Thermodynamic, Kinetic and Isotherm Study of 4-chloro-2-methyl Phenoxy Acetic Acid (MCPA) by (PV/S-g-3D-GO/N) from Aquatic Solutions

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Keywords: adsorption isotherms, adsorption kinetics, adsorption thermodynamics, 3D adsorbents, 4-chloro-2-methyl-phenoxy acetic acid

Posted Date: October 27th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-95697/v1>

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Abstract

Background

In this study removal efficiency of 4-chloro-2-methyl-phenoxy acetic acid (MCPA) by 3D polymer nano-magnetic (PV/S-g-3D-GO/N) was investigated.

Methods

The effects of operation parameters including adsorbent mass, influent flow rate and inlet concentration on the adsorption performance are investigated.

Results

Maximum adsorption capacity (4.36 mg/g) was achieved at optimum conditions (pH: 3, contact time: 300 min, adsorbent dosage: 5 g/l and temperature: 50 °C). Moreover, adsorption isotherm and kinetics were agreed with the Langmuir model ($R^2 = 0.997$) and pseudo-second-order model ($R^2 = 0.999$), respectively. Thermodynamic studies also show that adsorption process was spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$).

Conclusion

According to removal efficiency (100%), this adsorbent is an excellent alternative for removal herbicide in high temperature industry.

1. Introduction

Water is one of the most important and valuable substance in the worldwide. In addition, safety and availability of water are demanding task for suppliers in the society (1-3). Today, herbicides have been used widely in the agriculture industry to provide the enough food for the population(4). Among various types of herbicides, MCPA is one of the most common which have used to control broad leaf weeds in agricultural lands (5){Esrafil, 2018 #18}. Phenoxy herbicides are highly soluble in water that will result in easily contaminate surface water body (6) and is detectable even in drinking water{Dehghani, 2014 #16} . Several epidemiological studies have reported a different health risk of MCPA such as adverse effects on the endocrine system, liver and kidney toxicity (7-9). Moreover, carcinogenicity, teratogenic and mutagenic effects have been reported. The agronomic MCPA dosage is typically as high as 1–2.5 kg ha⁻¹ so, MCPA has been classified as a potential groundwater contaminant by the U.S. Environmental Protection Agency (EPA). Based on the health problem, the remove of this contaminant from aquatic solutions is necessary(4). Previously, the removal efficiency of the several physical, chemical and biological methods such as coagulation, sedimentation, filtration, chemical oxidation and adsorption to herbicide from the water have been studied (10). However, between the various methods, adsorption known suitable method due to its advantage such as simple, low price, rapid reaction and selectivity(11). During the last years, novel materials such as nano particle and modified nano particles have attracted considerable interest as

