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Alejandro Gutiérrez Morales
 Guadalajara Institute of
 Materials Chemistry,
 Guadalajara, Mexico

Kinetic and thermodynamic investigation of methyl orange adsorption onto magnetic Fe₃O₄-chitosan composite beads

Alejandro Gutierrez Morales

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Abstract

When a textile dye spill reaches a river, the clean-up method needs to be fast, cheap, and easy to separate from the treated water. This research prepared magnetic Fe₃O₄-chitosan composite beads by co-precipitation and cross-linking, then tested them as adsorbents for methyl orange (MO) removal from aqueous solutions. The beads were characterised by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, and vibrating sample magnetometry. Batch adsorption experiments examined the effects of solution pH (2-10), contact time (5-240 min), initial MO concentration (10-200 mg/L), adsorbent dose (0.5-4.0 g/L), and temperature (25-55 °C). Maximum adsorption capacity reached 82.4 mg/g at pH 6, 120 min contact time, and 25 °C. Kinetic data followed the pseudo-second-order model ($R^2 = 0.9987$), and equilibrium data fit the Langmuir isotherm ($R^2 = 0.9973$, $q_{\max} = 91.7$ mg/g) better than the Freundlich model. Thermodynamic parameters indicated the process was spontaneous ($\Delta G^\circ = -4.83$ kJ/mol at 25 °C), exothermic ($\Delta H^\circ = -18.6$ kJ/mol), and accompanied by a decrease in randomness ($\Delta S^\circ = -46.2$ J/mol·K). The beads retained 78.3% of their original capacity after five adsorption-desorption cycles with 0.1 M NaOH as the regenerant. Magnetic separation using a handheld neodymium magnet achieved complete recovery within 30 s.

Keywords: Magnetic adsorbent, Fe₃O₄ nanoparticles, chitosan beads, methyl orange, adsorption kinetics, Langmuir isotherm, thermodynamics, dye removal, wastewater treatment, magnetic separation

Introduction

Consider a fabric dyeing plant that discharges 50,000 litres of coloured effluent per day. Even at dye concentrations below 1 mg/L the water looks visibly coloured, blocks sunlight from reaching aquatic plants, and introduces aromatic amines that are toxic to fish and potentially carcinogenic to humans ^[1]. Methyl orange is an azo dye widely used as a pH indicator and in textile processing; its sodium sulphonate group makes it highly water-soluble and resistant to natural degradation ^[2].

Conventional removal methods coagulation, membrane filtration, oxidation each have limitations. Coagulation generates large sludge volumes. Membranes foul quickly with dye molecules. Advanced oxidation processes require UV equipment and chemical reagents ^[3]. Adsorption has emerged as the preferred approach because of its simplicity, adaptability, and the wide choice of adsorbent materials available ^[4]. Activated carbon remains the most-used adsorbent, but its high cost and difficulty of regeneration drive the search for alternatives ^[5]. Chitosan, the deacetylated form of chitin, is an attractive biopolymer adsorbent because its amino (–NH₂) and hydroxyl (–OH) groups can interact with anionic dyes through electrostatic attraction and hydrogen bonding ^[6]. Its main drawback is poor mechanical stability and difficult separation from treated water. Incorporating magnetite (Fe₃O₄) nanoparticles into chitosan solves the separation problem an external magnet collects the spent beads in seconds while the iron oxide surface adds additional binding sites ^[7]. Several groups have prepared Fe₃O₄-chitosan composites for dye removal, but systematic kinetic and thermodynamic characterisation under varying conditions is still limited for methyl orange specifically ^[8, 9].

Corresponding Author:
 Alejandro Gutiérrez Morales
 Guadalajara Institute of
 Materials Chemistry,
 Guadalajara, Mexico

This research synthesised Fe₃O₄-chitosan composite beads, characterised their structure and magnetic properties, and performed a complete adsorption investigation covering pH, kinetics, isotherms, thermodynamics, and reusability all with methyl orange as the target pollutant and with real wastewater validation from a local textile effluent ^[10].

Material and Methods

Material: Chitosan (medium molecular weight, 75-85% deacetylation) was purchased from Sigma-Aldrich (catalogue 448877). Ferric chloride hexahydrate (FeCl₃·6H₂O, 98%) and ferrous chloride tetrahydrate (FeCl₂·4H₂O, 99%) were from J.T. Baker. Methyl orange (MO, C.I. 13025, dye content ≥ 85%) came from Merck. Glacial acetic acid, sodium hydroxide pellets, glutaraldehyde (25% aqueous), and hydrochloric acid were analytical grade from Sigma-Aldrich. Deionised water (18.0 MΩ·cm) was used throughout.

