analysis.

Parameters	Values
pH	7.6
BOD (mg L^{-1})	25
COD (mg L^{-1})	40
NO_3^- (mg L^{-1})	63
PO_4^{3-} (mg L^{-1})	8.2
NO_2^- (mg L^{-1})	0

Synthesis of zeolite / Fe_3O_4 MNPs adsorbent

The zeolite used in this study was natural zeolite of Semnan (afrazand .co), with particles size of about 2-3 mm. The chemical precipitation used to make zeolite loaded with M- NC_s . First, natural zeolite was placed in a solution of

sodium chloride 2 M for 2 hours, until it comes to the cationic form. Then is washed with distilled water and was placed in a temperature of 105 °C for 10 h. For the deposition of MNPs on zeolite, iron sulfate and chloride solutions with respect $Fe_2/Fe_3 = 0.5$ was used in an alkaline environment, and under vacuum. Therefore, ferrous sulfate was mixed with iron chloride at a temperature of 75 °C for 30 min. The zeolite added to the solution and mixed for 20 minutes. To perform deposition process (forming of black precipitate), ammonia solution (25 %) was added slowly to solution and the solution pH was adjusted to 10. The precipitate was separated from the solution by filtration. To isolate troublesome salts, deposits were washed and dried at 100 °C for 2 h. All the experiments were performed in the presence of nitrogen gas(13).

Characterization of the adsorbent

The specific surface area of zeolite / Fe_3O_4 MNPs and raw zeolite were computed by Qunatachrome Nova Win 2 using N_2 vapor adsorption and BET analysis (see Fig. 1).The powder x-ray diffraction (PXRD) technique using (Quanta chrome, NOVA2000) with Cu $K\alpha$ radiation source over a range of 10-120 at a scan speed 1 s/step, 1.54 Å wavelength and 25 °C, was used to measure the crystallinity of samples and compound formation. Diffraction peaks were used to identify the structure of samples by matching their observed patterns with the standard pattern of zeolite (ICDD ASCII cards No (01-087-2334). the crystallite size D_{hkl} of the Fe_3O_4 loaded on zeolite was calculated by the Debye–Scherer formula (14).

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where β is the full-width at half-maximum (FWHM) value of XRD diffraction lines (see Fig. 2), λ (0.154056nm) is the wavelength and θ is the Bragg angle. Scanning electron microscopy (SEM AIS2300C, W.d=8.) was applied to analysis the surface physical morphology of Fe_3O_4 nanoparticles loaded on zeolite showed fig.3.

COD, BOD, NO_3^- , PO_4^{3-} adsorption optimization

Samples employed in this study, are prepared from Ekbatan municipal wastewater plant secondary effluent, Tehran, Iran. The secondary effluent characteristics are presented in Table 1. The experiments of adsorption of COD, BOD_5 , NO_3^- , NO_2^- and PO_4^{3-} on zeolite / Fe_3O_4 MNPs were performed by batch techniques. The effect of pH (3-9), contact time (10-120 min) and adsorbent dose (5-20 g/l) was screened in detail. Samples filtered before each test (Whatman filter) to prevent of turbidity interference in experiment results. The methods of (4500-B), (Vanadate - molybdate), (5210-A) and (5210-B) for Standard Methods for the Examination of Water and Wastewater used to determine final

amounts of nitrate, phosphorus, BOD₅ and COD respectively (15). All adsorption experiments were done at 20°C.

The amount of COD, BOD, NO₃⁻, NO₂⁻ and PO₄³⁻ adsorbed (q_e mg/g) on the zeolite /Fe₃O₄MNPs at each time and efficiency removal (%) of them were computed by the following equation 2 and 3 (16-18).

$$R\% = \frac{C_0 - C_e}{C_0} \quad (2)$$

$$q_e = \frac{(C_0 - C_e) v}{W} \quad (3)$$

Where C_0 and C_e are the initial and equilibrium (final) concentrations of COD, BOD₅, NO₃⁻, NO₂⁻ and PO₄³⁻ (mg/L) and W is the concentration of zeolite /Fe₃O₄ MNPs (g/L) (16, 17).

Adsorption isotherms

In order to investigate adsorption isotherm models, Langmuir and Freundlich adsorption isotherms were used to describe adsorption experimental data. The assumption of Langmuir isotherm is that the adsorption process occurs on homogenous adsorbent surfaces with constant energy whiles the assuming of Freundlich isotherm is that the adsorption process occurs on heterogeneous surfaces with non-uniform distribution of adsorption heat. The linear equations of two isotherms of Langmuir 5 and 6 Freundlich is following (16, 18).

$$\frac{C_e}{q_e} = \frac{1}{k_L q_0} + \frac{1}{q_0} C_e \quad (4)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (5)$$

Where q_e (mg/g) is the solid phase equilibrium concentration of COD, BOD₅, NO₃⁻, NO₂⁻ and PO₄³⁻ and k_L (L/mg) is Langmuir adsorption constant and C_e (mg/L) is the equilibrium concentration of the liquid phase. k_f (mg/g) (L/mg)^{1/n} and n (unit less) are the parameters connected to the adsorption capacity and intensity of Freundlich, respectively. The values of n demonstrate the type of adsorption to be favorable (range of 2–10), moderately difficult (range of 1–2) or poor adsorption ($n < 1$). The fundamental property of the Langmuir isotherm can be explain with the dimensionless separation factor RL : ($RL = 1 / (1 + k_L C_0)$) (4, 6). The factor of RL shows the type of the isotherm to be favorable ($0 < RL < 1$), unfavorable ($RL > 1$), irreversible ($RL = 0$) and linear adsorption ($RL = 1$).