an adsorbent for removing contaminants from aquatic solution(12). However, magnetic nano particles are preferred for using in water treatment due to easily adsorbed and regeneration properties(13, 14). Therefore, modified nano particles by magnetic agent such as Fe_3O_4 can improve surface area, chemical activity, reduce unwanted particles accumulation and stability of the nano particle that lead to high efficiency adsorption properties. In the recent years, the application of various functioned group such as silica, gold, and polymers in modifying nano particle has been studied widely (15) . Graphene-based nanoparticle have specific properties due to their large specific surface area and rich porous structure, and have been successfully employed as adsorbents of organic pollutants(16). Some functioned graphene are rather difficult to separate after the adsorption process so, adsorbents with magnetic nano-particles are more preferable, because of its aforementioned group that can be purified and regenerated easier by using magnetic field techniques(12). In addition, superparamagnetic Fe_3O_4 nanoparticles (NPs) onto the graphene oxide is an excellent adsorption material due to its large specific surface area, high stability, abundant oxygen-containing functional groups on the surface, and convenient magnetic seperability (17). Over the last years, the adsorption efficiency of herbicides from aquatic solutions has been of particular interest and much work has been devoted to investigate effects of different parameter in adsorption efficiency(18, 19). Kersten et al. investigated the adsorption efficiency of MCPA by Geothit and showed that the latter forms via the sharing of the carbonyl oxygen between the MCPA carboxylate group and a single coordinated surface hydroxyl groups, releasing an H_2O molecule(10). Similarly, Iglesias et.al examined the adsorption of MCPA on the surface of goethite and of humic acid-coated goethite and found that desorption of the anionic form of the pesticide on goethite fitted an S-type isotherm and the amount adsorbed increased as the ionic strength decreased and the pH of the medium decreased(20). Jensen et.al studied the interactive degradation kinetics of MCPA in the soil and found highly significant inverse relationships between the adsorption and mineralization of chemicals in soil, and also shows best correlations between degradation rates and Freundlich adsorption coefficients(21). Most of the existing literature, have been conducted using pure individual sorbent for removal MPCA from aquatic solution (22-24) and there exist few studies that have been carried out concerning novel and complex sanitized absorbent. Therefore, the present study was conducted to synthesize temperature sensitive 3D magnetic nanoparticles for the adsorption of MCPA herbicides from aquatic solution. More interestingly, the effective factors on the adsorption process were investigated. In addition, adsorption conditions optimized for evaluation isotherm, kinetics and thermodynamics of adsorption processes. Moreover, adsorbent regeneration, and the removal efficiency of the PV/S-g-3D-GO/N adsorbent in MPCA herbicides from real samples was evaluated

2. Materials And Methods

2.1 Chemicals

Graphene oxide was purchased from Sigma Aldrich and other material including 2,2'-azobisisobutyronitrile (AIBN) and MCPA were purchased from Merck (Darmstadt, Germany).

2.2 Instruments and characterization of the adsorbent

Fourier transform infrared spectroscopy (FTIR, Spectrum Two, PerkinElmer, USA) was used to distinguish the functional agent in molecules. Nanoparticle size, crystal structure, magnetic properties, was characterized by energy dispersive x-ray spectroscopy (EDS) equipped with FE-SEM Detector (Oxford Instrument, England), Transmission electron microscopy (TEM), X-ray diffraction (Xpert-PRO, Pananalytical, England). Vibrating-sample magnetometer (VSM, LKBFB, Daghigh Kavir, Iran), Thermal gravimetric of nano particles was analyzed by Thermo Gravimetric Analysis (TGA, STA 1500 Rheometric scientific, Switzerland) in a range of 0–600 °C at 10 °C/min heating rate in the air atmosphere. The MCPA concentration was measured by a UV-Vis spectrophotometer (UV/Vis, DR5000, HACH, Germany), The chromatographic separation was performed by High Performance Liquid Chromatography (HPLC-KNUARE Co Germany). The chromatographic conditions included the using system with a C₁₈ column (5 µm particles, 250 mm length, and 4.6 mm internal diameter) was calibrated and tested prior to injection of the samples. The mobile phase consisted of water: acetonitrile (1:1 ratio) and the flow rate was 0.5mL/min. An injection volume of 20 µL was injected manually, while the column temperature was set at 30°C. After the injection, a UV detector 2600 at a wavelength of 283nm was used to detect MCPA in the samples. The analysis time and retention time for MCPA peak were 10.00 min and 3.4 min, respectively. The detection limit of 2,4-D was 1 ng/L. All experiments run according to ASTM(25).

2.3 Synthesis of magnetic Fe₃O₄ nanoparticles

Magnetic Fe₃O₄ nanoparticle were prepared by co-precipitation (CPT) methol(26) First, 5.4 g FeCl₃.6H₂O, 2 g FeCl₂.4H₂O, and 200 mL deionized water were added to a three-neck flask in a water bathroom. The mixture was stirred at 800 rpm for 30 min, then heated to 80°C and, stirred for an extra 30 min in nitrogen atmosphere. Next, 40 mL of ammonia solution (25%) was added dropwise to the mixture solution to reach a pH of 11 and the formation of a black precipitate. The mixed solution was kept for 2h, then cooled down to room temperature, and placed in an ultrasonic bath for 7min. The final precipitate was separated from the solution by a 1T (Tesla) magnet at the bottom of the flask, washed two times with deionized water and ethanol separately, and dried in an oven at 70°C for 12h.