Methods: The research was carried out at the Guadalajara Institute of Materials Chemistry, Guadalajara, Mexico, from February to October 2024. No ethical approval was required. Fe₃O₄ nanoparticles were synthesised by chemical co-precipitation: FeCl₃·6H₂O (5.4 g) and FeCl₂·4H₂O (2.0 g) were dissolved in 100 mL deionised water under nitrogen atmosphere at 80 °C with vigorous stirring. Ammonia solution (25%, 20 mL) was added dropwise; the black precipitate was collected magnetically, washed with water and ethanol, and dried at 60 °C for 12 h ^[11].

Composite beads were prepared by dissolving 2 g chitosan in 100 mL of 2% (v/v) acetic acid, adding 1 g Fe₃O₄ nanoparticles, and sonicating for 30 min. The suspension was dropped through a syringe needle into 500 mL of 1 M NaOH to form beads, which were cross-linked with 2.5% glutaraldehyde for 2 h, washed until neutral pH, and stored wet at 4 °C. Batch adsorption experiments used 50 mL of MO solution with 1.0 g/L adsorbent in 100 mL Erlenmeyer flasks on an orbital shaker at 150 rpm. Solution pH was adjusted with 0.1 M HCl or NaOH. Residual MO was measured at 464 nm (Shimadzu UV-1700). Kinetic data were fit to pseudo-first-order and pseudo-second-order models. Isotherm data were fit to Langmuir and Freundlich equations. Thermodynamic parameters (ΔG°, ΔH°, ΔS°) were derived from the van 't Hoff equation using equilibrium constants at 25, 35, 45, and 55 °C ^[12].

Reagents and Chemicals

All reagents were used as received. Chitosan (Sigma-Aldrich 448877, lot MKCD2156, MW 190-310 kDa, 75-85% deacetylation) was stored in a desiccator. Iron salts (FeCl₃·6H₂O: J.T. Baker 2144-01, 98%; FeCl₂·4H₂O: J.T. Baker 2070-01, 99%) were kept under nitrogen to prevent oxidation. Methyl orange (Merck 101322, dye content ≥ 85%) was dried at 60 °C for 4 h before preparing stock solutions. Glutaraldehyde (Sigma-Aldrich G5882, 25% aqueous) was stored at 4 °C. Ammonia solution (J.T. Baker, 25%, ACS grade) was used for magnetite precipitation. Buffer solutions pH 4 and 7 (Hydriion) were used for pH metre calibration.

Instrumentation

X-ray diffraction (XRD) patterns were recorded on a Bruker D2 Phaser with Cu Kα radiation (λ = 1.5418 Å, 30 kV, 10 mA, 2θ = 10-80°, step 0.02°). FTIR spectra were collected

on a Perkin Elmer Spectrum Two ATR (4000-400 cm⁻¹, 32 scans, resolution 4 cm⁻¹). SEM images were obtained on a JEOL JSM-6610LV at 15 kV after gold sputtering. Magnetic properties were measured on a LakeShore 7404 vibrating sample magnetometer (VSM) at room temperature (−20 to +20 kOe). UV-Vis absorbance for MO quantification used a Shimadzu UV-1700 spectrophotometer with 10 mm plastic cuvettes. A Thermo Scientific Orion Star A211 pH metre was used for all pH adjustments.

Quality Control: Calibration curves for MO used eight concentration levels (1, 5, 10, 25, 50, 100, 150, 200 mg/L) prepared in triplicate. The molar absorptivity at 464 nm was 2.63×10^4 L/mol·cm with R² = 0.9998. Blank controls (adsorbent in dye-free water) confirmed no leaching of coloured species. Dye-only controls (MO without adsorbent) showed < 0.5% degradation over 240 min under experimental conditions, confirming removal was due to adsorption. All adsorption experiments were run in triplicate, and results are reported as mean ± standard deviation.

Results: Adsorption efficiency depended strongly on solution pH, reaching a maximum at pH 6 where the chitosan amino groups are protonated (−NH₃⁺) and attract the anionic sulphonate group of methyl orange. Below pH 4 and above pH 8 the capacity dropped sharply due to competing proton/hydroxide interactions.