Adsorption kinetics

The first-order and second order sorption kinetic of adsorption process of COD, BOD₅, NO₃⁻ and PO₄³⁻ on zeolite /Fe₃O₄ MNPs were used to make the best fitted model for the experimental data. The linear equation form of two models can be expressed as for equation 6 and 7.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_e and q_t (mg/g) are the amount of material adsorbed at equilibrium and at time t (min), respectively. k_1 (1/min) and K_2 (g/(mg.min)) are rate constants of the first order and second order adsorption, respectively (16, 17).

Zeta potential measurements

The zero point of charge for adsorbent was determined to investigate the surface charge of adsorbent material depended on pH. To determine of pH_{zpc} , potassium nitrate (0.01M) solution to gather with HCl and NaOH solutions to adjusted pH were used according to method of Ngah & Hanafiah (2008) (9).

Result and Discussion

Characterization of the adsorbent

The results of XRD analysis of Semnan zeolite and zeolite loaded with MNP_s are displayed in Fig. 2. The XRD diffraction pattern of zeolite sample shows that the crystalline phase of clinoptilolite with the empirical formula $((\text{Al}_{6.59}\text{Si}_{29.41}\text{O}_{72})_{28}(\text{H}_2\text{O}) \cdot (\text{Na}_{0.52}\text{K}_{2.44}\text{Ca}_{1.48}))$ is 70% of zeolite sample. Other components are also found and identified as Ramsdellite (3%), Silicon oxide (8%), Potassium Aluminum Silicate (9%). It indicates the Semnan zeolite is mainly composed of clinoptilolite (Fig. 2a). As presented in Fig. 2b.

The highest peaks of zeolite/ Fe_3O_4 MNP_s with the nature of the fine are $2\theta = 18^\circ, 30^\circ, 35^\circ, 37^\circ, 43^\circ, 47^\circ, 53^\circ, 56^\circ, 63^\circ, 65^\circ, 70^\circ, 73^\circ, 74^\circ, 78^\circ, 81^\circ$ and 89° which confirm the presence of particles of MNP_s (magnetic nanoparticles Fe_3O_4). These reflections at 2θ are found and identified as MNP_s with cubic crystal formation when compared with the standard (ICDD ASCII card No (01-087-2334). This pattern indicates that Fe_3O_4 magnetic nanoparticles on zeolite are successfully loaded. The same results have been reported by other researcher, In previously studies (2).

Scanning electron microscopy (SEM, AIS2300C, W.d=8.8) at 20 keV (Fig 3) shows the nearly uniform distribution of Fe_3O_4 nanoparticles on surface of the zeolite and also show the particles with similar shapes. using the Debye-Scherrer formula, The crystallite size of iron oxide particles loaded on zeolite was obtained to be 30-80 nm(2). Very thin peaks of sample confirm fine nature and small crystallite of particles also (2, 8). In XRD pattern, diffraction patterns of other iron oxides, such as Fe_2O_3 , were detected that caused the XRD pattern of magnetite can deviate slightly from the standard mode.

The X-ray fluorescence (XRF) analysis showed SiO₂ and Al₂O₃ as main components of natural zeolite (table.2). The specific surface area of zeolite /Fe₃O₄ MNPs adsorbent, and raw zeolite, was determined by BET (fig1). The results of the analysis indicated that the highest surface area of zeolite /Fe₃O₄ MNPs is 32 m² g⁻¹, whereas surface area for natural zeolite was obtained 20.74 m² g⁻¹. Increasing of surface area of zeolite /Fe₃O₄ MNPs can be due to presence of Fe₃O₄ nanoparticles in the structure and surface of zeolite.

The N₂ adsorption/desorption isotherm and BET plots of zeolite/ Fe₃O₄ MNPs are presented in Fig. 1. The volume and diameter of pore were estimated to be 0.1 cm³ g⁻¹ and 20 nm respectively. According to the classification of IUPAC, adsorption isotherm associated with the adsorbent is consistent with type IV isotherm (2 nm < pore diameter < 50 nm), which is characterized as the mesoporous material

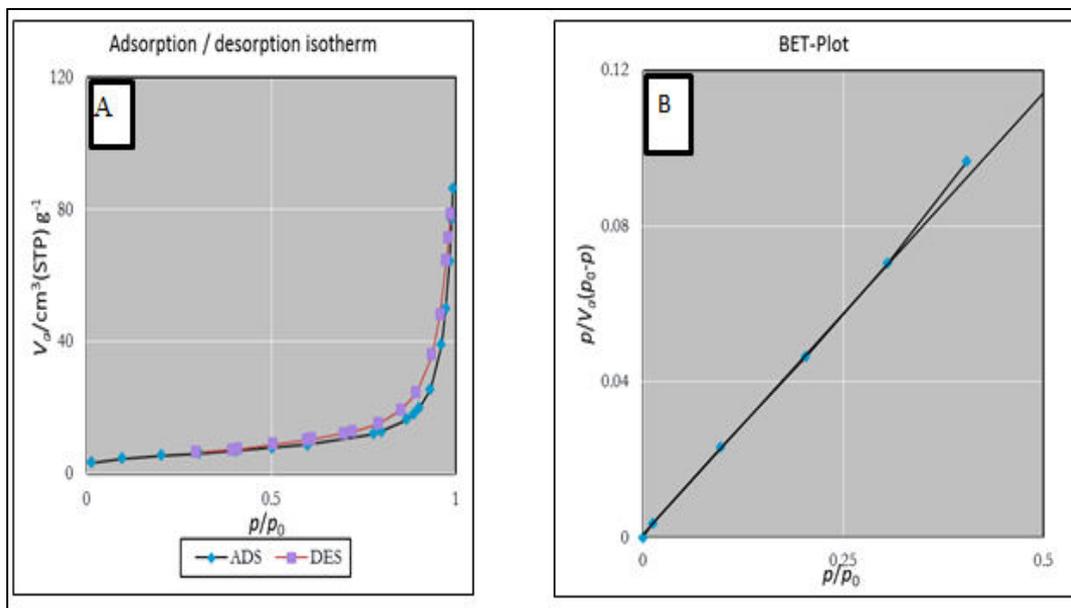


Fig.1. The plots of N₂ Adsorption/Desorption isotherm (a) and BET (b) of zeolite/ Fe₃O₄ MNPs.