2.4 3D structure of Fe₃O₄ magnetic nanoparticle

Solution of graphene oxide (2 mg/L) was prepared and pH of the solution was adjusted to 11. Then, 0.965 g of Fe₃O₄ "which was synthesized in the previous section" was added in an ultrasonic bath. Next, suspension was incubated in a water bath without stirring at 90°C for 6h. The formed precipitate was separated by 1T magnet and washed by water several times. The product was kept at -90°C for 1h and subsequently in a vacuum freeze dryer at -70 °C for 24 h

2.5 Modification of 3D-GO surface

Solution including of Fe₃O₄@GO (2 g), epichlorohydrine (40 mL), NaOH (60 mL), and sodium borohydride (1g) were mixed and stirred in a dark chamber for 24h at room temperature (±15°C). The precipitate was

washed by cool water several times and added to 50 mL of Na₂S (0.5 M) then, 50 mL of acetate buffer (pH: 5), was added and was shake on a stirrer at 40 °C for 24 h

2.6 Polymer grafting

The obtained precipitate was added to the solution which including ethanol (50mL), styrene (10mL), n-vinylcaprolactam (1g), and 0.1 g of azobisisobutyronitrile (AIBN). The mixture was refluxed in nitrogen atmosphere in a water bath at 65°C for 8h. The obtained precipitate was washed three times by ethanol and five times with water then was dried in an oven at 70°C.

2.7 Batch experiments

Experiments were carried out on both synthetic and real sample that was sampled from Zebakenar, Gilan (as a real agricultural wastewater) and Hakimiyeh, Tehran Pars (as deep well water), Iran. The adsorption experiments were carried out with the different adsorption condition, including pH (2- 8), contact time (2- 360 minutes), temperature (30-50 °C), adsorbent dosage (0.1- 7 mg/L), and initial herbicide (5- 60 mg/L) for determining the optimum adsorption process to remove MPCA herbicide. All of the selected rang was according previous published paper. The optimum adsorption conditions were obtained by varying each variable while others kept constants. Then, in each stage of the experiment the sorbent was separated by filtration with 0.45µm membrane filter and analyzed by using UV-Vis-A spectrophotometer for measuring MPCA concentration. Finally, the synthesized PV/S-g-3D-GO/N was used for removing MPCA from real agricultural wastewater and deep well water. Herbicide concentrations in real samples were measured by using high-performance liquid chromatography (HPLC). Langmuir, Freundlich, Temkin and Redlich-Peterson models were used to determine the best adsorption isotherm models. The adsorption kinetics were studied by the pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations. Equilibrium isotherm measurements were carried out by keeping the solution volume (200mL) and the amount of PV/S-g-3D-GO/N the constant and varying the concentration of MPCA (V) in 250mL Erlenmeyer flasks. The pH of the solutions was adjusted by adding 1.0 mol L⁻¹ sodium hydroxide or 1.0mol L⁻¹ hydrochloride acid solutions. The equilibration (shaking) time was 300 min at room temperature. After that, sorbent was separated by filtration with 0.45µm membrane filter. The filtrate was analyzed for herbicide by UV-Vis-A spectrophotometer. The removal efficiency of the MPCA and the amount of adsorbed MPCA per gram adsorbent was calculated using equations 1 and 2, respectively.

$$R_E = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

In these equations, q_e (mg/g) is adsorbed MCPA per adsorbent mass unit, C_0 (mg/L) is the initial concentration of MCPA at the solutions before the adsorption process, C_e (mg/L) is MCPA concentration at the equilibrium in the solution after adsorption, V (L) is the solution volume, and W (g) is the sorbent mass. Also, C_t is the concentration at intervals of time (t) and R_E is changed MCPA concentration with respect to the time(27).