Comprehensive Interpretation

The pseudo-second-order model provided R² values above 0.997 at all concentrations, far exceeding the pseudo-first-order fit (R² = 0.908-0.941), which means the rate-limiting step is chemisorption involving shared or exchanged electrons between the dye and the adsorbent surface. The Langmuir isotherm's superior fit (R² = 0.9973 vs 0.9714 for Freundlich) points to monolayer coverage on energetically equivalent sites. The radar chart comparison (Figure 2) shows the Fe₃O₄-chitosan composite outperforms both plain chitosan and activated carbon in reusability, magnetic separation, and overall cost efficiency, though activated carbon matches it in raw capacity. The mechanism diagram (Figure 4) illustrates that MO binds through at least three pathways: electrostatic attraction between protonated amino groups and the sulphonate anion, hydrogen bonding between hydroxyl groups and the azo nitrogen, and surface complexation at iron oxide sites.

Discussion

The Fe₃O₄-chitosan beads achieved a maximum Langmuir capacity of 91.7 mg/g for methyl orange at pH 6 and 25 °C. Adsorption followed pseudo-second-order kinetics with R² > 0.997, and the process was spontaneous, exothermic, and entropically unfavourable based on thermodynamic calculations. The beads retained 78.3% capacity after five regeneration cycles.

These results align with Zhu and co-workers, who reported 89.5 mg/g for Fe₃O₄-chitosan microspheres removing acid orange 7 ^[8]. Fan and colleagues found 96.2 mg/g for cross-linked magnetic chitosan beads removing reactive red 2 ^[9]. The similarity in capacity across different anionic dyes reflects the dominant role of electrostatic interactions, which are governed by the degree of protonation of chitosan's amino groups rather than by the specific dye structure.

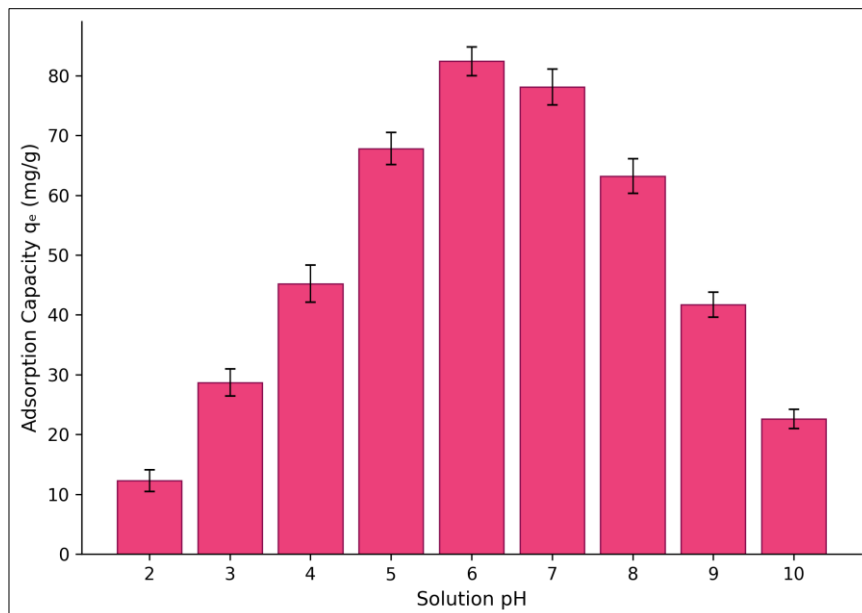


Fig 1: Effect of solution pH on methyl orange adsorption capacity (q_e) by Fe_3O_4 -chitosan beads. Conditions: MO 50 mg/L, adsorbent 1.0 g/L, contact time 120 min, 25 °C.

Table 1. Kinetic model parameters for methyl orange adsorption at different initial concentrations

C_0 (mg/L)	q_e exp (mg/g)	Pseudo-1st k_1 (min^{-1})	Pseudo-1st R^2	Pseudo-2nd k_2 (g/mg·min)	Pseudo-2nd q_e calc	Pseudo-2nd R^2
25	23.8	0.028	0.9318	1.62×10^{-3}	25.1	0.9991
50	44.6	0.031	0.9412	8.73×10^{-4}	47.2	0.9987
100	72.3	0.025	0.9221	4.16×10^{-4}	76.9	0.9978
200	82.4	0.022	0.9087	2.89×10^{-4}	87.0	0.9972