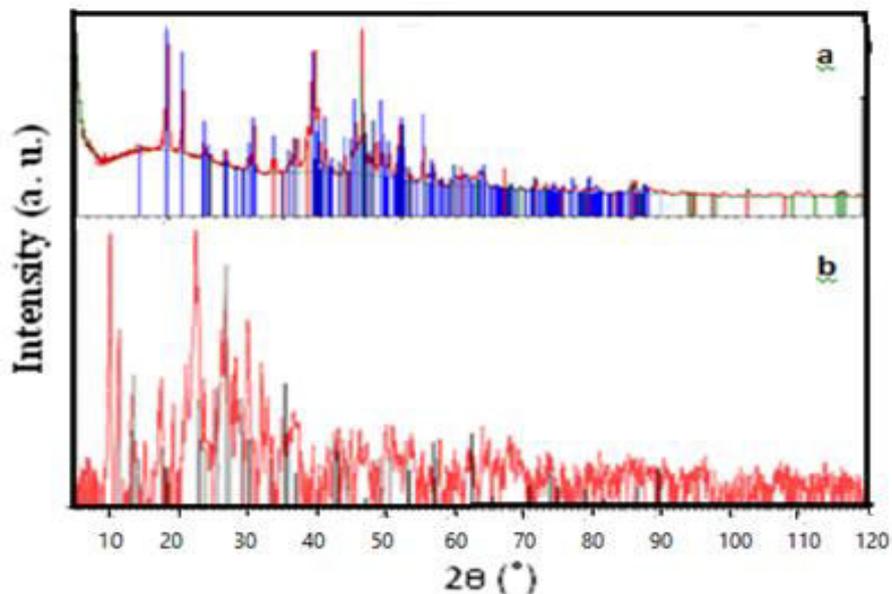


Fig.2. XRD patterns of Semnan zeolite (a) and zeolite/MNPs(b).

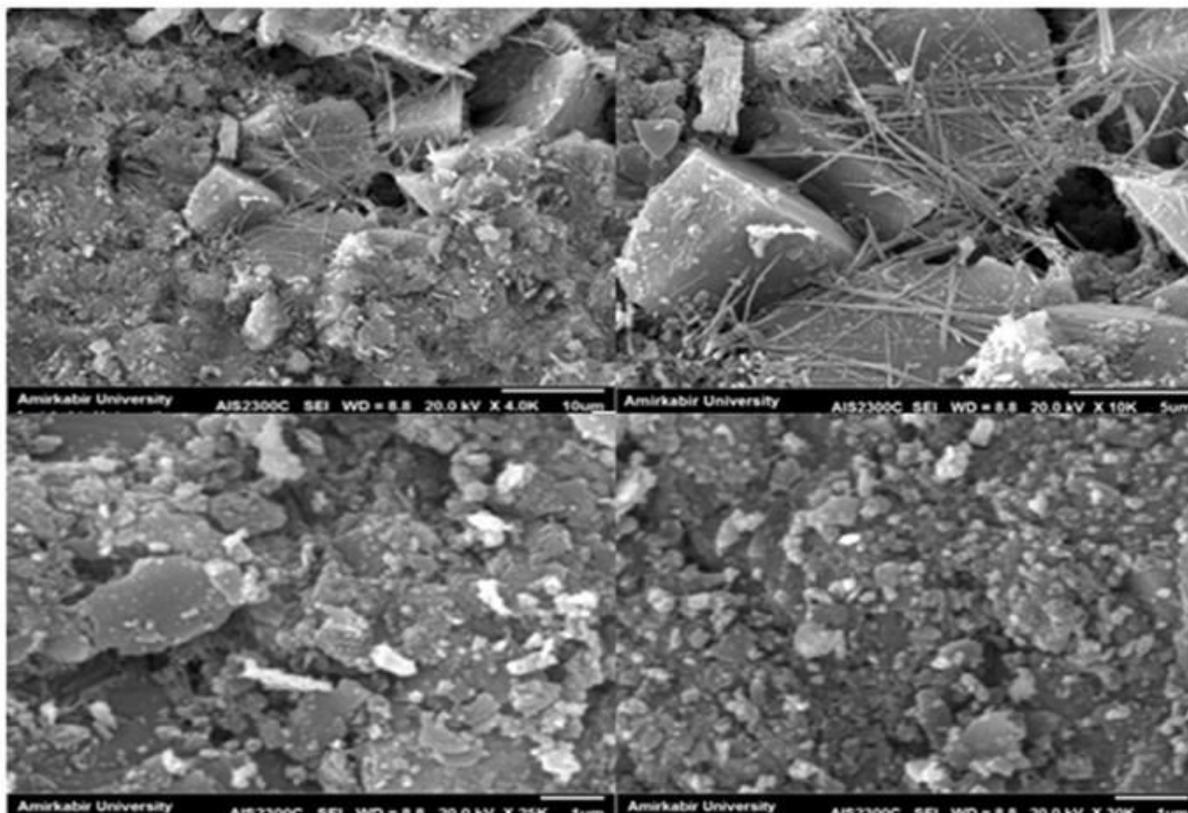


Fig.3. SEM images of zeolite / Fe₃O₄ MNPs.