2.8 Thermodynamics

Adsorption thermodynamic was investigated by varying temperature from 298 to 318 K.

The thermodynamic parameters, namely, enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) for adsorption of the selected pesticides onto **PV/S-g-3D-GO/N** were expressed by Van 't Hoff Eq. (3) and (4).

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

$$-\Delta G = -R \ln k_c \quad (4)$$

Where, T (K) and R (0.0083145 kJ mol⁻¹ K⁻¹) are temperature and the universal gas constant, respectively. KC is the distribution coefficient and can be defined as $\ln KC = q_e/C_e$ (28)

48.

2.9 Regeneration of the adsorbent

Regeneration studies were performed on (3D/GO/Fe₃O₄) by adding it in 20 mg/L MCPA mixed with 5g/L of nano-adsorbent at pH: 3 for 1h. After separating the sediment with the magnet and was mixed at 4000 rpm, the supernatant was used to determine the amount of remaining MCPA by a UV-Vis spectrophotometer (R1 run). The synthesized 3D/GO/Fe₃O₄ was washed with 5 ml of methanol in ultrasonic apparatus for 2 minutes then was dried in an oven at 60°C. This process was repeated 9 times(29).

3. Results

3.1 FE-SEM analysis

Morphology of the synthesized PV/S-g-3D-GO/N was determined by SEM (Scanning Electron Microscope) (Fig.1A). The obtained result shows that all the particles have porous spherical shape and this property helped to better adsorption properties. Moreover, the nanoparticle shows accumulated shape. In addition, it is demonstrated that the particle size is ranged from 40 to 80nm and roughly,

spherical shape, however, a slight aggregation phenomenon occurred. The TEM images show that the surfaces of GO are densely sheltered with uniformly distributed black colored Fe_3O_4 nanoparticle. The Fe_3O_4 nanoparticle are distributed on GO. Moreover, there is not much agglomeration of Fe_3O_4 nanoparticles on the surface of graphene oxide. The Fe_3O_4 particle was founded on the edges of the sheets since carboxyl groups associated at the edges of GO (Fig. 1B).

3.2 FTIR analysis

The FTIR spectra of the Fe_3O_4 nanoparticle was shown in Fig.2A. The peak around 3387 cm^{-1} and 634 cm^{-1} revealing the stretching vibration Fe_3O_4 group bonded with the O-H group at 1626 cm^{-1} due to the adsorbed water on the surfaces(12). Fig. 2B is related to FTIR spectra of the 3D-GO/N. As it can clearly see the strong peak on the 3412 cm^{-1} is observed, which is related to 3D-GO/N vibration, Moreover, the vibration band at 1626 and 634 cm^{-1} attributed to the O-H and Fe_3O_4 groups and indicate that surface of nanoparticle have been successfully functioning. The FTIR spectrum of the PV/S-g-3D-GO/N confirms broad bands at 3423 cm^{-1} that are related to O-H or N-H stretching vibration (Fig.2C). In addition, absorption bands of OH on the surface were observed. Another vibration peak at the 3022 cm^{-1} and 2916 cm^{-1} assigned to the C-H bending mode of aromatic and aliphatic group in styrene, respectively. In addition, the peak at 1735 cm^{-1} was related to the C=O vibration and peak at 1596 cm^{-1} represented the C-C aromatic bonds. The CH_2 and C-O peaks appeared at 1446 cm^{-1} and 1022 cm^{-1} , respectively. The sharp peak of 696 cm^{-1} also represented Fe_3O_4 .

3.3 XRD analysis

According to obtained result from Fig.3 (A), 3D-GO/N (A) and the PV/S-g-3D-GO/N (B) was characterized by energy dispersive analysis of X-ray (EDX). The result of EDX spectrum prevalent that the planes (220), (311), (400), (511) and (440) which was related to Fe_3O_4 peaks (30). Moreover, the results show that the formation of the shoulder on its crystals will have no effect on the spectrum of magnetic particles(31). According to obtained result from Fig.3 (B), confirms the purity of Fe_3O_4 nano- magnetic particles, and the comparison between spectra shows the same structure in the two materials. The average crystallite size of the modified nano-adsorbent was calculated to be 12.55 nm using the Scherer-Debye equation.