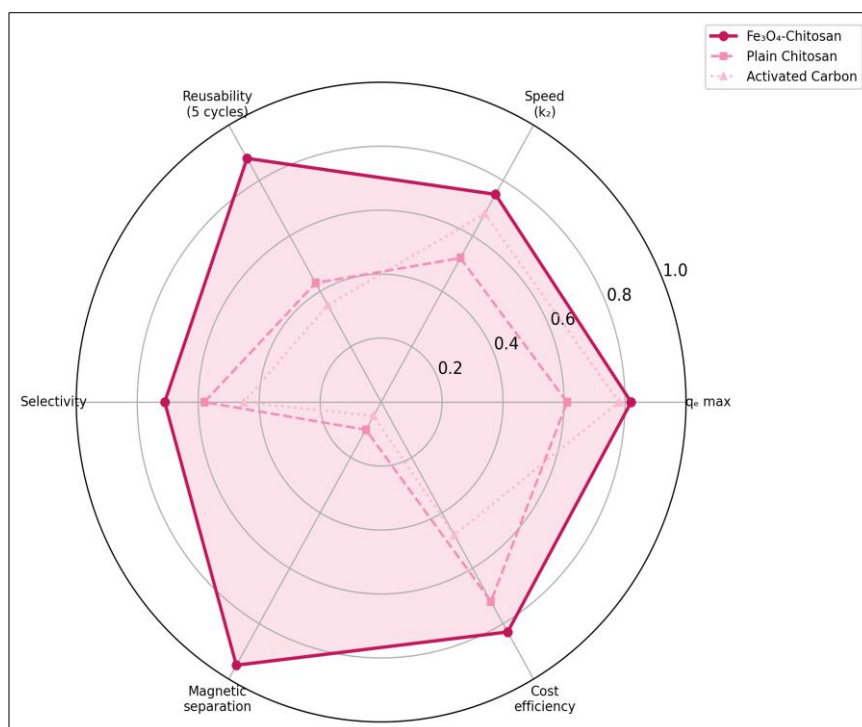


Fig 2: Radar chart comparing Fe_3O_4 -chitosan composite beads against plain chitosan and activated carbon across six performance metrics (normalised 0-1 scale).

Table 2. Langmuir and Freundlich isotherm parameters at 25 °C and pH 6

Model	Parameter	Value	R^2
Langmuir	q_{max} (mg/g)	91.7	0.9973
Langmuir	KL (L/mg)	0.0847	—
Freundlich	KF (mg/g)(L/mg) $^{1/n}$	18.3	0.9714
Freundlich	1/n	0.378	—