Table-2: Semi-quantitative XRF analysis results of Semnan zeolite.

Constituent	Percent
SiO ₂	66.5
Al ₂ O ₃	11.81
Fe ₂ O ₃	1.3
CaO	3.11
MgO	0.72
Na ₂ O	2.01
K ₂ O	3.12
P ₂ O ₅	0.01
MnO	0.04
TiO ₂	0.21
LOI*	12.05
*Loss on ignition	

Optimal conditions of COD, BOD₅, NO₃⁻, PO₄³⁻ adsorption on zeolite/Fe₃O₄ MNPs

Effect of pH

First, in an exploratory experiment, the equilibrium time need for the adsorption of COD, BOD₅, NO₃⁻, and PO₄³⁻ was determined in the range of 20-120 min with dosage 10 g/l and pH: 5. The effect of solution pH was studied at temperature 20°C, constant initial concentration, amount of adsorbent (10 g/l) and 200 rpm agitation speed. The range of solution pH was set between 3 and 9. The initial concentration of matter existing in wastewater is according to

table (1). Fig 4 shows the effect of pH for adsorption of COD, BOD₅, NO₃⁻ and PO₄³⁻, as seen in low pH, The Removal efficiency of COD and BOD₅ were high. The most uptake of COD, BOD₅ were in pH = 3 (69, 60 % respectively). In this domain, the adsorption capacity was 3 and 1.5mg/g respectively. Lowest amount of adsorption capacity related to pH = 7. The Removal efficiency of PO₄³⁻ in acidic pH was increased with increasing pH from 3 to 5. Then, the adsorption efficiency decreased in higher pH. In very low pH, Electrostatic force between the positive protons of the surface of zeolite / Fe₃O₄MNPs and molecules of organic materials lead to increase of adsorption capacity (20). On the other hand, in alkaline conditions, reducing the adsorption of COD and BOD₅ may be due to the presence of excess OH⁻ ions and the organic molecules for the adsorption sites which produces the repulsion force of negative charges on the adsorbent surface and Organic materials (21). However, under alkaline pH, a small of the adsorption of organic matter exist, which indicates the presence of organic matter having positive charge. Zhang et al(2009) and Ahmad Jonid Jafari et al(2013) stated that the acidic and neutral conditions are favorable condition of removal of aniline using nanoparticles of Fe₃O₄(22, 23). An important role of the pH on degradation of organic contaminants is reported by other researcher (23, 25). A similar result is proposed in magnetic removal of surfactants from wastewater using micrometric iron oxide (26). In research of Sasha, Sakia& Das (2011), the maximum adsorption capacity of different dyes is achieved at pH: 4-5 using iron oxide nanoparticles and then is decreased with increasing pH (27). In acidic conditions, with increasing pH, sorption of phosphorus increases, and then reduces, due to the positive protons of the surface of adsorbent. This is because that at pH < p*H*_{pzc} the positive groups on the zeolite/Fe₃O₄MNPs surface are prevailing than the negative ones which generate a relevant electrostatic force to uptake the negative charge of the adsorbent surface (28). In the natural condition, rate of phosphorus adsorption was decreased due to neutralization of zeolite/Fe₃O₄MNPs adsorbent surface. At high pH, adsorbent particle are predicted to be negatively charged. Nevertheless, there is still a small amount of phosphorus adsorption. This adsorption mechanism occurs due to replacement of hydroxyl groups by P species and formation of inner -sphere surface complexes at water /oxide interface. The same result are reported by other (29, 30). So P adsorption is to depend on pH, while maximum adsorption occur under acidic condition and decrease with increasing pH. Drenkova. et al (2013) demonstrated that the more rapid absorption kinetics of phosphate from wastewater with modified super magnetic particles in the pH= 4-5. So that 90% of the phosphate was removed in the first 45 minutes (12). Use of zeolite/ Fe₃O₄ MNPs was not effective for removal nitrate. Perhaps because removal mechanism of nitrate is a reduction in which electron transfer takes place (17). This result is the same as result of Y.H. Huang. et al (2003) (1).

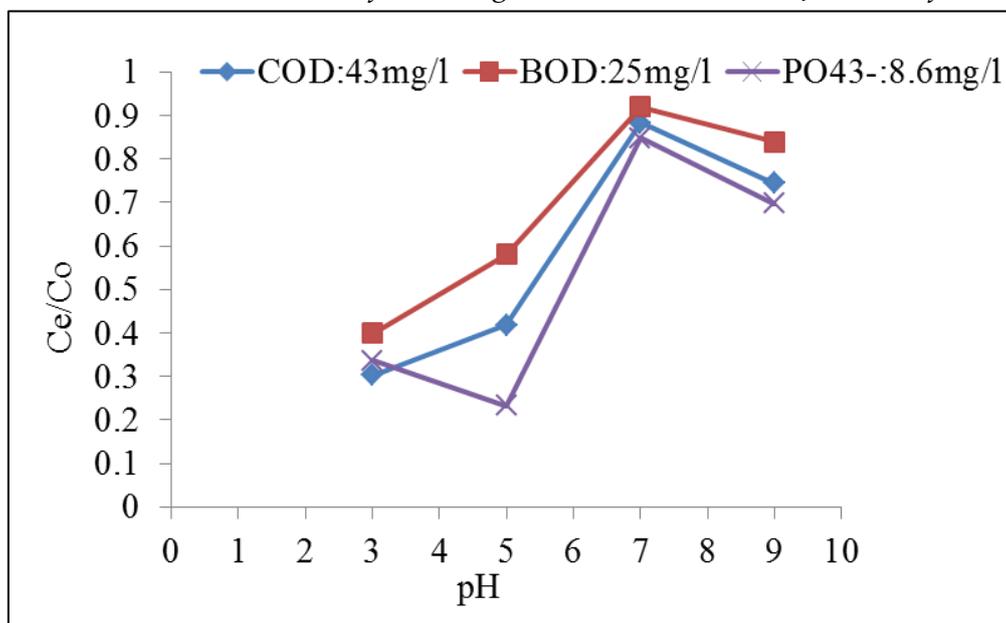


Fig.4. Effect of pH on COD, BOD₅ and PO₄³⁻ adsorption on zeolite /Fe₃O₄ MNPs W=10g/l, time =80 min , T=20⁰.