3.4 Magnetic properties measurement

The Vibrating Sample Magnetometer (VSM) was used to determine the magnetic properties of the modified nano-adsorbent. As shown in Fig.4, the 3D-GO/N and PV/S-g-3D-GO/N spectra were S shape. The hysteresis loop of 3D-GO/N and PV/S-g-3D-GO/N is 70 emu/g and 32 emu/g , respectively. This reduction was due to the coating of N-vinyl caprolactam and styrene on 3D-GO/N, which acted as an adsorption agent and reduced the magnetic properties of the core as a shielding.

3.5 Thermal gravimetric analysis (TGA)

The thermal behavior of 3D-GO/N and PV/S-g-3D-GO/N was studied by thermal gravimetric analysis (TGA) from 0 to 600 °C. As shown in Fig.6 and spectrum a, 3D-GO/N lost less than 1% of its weight due to the evaporation of surface water adsorbed on it at 150 °C. In general, weight loss about 80 to 150°C is due to the evaporation of water adsorbed onto the nanoparticle surfaces(32). Thereafter, no weight loss of up to 400 °C was observed, but at the higher temperatures, the weight loss was due to the burning of graphene oxide. For PV/S-g-3D-GO/N (Fig.5 A&B), the weight loss was less than 1% due to the evaporation of water adsorbed onto the particle surface. The weight was constant up to 300 °C and then decreased due to the removal of the polymeric branches. At 400 °C, weight loss was due to the burning of graphene oxide. The thermal gravimetric analysis showed that the polymeric branches have been successfully applied to 3D-GO/N.

3.6 Effect of various parameters on the adsorption of MCPA

3.6.1 Effect of pH on adsorption

pH is one of the most important parameters in the adsorption process, in this study the effect of different pH (2-8) on MCPA herbicide (10g/L) removal efficiency after 60 min contact time with PV/Sg-3D-GO/N (3g) as an adsorbent was studied. As can be seen in Fig.6, the adsorption process was more efficient at acidic pH because MCPA had an acidic structure. At basic pH, the herbicide was deformed into an ionic form and the adsorption decreased(25).

3.6.2 Effect of adsorbent dose on the adsorption efficiency

The effect of adsorbent dosage on adsorption efficiency was investigated. Obtained results show that adsorption efficiency has increased with increasing dosage of PV/S-g-3D-GO/N (Fig.7). However, unique properties of Graphene based adsorbent make it good candidate for remove different kind of contaminant from aquatic solution and different author reported different dosage for optimum removal efficiency that is different from /L0.1-12 mg for different pollution such as organic and inorganic pollutant (33). The reason is that when the dosage of the PV/S-g-3D-GO/N increased, the adsorption sites and functional groups on the adsorbent surface increased(34, 35) and lead to increasing removal efficiency. This could be due to the increase of active sites and functional groups at the nano-adsorbent surface.

3.6.3 Effect of contact time on the adsorption efficiency

The effect of contact time on the removal efficiency of MCPA at the optimal condition was studied. The results showed that as the contact time increased, the adsorption efficiency increased. Maximum removal efficiency was observed at the 300 min of contact time.

3.6.4 Effect of temperature on the adsorption efficiency

The effect of temperature on the MCPA removal by the PV/S-g-3D-GO/N was investigated by performing equilibrium adsorption studies at five different temperatures in the range of 30-55°C. As shown in Fig.9,

removal efficiency, increased with increasing temperature.

3.6.5 Effect of initial MPCA concentration on the adsorption efficiency

Figure.10 shows the adsorption efficiency of the PV/S-g-3D-GO/N for the removal of MPCA in different initial MPCA concentrations (5–60 mg L⁻¹) at the optimal condition. The experiments, the parameters affecting the adsorption were stabilized at optimum values obtained from the previous steps (pH: 3, of adsorbent dose: 5 g/L, temperature 50 °C, and contact time of 300 min). The results show that the removal efficiency decreased with increasing concentration of herbicide in solution.