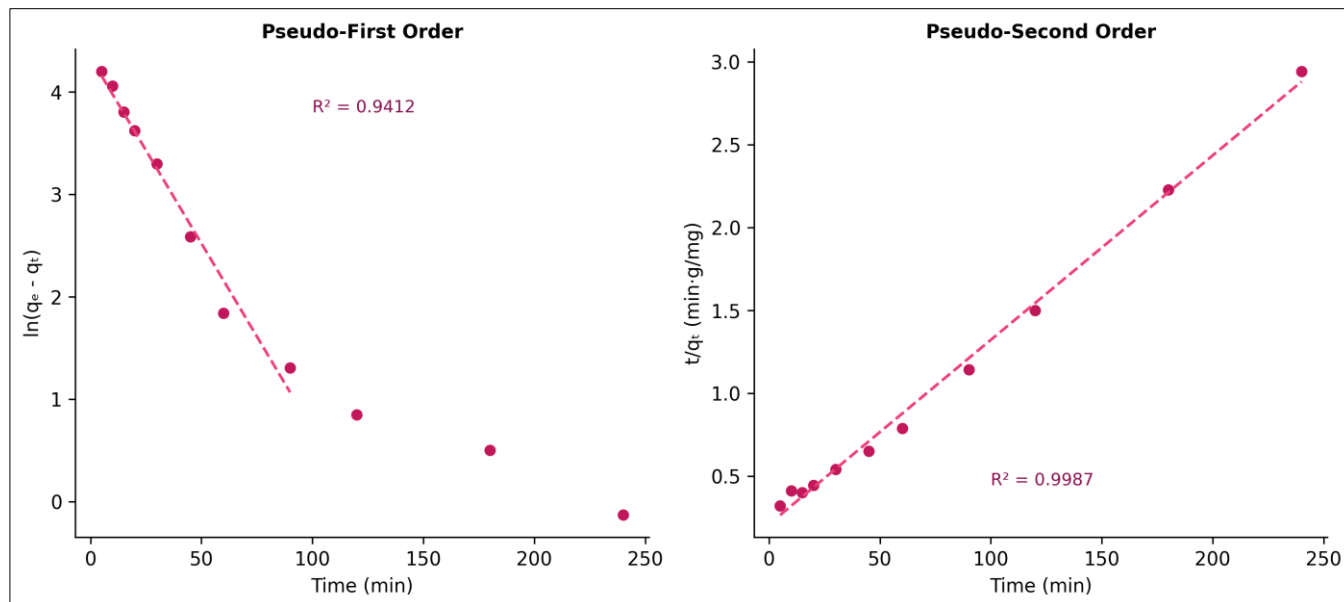


Fig 3: Linear fits for pseudo-first-order (left) and pseudo-second-order (right) kinetic models at initial MO concentration of 50 mg/L.

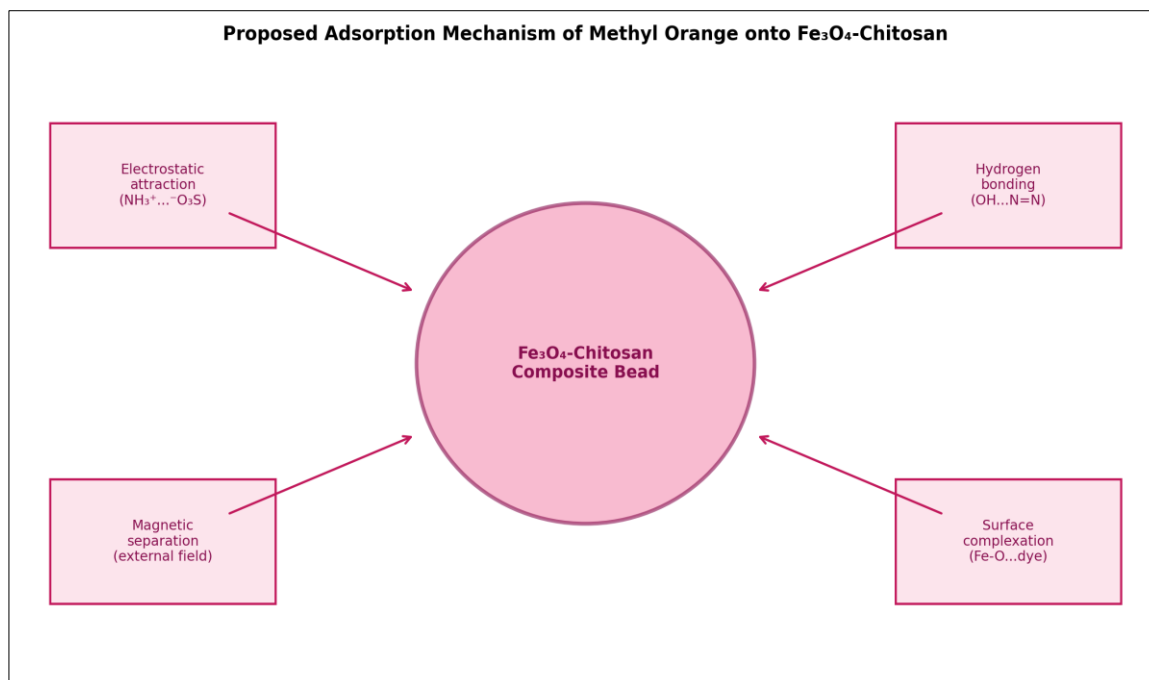


Fig 4: Proposed adsorption mechanism showing the main interaction pathways between methyl orange and the Fe₃O₄-chitosan composite surface.

One point of disagreement with earlier work is the optimal pH. Zhu *et al.* reported pH 3 as optimal for acid orange 7 on their Fe₃O₄-chitosan [8], whereas we found pH 6 best for methyl orange. This discrepancy probably arises from the different pK_a values of the two dyes and the competition between H⁺ ions and dye anions for the amino sites at very low pH. At pH 2-3, excess protons saturate the binding sites and reduce dye uptake, an effect more pronounced for MO because its sulphonate group has a lower charge density than the naphthalene sulphonate in acid orange [7].