Optimal contact time for adsorption

It is important to determine the required optimum time for the adsorption of COD, BOD₅, NO₃⁻, PO₄³⁻. removal efficiency obtained after the analysis of sample of treated solution under different constant time is shown in fig.5. The required time for arrive at an equilibrium state was screened in range 10-120 min after contact with certain amount of adsorbent (10 g/L) and pH:5. by increasing the time from 10 to 120 min, adsorption ratio of COD, BOD₅ and PO₄³⁻ were increased and it was reached to equilibrium state in 60-80 min for COD,BOD₅ and 80 min to PO₄³⁻. in this time period, absorption was completed because absorptive capacity remained constant, but over 80 mint a small sum of adsorption ratio of COD and BOD₅ were decreased which indicate desorption of organic material . So, the optimal contact time of absorption using zeolite /Fe₃O₄MNPs was selected 80 min.

The various contact time in range 15-300 min for removal of different component (for example: aniline, organic load and phenolic compounds, surfactants, humicaicd, acid dye, phosphorus component and total organic carbon) using Fe₃O₄MNPs alone and Fe₃O₄ composite with different absorbent (activated carbon, chitosan and) were achieved by other reports (21, 22, 24, 28-31).

The reaction time is different, in variation of adsorbent, because of the absorbent structure, reactivity degree of pollutants, absorbing solubility, concentration gradient, the saturation degree of the adsorbent surface, homogenous or non-homogenous uptake and reversible or non-reversible absorption process (32-35). Removal efficiency of COD, BOD₅, NO₃⁻ and PO₄³⁻ with initial concentrations of 43, 25, 60, 8.6mg/l was 62, 52, 0, 75%, respectively.

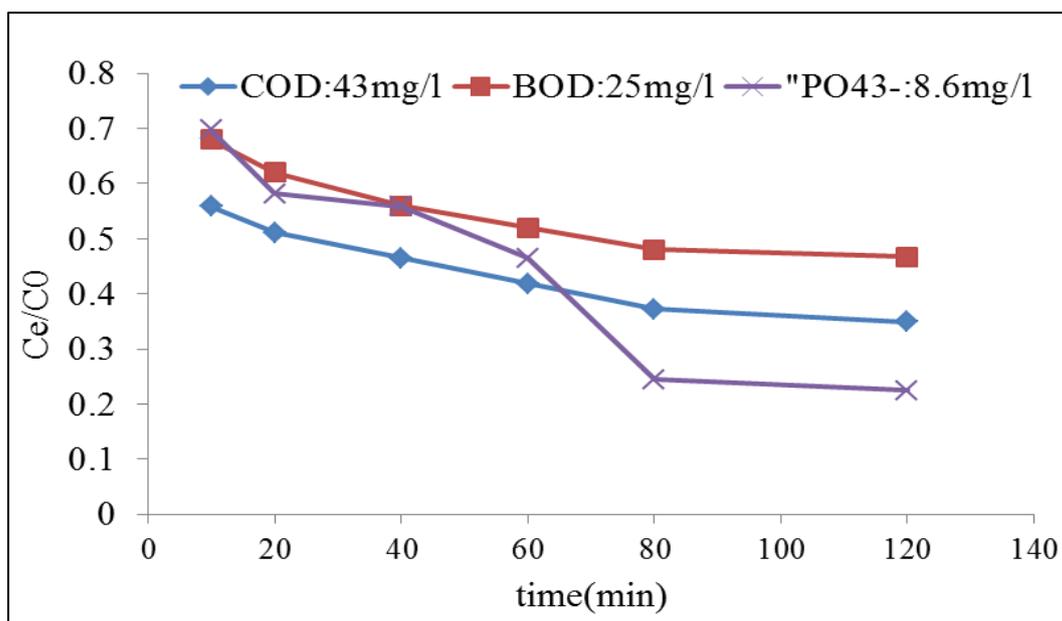


Fig.5. Effect of contact time on COD, BOD₅ and PO₄³⁻ adsorption on zeolite /Fe₃O₄ MNPs W=10g/l, pH=5, T=20 °C.

Effect of adsorbent dose

Figure.6 shows the adsorption efficiency of COD, BOD₅, NO₃⁻, and PO₄³⁻ with various dosage of zeolite /Fe₃O₄MNPs. Increasing zeolite /Fe₃O₄MNPs dose from 5g/ L to 20 g /L increased the adsorption efficiency of COD, BOD₅ and PO₄³⁻. And then leveled off with the further dose of zeolite /Fe₃O₄MNPs adsorbent. Also shows that increase of adsorbent dose, in initial concentration of adsorbate, enhance the removal efficiency from 37, 48 and 18 to 81, 76.2 and 78.14 % for COD, BOD₅ and PO₄³⁻ respectively. The increasing of adsorbent dose will increase a number of active sites, adsorbent surface and availability of molecules to adsorbent surface. So adsorption efficiency was increased with raising the adsorbent dose, as result of increased adsorption efficiency but the absorption capacity decreased due to the unsaturated stay active parts of the absorbent (23). The difference in absorption BOD₅ and COD is due to differences in the carbon chain, the solubility of ingredients them and surface tension to the absorbent surface .The similar results were reported in elimination of aniline and surfactant and total organic carbon with Fe₃O₄ nanoparticles and activated carbon-Fe₃O₄ (5, 22, 23, 26, 28). Fig. 6 shows that the adsorption process consists of two stage; an initial stage that is fast and a second stage that state uptake is achieved. Because the highest removal (during 80 min of adsorption and dosage 10 g/l) was at The first stage, So amount 10 g/l of absorbent was selected as optimal concentration of adsorbent. The Analysis of sample for all four factor COD,BOD₅,NO₃⁻, PO₄³⁻ showed that at doses more than 10g/l, the adsorption capacity remained constant ,with little change.as seen Fig.6.