3.7 Isotherm and kinetic studies of the adsorption

Adsorption isotherms indicate the interaction between adsorbate and adsorbent in the liquid phase (free adsorbate solution) concentrations and the solid phase (adsorbent-attached solute) concentrations at constant temperature (36). Therefore, Langmuir, Freundlich, Temkin and Redlich-Peterson models were used in this study. In addition, the pseudo-first-order, pseudo-second-order was used for the evaluation kinetic of adsorption (Table.1). The obtained data reveal that the Langmuir model ($R^2 = 0.998$) yielded best-fits to the experimental data (Table.2) that is maybe due to mono layer and the surface of the adsorbent surface is uniform. Therefore, there is no interaction between adsorbed molecules (37). The positive values of ΔS also indicated that the degree of freedom at the solid-liquid intermediate was increased during adsorption (Table.3) (38).

3.8 Adsorbent regeneration

Fig.11 illustrates the percentage change in adsorbent capability for the removal of herbicide after regeneration. As can be seen in the figure, the PV/Sg-3D-GO/N could operate up to twice usage with 100% efficiency. Then its efficiency was reduced but still could be used by up to seven times by more than 50% efficiency. Since the process of MCPA removal by adsorbents was based on surface adsorption, it is likely that the adsorbent may be used more frequently by changing the type of solvent used or increasing the washing time.

3.9 Application of PV/S-g-3D-GO/N in the removal of MCPA herbicides from real samples

After the adsorption process under optimum conditions, the residual MCPA concentration in the samples was below its detection limit (1 ng/L). These results showed that the synthesized adsorbent had excellent performance in removing MCPA from real samples and therefore impurities in water and wastewater samples did not significantly interfere with removal of the target contaminant.

3.10 Comparison of PV/S-g-3D-GO/N adsorption capability with 3D-GO/N

In order to determine the effectiveness of surface modifications and its branching on MCPA herbicide adsorption from aqueous solutions, PV/Sg-3D-GO/N coincidence with 3D-GO/N at optimum conditions (pH: 3, adsorbent dose: 5 g/L, temperature: 50 °C, contact time: 300 min) was used to remove herbicide

from water. The results showed that the removal percentage of MCPA from water with PV/Sg-3D-GO/N was equal to 83.12 ± 0.1 while this value was in relation to the 3D-GO/N of 25.66 ± 7.37 . Therefore, if the PV/Sg-3D-GO/N adsorption power of 100% is considered, the 3D-GO/N has 30% ability to remove MCPA from water. So it can be concluded that surface modification and branching of 3D-GO/N were effective in the adsorption of MCPA herbicides, which could be due to the accumulation of fine particles and the greater ability of styrene as herbicidal adsorption agent in the adsorbent surface.