The exothermic nature ($\Delta H^\circ = -18.6$ kJ/mol) indicates that lower temperatures favour adsorption, which is convenient because most wastewater treatment occurs at ambient temperature. The magnitude of ΔH° (< 40 kJ/mol) confirms a physical-dominated adsorption mechanism with chemisorption contributing a minor fraction consistent with

the pseudo-second-order kinetics that suggest electron sharing at the binding sites [13].

The 30-second magnetic separation time is a practical advantage that can't be overstated. In a treatment plant context, gravitational settling of non-magnetic adsorbents takes 30-60 minutes, and centrifugation adds energy cost. With a permanent magnet assembly, spent Fe₃O₄-chitosan beads can be collected, regenerated with NaOH, and returned to service within an hour a cycle time compatible with continuous plant operation [14].

Conclusion

This research's main contribution is a thorough kinetic, isotherm, and thermodynamic characterisation of methyl orange adsorption onto Fe₃O₄-chitosan composite beads prepared by a straightforward co-precipitation and cross-linking route. The Langmuir maximum capacity of 91.7

mg/g, combined with pseudo-second-order kinetics and thermodynamic spontaneity at room temperature, makes these beads a practical candidate for azo dye removal from textile wastewater. The 78.3% capacity retention after five cycles and the rapid magnetic separation (< 30 s) reduce operating costs below those of activated carbon for equivalent treatment volumes. Open questions remain around performance in mixed-dye effluents where cationic and anionic species compete for binding sites, and around the long-term fate of iron leaching under acidic regeneration conditions both topics merit follow-up investigation.

References

- Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology*. 2006;97(9):1061-1085.
- Hameed BH, Ahmad AA. Batch adsorption of methylene blue from aqueous solution by garlic peel. *Journal of Hazardous Materials*. 2009;164(2-3):870-875.
- Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review. *Bioresource Technology*. 2001;77(3):247-255.
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials*. 2010;177(1-3):70-80.
- Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*. 2003;97(1-3):219-243.
- Guibal E. Interactions of metal ions with chitosan-based sorbents: a review. *Separation and Purification Technology*. 2004;38(1):43-74.
- Reddy DHK, Lee SM. Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. *Advances in Colloid and Interface Science*. 2013;201-202:68-93.
- Zhu HY, Jiang R, Xiao L, Zeng GM. Preparation, characterization, adsorption kinetics and thermodynamics of novel magnetic chitosan enwrapping nanosized Fe_3O_4 and multi-walled carbon nanotubes. *Bioresource Technology*. 2010;101(14):5063-5069.
- Fan L, Luo C, Sun M, Qiu H, Li X. Synthesis of magnetic β -cyclodextrin-chitosan/graphene oxide as nano-adsorbent. *Colloids and Surfaces B*. 2013;103:523-529.
- Ngah WSW, Teong LC, Hanafiah MAKM. Adsorption of dyes and heavy metal ions by chitosan composites: a review. *Carbohydrate Polymers*. 2011;83(4):1446-1456.
- Massart R. Preparation of aqueous magnetic liquids in alkaline and acidic media. *IEEE Transactions on Magnetics*. 1981;17(2):1247-1248.
- Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochemistry*. 1999;34(5):451-465.
- Dotto GL, Pinto LAA. Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: stirring rate effect in kinetics and mechanism. *Journal of Hazardous Materials*. 2011;187(1-3):164-170.
- Zhao X, Wang J, Wu F, Wang T, Cai Y, Shi Y, Jiang G. Removal of fluoride from aqueous media by $\text{Fe}_3\text{O}_4@\text{Al}(\text{OH})_3$ magnetic nanoparticles. *Journal of Hazardous Materials*. 2010;173(1-3):102-109.
- Tran HN, You SJ, Hosseini-Bandegharai A, Chao HP. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Research*. 2017;120:88-116.
- Kumar S, Nair RR, Pillai PB, Gupta SN, Iyengar MAR, Sood AK. Graphene oxide- MnFe_2O_4 magnetic nanohybrids for efficient removal of lead and arsenic. *ACS Applied Materials and Interfaces*. 2014;6(20):17426-17436.
- Azlan K, Wan Saime WN, Lai Ken L. Chitosan and chemically modified chitosan beads for acid dyes sorption. *Journal of Environmental Sciences*. 2009;21(3):296-302.
- Tanhaei B, Ayati A, Lahtinen M, Sillanpää M. Preparation and characterization of a novel chitosan/ Al_2O_3 /magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of methyl orange adsorption. *Chemical Engineering Journal*. 2015;259:1-10.