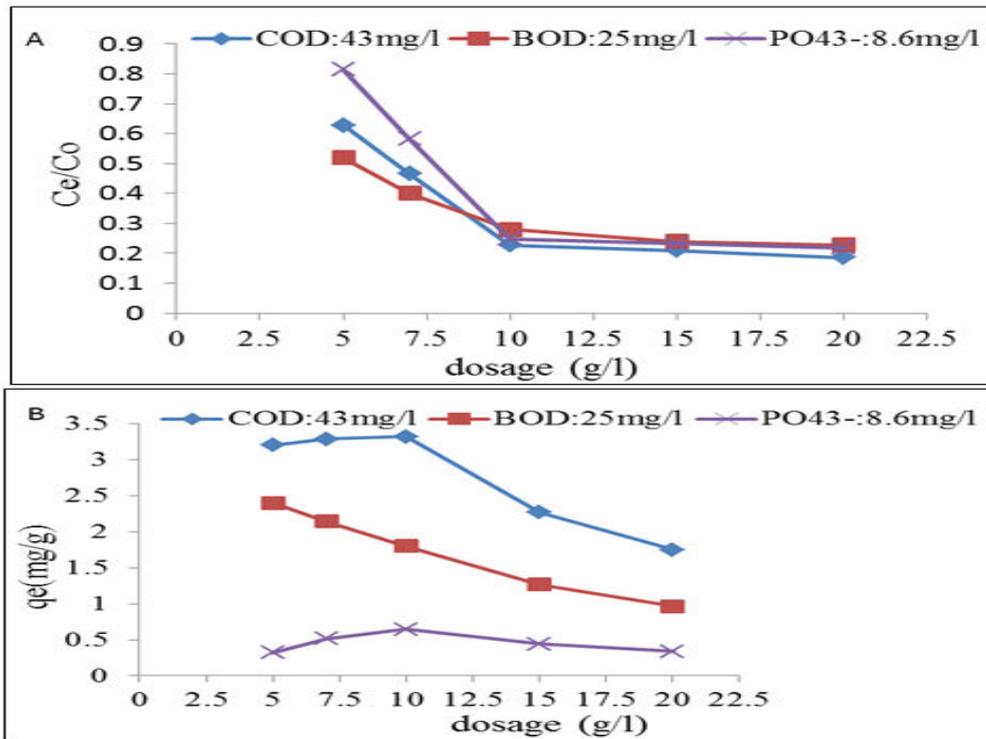


Fig.6. Effect of differential dosage of adsorbent on COD, BOD₅ and PO₄³⁻ Ce/Co(A) and adsorption capacity(B) on zeolite /Fe₃O₄ MNPs time =80 min ,pH=5 ,T=20 °C.

Adsorption equilibrium isotherms

In order to investigate how adsorbate interacts with adsorbent, adsorption isotherms were studied (fig.7). These mathematical functions establish actual forecasts of adsorption parameters and adsorption conduct for different adsorbent systems (18). The equation parameters of these models often characterize the adsorption mechanism, affinity of the adsorbent and surface properties. In this study, Two of the most common models were used for characterize the adsorption mechanism, Langmuir and Freundlich models. The Langmuir isotherm model presumes that the forces of interaction between the adsorbed molecules are insignificant and once the molecule occupies the adsorption site, greater absorption does not occur (36). And adsorption can only occur at a finite number of definite localized sites. In the model, the strength of the intermolecular attractive forces will decrease with distance (36).Langmuir isotherm equation and the linear form of Langmuir isotherm is given in section above. Freundlich isotherm model is an empirical isotherm which describes non-ideal adsorption on heterogeneous surfaces, reversible adsorption, and not limited to the formation of monolayer (36). Freundlich isotherm equation and the linear form of freunlich isotherm are given in section above. Table 2 shows that the correlation coefficients in Longmuir model, for all three parameter COD, BOD₅ and PO₄³⁻ are 0.98, 0.95 and 0.91. The values of RL are funded between 0 and 1. This shows that the COD, BOD₅ and PO₄³⁻ removal process are favorable on adsorbent. According to the regression coefficients obtained from Langmuir and Freundlich models, the adsorption process of COD, BOD₅ and PO₄³⁻ follows better from Langmuir model. This result shows that adsorption of COD, BOD₅ and PO₄³⁻ on zeolite /Fe₃O₄

are monolayer. The k_1 values, the correlation coefficients, R_2 , and the predicted and experimental q_e values are given in Table 3. The b values in Table.4 represent the enthalpy of adsorption process (adsorption stability) and tend to attract COD, BOD₅, and PO_4^{3-} on exchange sites that highest of it is related to phosphate. The highest q_{max} is related to COD. The results of this study and similar studies can be concluded that a single model cannot be offered to attract contaminants by adsorbent. Adsorption model available depend on the type of pollutants, adsorbent used and the modified procedure of adsorbent structure.