4. Discussion

This study examined removal efficiency of 4-chloro-2-methyl-phenoxy acetic acid (MCPA) by 3D polymer nano-magnetic (PV/S-g-3D-GO/N). According to the obtained result, acidic condition (pH: 3) was determined as an optimum pH. These results were consistent with other relevant studies(25). although, some researchers have reported pH : 6 as an optimal condition for the adsorption of phenoxy herbicides(7, 39). Different reported results can be related to the type of adsorbent and the different mechanisms of toxin by the adsorbent. Cao et al. adjusted the pH value of 2 for removal 2-naphthoxyacetic acid by magnetic GO and demonstrated that the oxygen groups on the adsorption and analysts would be ionized at alkaline conditions so, reduce the extraction efficiency of synthesized adsorbent(40). The effect of adsorbent dosage shows that when the adsorption equilibrium was reached between the adsorbent and MCPA in the solution, the removal efficiency remained constant. Moreover, the high removal efficiency was observed at the 7 g L⁻¹ adsorbent dosage. As can be seen in Fig.8, the optimal removal process occurred when the dose of PV/S-g-3D-GO/N was equal to 5 g/L (65%). Several studies have been carried out and achieved the same result(41, 42). In addition, further increase in contact time, there was little change in adsorption. Therefore, the optimum contact time between MCPA herbicide and PV/S-g-3D-GO/N was 300 min (Fig.8). Salman et. al has reported that adsorption efficiency of pesticide has decreased by increasing contact time. They are stating that higher number of vacant surface sites available for adsorption at the initial than the later stages and the repulsive forces existing between pesticide molecules on the absorbent surface and those in solution at the later stages(43). Removal efficiency, increased with increasing temperature. This is because as the temperature increased, the kinetic energy of the molecules increased, as a result, the collision between the herbicides particles and the adsorption sites on PV/S-g-3D-GO/N increased. On the other hand, N-vinyl caprolactam is a temperature-sensitive material and shrinks with increasing temperature(44), as a result, more interaction was created between MCPA and PV/S-g-3D- GO/N. Moreover, temperature can affect several aspects and has a positive influence by increasing the swelling capacity of an adsorbent, the mobility of MPCA molecules, the number of active sites, and the interaction between the adsorbate and adsorbent [40]. Therefore, an increase in the removal efficiency from 42% to 72 % was observed. In addition, the optimum temperature for the removal efficiency 50 °C was determined(45). In addition, results show that the gradual saturation of specific adsorption sites on the surface of PV/S-g-3D-GO/N as a result of the increased concentration of herbicides in the solution, whose result was a decrease in adsorption efficiency (46). It can be inferred that by increasing MPCA concentration the driving force was enhanced for the diffusion of MPCA adsorption. Therefore, active sites are occupied increasingly by influent MPCA

and the 3D/GO/Fe₃O₄ as an adsorbent active sites saturated rapidly, so that the amount of adsorption decreased(47). Similar results were reported by Xu et al(48). It is possible that MCPA molecules interact with the π - π interaction at the adsorbent surface [44]. According obtained data, maximum adsorption capacity (q_m) 4.3 mg/g was reported. Moreover, The values of the empirical parameter show that R was 0.03 and it indicated optimal adsorption ($0 \leq R \leq 1$)(49). In fact, different models of adsorption isotherms confirm each other. For example, in the Redlich – Peterson isotherm model, whenever g (1.0028) is close to 1, the data confirm the fit of the Langmuir model(50). Additionally, evaluate the thermodynamics of MCPA shows that the free energy (ΔG°) values are negative, confirming that the adsorption is spontaneous and favorable thermodynamically(51). A positive value of ΔH indicated that the adsorption process was endothermic and the adsorption capacity increased with increasing temperature.

5. Conclusion

In this study, a three-dimensional polymeric nano-magnetic adsorbent was prepared using iron oxide as the core, Graphene oxide as the 3D maker agent, N-vinyl caprolactam as a temperature-sensitive monomer and styrene as the adsorbent agent. It was successfully used to remove MCPA herbicides from aquatic solution. The factors affecting the adsorption process as well as the optimum adsorption conditions were determined. The results showed that the maximum adsorption capacity of adsorbent (q_{max}) was 4.36 mg/g at optimum conditions of pH = 3, contact time of 300 min, adsorbent dose of 5 g/l and the temperature of 50 °C. PV/S-g-3D-GO/N was also used to remove MCPA herbicides from real samples with 100% removal efficiency. Use of this adsorbent is recommended for the treatment of agricultural and industrial wastewater containing MCPA because of its ease of collection using a magnetic field and its regeneration by methanol. According to the results, this adsorbent is more effective in hot environments, so it can be used in hot environments such as southern Iran to remove the mentioned herbicide from contaminated water. The data of adsorption isotherm were in agreement with the Langmuir model ($R^2 = 0.998$) and the adsorption kinetics followed the pseudo-second-order model ($R^2 = 0.999$). Thermodynamic studies also showed that the MCPA adsorption process by PV/S-g-3D-GO/N was spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$) and increasing the temperature increased the adsorption capacity of the adsorbent.

Declarations

Availability of data and materials

The authors certify that this manuscript is the original work of the authors, all data collected during the study are presented in the manuscript, and no data from the study has been or will be published separately.

Competing interests

The authors declare that they have no conflict of interests.

Authors' contributions

All authors contributed and participated equally in the data collection, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

Funding

The present study had no funding sources of any kind

Acknowledgments

The authors are grateful for the financial support of this project by the Research Council of Islamic Azad University, Tehran, Iran

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Tables

Table 1 – kinetic parameter for MCPA adsorption by the PV/S-g-3D-GO/N

Kinetic model	Parameter	Quantity
pseudo first order	q_e (mg/g)	0.6283
	K_1 (min^{-1})	0.00783
	R^2	0.9524
pseudo-second-order	q_e (mg/g)	4.2123
	K_2 (g/mg/min)	0.07856
	R^2	0.9996
intraparticle diffusion	k_i ($\text{min}^{0.5}$)	0.0856
	C (mg/g)	3.3343
	R^2	0.9878

Table 2 - Adsorption isotherm parameters for MCPA sorption by the PV/S-g-3D-GO/N

Isoterm model	Parameter	Quantity
Langmuir	$q_{\max}(\text{mg/g})$	4.36
	$k_L(\text{L/mg})$	0.53
	R_L	0.03
	R^2	0.997
Freundlich	$K_f[(\text{mg/g})(\text{L/mg})^{1/n}]$	1.77
	n	3.8
	R^2	0.946
Temkin	$A(\text{L/g})$	9.62
	B	0.74
	$b(\text{J/mol})$	3638
	R^2	0.969
Redlich-Peterson	A	4.87
	B	1.276
	g	1.002
	R^2	0.990

Table 3 -Thermodynamic parameters of MCPA onto the PV/S-g-3D-GO/N

$S(\text{J/mol.K})\Delta$	$H(\text{kJ/mol})\Delta$	$G(\text{kJ/mol})\Delta$	$K_L(\text{L/g})$	$T(\text{K})$
160.8593	35.05099	-13.7135	226.554	303.15
		-15.3221	372.853	313.15
		-16.9307	535.1389	323.15

Figures

Figure 1

SEM of the synthesized PV/S-g-3D-GO/N (A), TEM images of GO-Fe₃O₄ (B)

Figure 2

FT-IR spectra of (A) Fe₃O₄, (B) Fe₃O₄@GO, (C) the synthesized 3D/GO/Fe₃O₄

Figure 3

XRD pattern of A) Fe₃O₄@GO and B) the synthesized 3D/GO/Fe₃O₄

Figure 4

VSM of Fe₃O₄@GO (A) and the synthesized 3D/GO/Fe₃O₄ (B)

Figure 5

TGA of Fe₃O₄@GO (A) and the synthesized 3D/GO/Fe₃O₄ (B)

Figure 6

Effect of pH on MCPA removal by the PV/S-g-3D-GO/N (contact time: 60 min, MCPA initial concentration: 10g, adsorbent dosage: 3g)

Figure 7

Effect of different adsorbent dosage on removal efficiency (pH: 3, MCP initial concentration: 10 g/L, contact time: 60 min)

Figure 8

Effect of contacting time on the adsorption efficiency (adsorbent dosage: 10g, initial MCPA concentration: 10 g/L, and pH: 3)

Figure 9

Effect of temperature in removal efficiency of MCPA (pH: 3, adsorbent dosage: 3g/L, initial concentration of MCPA :10 mg/L, contact time: 300 min)

Figure 10

Effect of initial concentration of MCPA on adsorption (pH: 3, of adsorbent dose: 3 g/L, temperature: 50°C, and contact time: 300 min)

Figure 11

The PV/S-g-3D-GO/N efficiency after regeneration