Table-3: Langmuir, Freundlich isotherm constants and separation factors (RL) for adsorption of COD, BOD, NO₃⁻, PO₄³⁻ on zeolite /Fe₃O₄ MNPs. T 20°.

Zeolite/Fe ₃ O ₄	Langmuir					Freundlich		
	R ²	R _L	B	q _{max} (mg/g)	q _{cal} (mg/g)	R ²	n	K _f (mg/g)(lmg) ^{1/n}
COD	0.98	0.07	.032	2.27	3.7	0.55	0.92	9.5
BOD	0.95	0.17	0.2	1.27	0.83	0.86	1.3	2.6
NO ₃ ⁻	-	-	-	-	-	-	-	-
PO ₄ ³⁻	0.91	0.11	.089	0.44	0.3	0.41	3.3	1.4

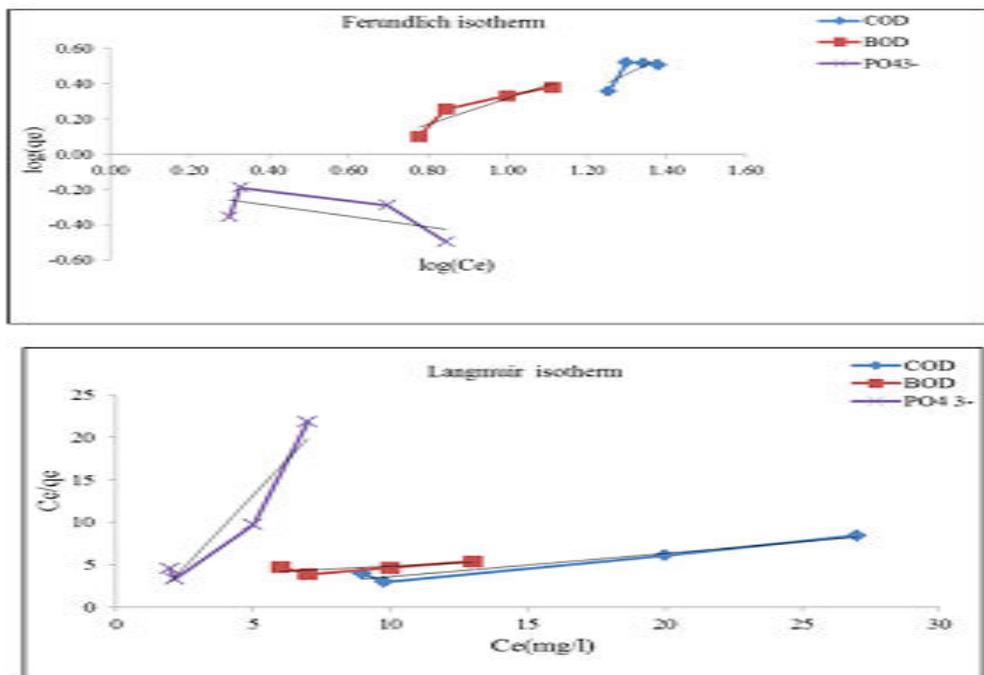


Fig.7. Freundlich and Langmuir isotherm for adsorption of COD, BOD₅ and PO₄³⁻ on zeolite /Fe₃O₄ MNPs, T 20 °C.

Adsorption kinetics

In order to analysis the sorption kinetics of COD, BOD₅ and PO₄³⁻, the kinetic models including the pseudo-first-order equation and the pseudo-second-order equation, were used to the experimental data (fig.8). The effect of the initial concentrations of COD, BOD₅, NO₃⁻, PO₄³⁻ and time were used to calculate the constants k_1 , k_2 of pseudo-first-order

equation and the pseudo-second-order. The kinetic parameters of models and correlation coefficient at 20°C are indicated in table 4. The R^2 value of the pseudo-second-order adsorption kinetics has high value (>0.98) for COD, BOD₅ and 0.85 for PO₄³⁻. It is clear from table that the calculated adsorption capacity is approximately equal to the capacity of the experimental. Therefore it can be stated that zeolite/MNPs follows second-order chemisorption and this model considers the rate limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent.

Table.4: Pseudo-first-order and pseudo-second-order adsorption rate constants and the calculated and experimental q_e values for adsorption of COD, BOD, NO₃⁻, PO₄³⁻ on zeolite /Fe₃O₄MNPs. T: 20°C.

zeolite/Fe ₃ O ₄	Pseudo-first –order kinetic				Pseudo-second–order kinetic		
	R ²	K ₁ (g/gmin)	Q _{cal} (mg/g)	Q _{exp} (mg/g)	R ²	K ₂ (g/gmin)	Q _{cal} (mg/g)
COD	0.94	0.027	1.34	2.7	0.993	0.07	3.5
BOD	0.98	0.036	0.77	1.4	0.996	0.075	1.4
NO ₃ ⁻	-	-	-	-	-	-	-
PO ₄ ³⁻	0.69	0.043	0.95	0.66	0.85	0.05	0.76

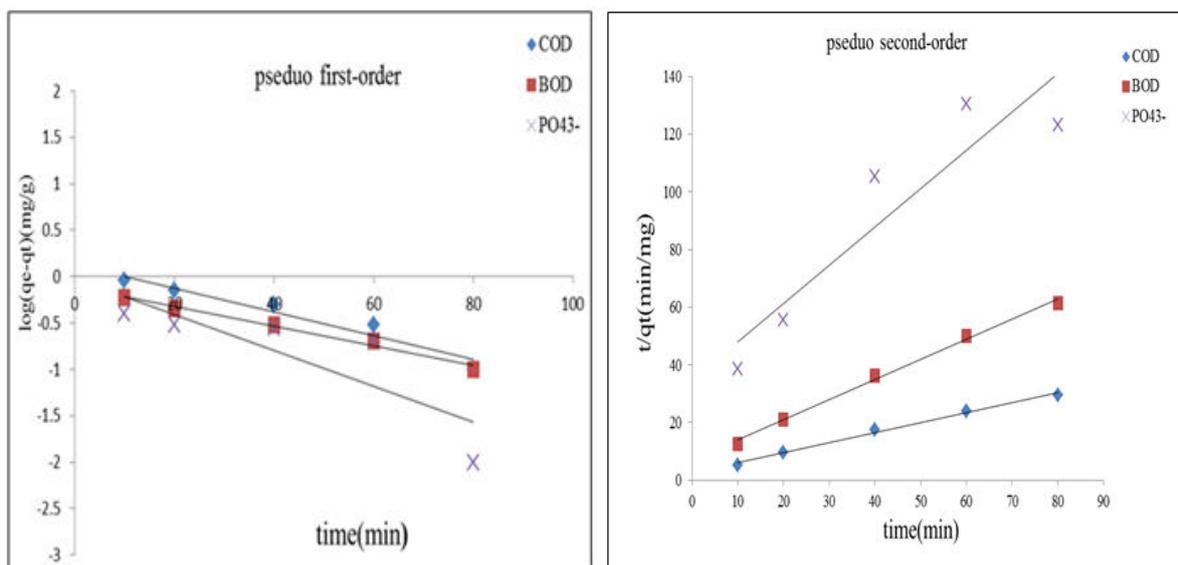


Fig.8. Pseudo-second-order and Pseudo-first-order kinetics for adsorption of COD, BOD₅ and PO₄³⁻ on zeolite /Fe₃O₄MNPs. T 20 °C

Determine the amount of iron ion leakage from zeolite/M-NC_s adsorbent

To determine of iron ion leakage amount from zeolite/MNPs adsorbent, the amount of leakage was measured in blank and treated effluent samples for 10 to 120 min. The amount of measured iron ion to blank sample was equal to treated effluent sample and 0.2 to 0.35 mg L⁻¹, that indicates the magnetite nanoparticles were well doped on surface and

inside of adsorbent and leakage of iron is very low. This prevents from entering iron ions in treated effluent and thus will not create further problems. Figure 9 shows iron ion leakage amounts from zeolite/MNPs adsorbent in blank and treated effluent samples.

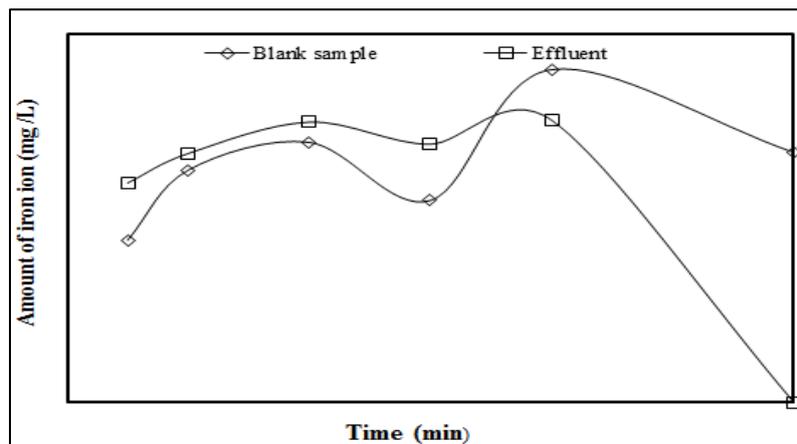


Fig-9: Iron ion amount of presence in blank and effluent samples.

Conclusions

In summary, a facile method was employed to prepare zeolite /Fe₃O₄MNPs adsorbent. The pore structure analysis by nitrogen isotherm data and SEM images showed that the magnetite particles were successfully intercalated into the interior of zeolite. The X-ray fluorescence (XRF) analysis showed SiO₂ and Al₂O₃ as main components of natural zeolite. The XRD diffraction pattern of zeolite sample shows that clinoptilolite is most of zeolite sample. Adsorption COD, BOD₅ and PO₄³⁻ was dependent in pH. At lower pH, zeolite /Fe₃O₄MNPs adsorbent acted as a good adsorbent, however, at higher pH it gave low adsorption capacity. The pH analysis showed that the adsorption process involved electrostatic interaction between the protonated groups of zeolite /Fe₃O₄MNPs surface and the negative groups of organic matter and PO₄³⁻. Other mechanisms such surface adsorption also can play an important role during the adsorption process. Results revealed that the adsorption efficiency of COD, BOD₅ and PO₄³⁻ on this adsorbent was enhanced with increasing the contact time and adsorbent dosage. Zeolite /Fe₃O₄MNPs were found to have a much higher adsorption capacity for removing COD, BOD₅ and PO₄³⁻ but NO₃⁻. Using zeolite /Fe₃O₄MNPs beads alone for removal nitrate is not effective.

The analysis of the sorption kinetics indicated that predominant mechanisms for zeolite/MNP_s are pseudo-second order kinetic models. Among the tested isotherms, linear regression analysis showed that the removal of pollutant follows a Langmuir for restructured zeolite. It can be concluded that zeolite /Fe₃O₄MNPs beads have great ability to adsorb COD, BOD₅ and PO₄³⁻. It can be concluded that zeolite /Fe₃O₄MNPs have features such as easy separation

form solution without filtration, proper porosity, high surface area and also good adsorption capacity to adsorb COD, BOD₅ and PO₄³⁻ but NO₃⁻. This adsorbent can be used as effective and efficient adsorbent to remove most contaminants, especially organic pollutants from aquatic environment and wastewater, As a supplement is used together with conventional treatment system.

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