



Adsorption of agricultural wastewater contaminated with antibiotics, pesticides and toxic metals by functionalized magnetic nanoparticles



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ABSTRACT

Functionalized magnetic nanoparticles (MNPs) as new-generation adsorbents have been widely used in environmental problems treatment processes due to their unique physical and chemical properties. MNPs have excellent efficiency towards the elimination of pesticides, antibiotics as well as toxic metals in agricultural wastewater because various specific functional groups anchoring the surface of magnetic nanoparticles, which can efficiently remove contaminants. Herein, this work aims to: (i) summarize the literatures about the sorption of pesticides, antibiotic and toxic metals; (ii) discuss the sorption mechanism and influence factors; (iii) pointed out prospective research necessities and challenges on the adsorption of agricultural wastewater pollutants by MNPs. To make feasibility of MNPs at large scale application, more efforts should be made to afford the relevant research in this field.

1. Introduction

Recently, the problem of agricultural wastewater has been aroused more and more attention. The sources of agricultural wastewater are used universally and unconsciously, involving crop farming, aquaculture, agricultural products processing industry, livestock as well as poultry breeding. Those complicated compositions (e.g. antibiotics, pesticides and toxic metals) are generally traced quantities as well as not easy to be degraded in nature, which has tremendously threatened environmental stability and human health [1–4]. For example, toxic metals like Pb, Ni, Zn, Cr, Cu, Cd, have caused serious environmental problems and posed serious risks to human health even at low concentrations [3]. As for antibiotics, even at very low levels it also could induce toxic effects, chronic allergic reactions and latent growth of antibiotic-resistant bacteria in the long-term [5,6]. And the high toxicity of pesticides can harm respiratory tract, cardiovascular system and nervous system, just like organ failure and deadly results [7,8]. Hence, to maintain ecological stability and people safety, successfully removing antibiotics, pesticides and toxic metals from agriculture water is still a very important and challenging project.

In recent years, a variety of methods including biodegradation [9,10], photodegradation [11], chemical precipitation [12], hydrolysis

and oxidative degradation [13], ion exchange [14,15], flocculation [16], neutralization [17,18], membrane separation [19], ultrafiltration [20,21], and adsorption strategies [1,22,23] have been applied for the treatment of agricultural wastewater. Among these techniques, adsorption technique, a simple and effective tool, is a most attractive alternative method for agricultural wastewater treatment due to its widespread adaptability, environment-friendly and low cost [1,23]. Adsorption is actually a time-dependent process [24]. Adsorption kinetics describe the solute uptake rate, controlling the residence time of adsorbate uptake at the solid-solution interface, which can illustrate the mechanism and reaction pathway of adsorption process. The pseudo-second-order kinetic model is fit for the whole adsorption process, indicating the adsorption rate was much controlled by chemical mechanism [25]. The two-parameter Langmuir and Freundlich isotherm models were frequently adopted to analyse the adsorption equilibrium data [26–28]. The Langmuir model was assumed monolayer adsorption with a finite identical adsorption sites on a uniform surface, demonstrating that chemical adsorption might be an important adsorption process [29]. The Freundlich model was applied to multilayer adsorption on non-uniform surface, illustrating physical interaction also affect the adsorption mechanism [29–31]. Therefore, adsorption technique has been broadly applied to remove contaminants from water solutions

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in environmental remediation.

To the best of our knowledge, lots of researchers have used MOFs [32], laterite soil [13], clay [33–38], polymers [39,40], peanut hull carbon [41], activated carbon [42–47], coirpith carbon [48], activated carbon composites [12], graphene oxide [49], zeolite [50,51], biochar [52–54] MWCNTs [55–57], sawdust [58], rice husk ash [59], spent mushroom substrate [60], coal fly ash [61–63], soil–fly ash mixtures [64], nonliving biomass [65] and biosorbent [66–68] as efficient adsorbents to separate antibiotic, pesticides and toxic metals from agricultural wastewater. Magnetic nanoparticles as an environmentally friendly material [69–72], have been used successfully to treat various antibiotics, pesticides and toxic metals in aqueous solutions, such as tetracycline [1], sulfonamide [5], phenylurea herbicides [72], Cd(II), Cu(II), Ni(II) [69,70], due to their large surface area, unique magnetic force and rapid phase separation by external magnetic field [31,73,74]. Due to their magnetic properties, they are useful in many fields such as information storage, magnetic resonance imaging, electronic devices, chemical sensors, drug delivery and catalysis [75]. However, the unmodified magnetic nanoparticles are generally unstable in strong acidic solutions, shorter lifetime after undergoing leaching and low surface energy, which limit the large-scale application of magnetic nanoparticles [27,75].

Thus, a good deal of functionalized magnetic nanoparticles (MNPs) with new structures and surface properties has been produced in many researches to overcome the shortcomings of magnetic nanoparticles, provide more active sites, improve aqueous stability and meet a higher demand for effective elimination treatments of agricultural pollutants [27,76–78]. Lately, many types of studies have been dedicated to the manufacture of MNPs which can eliminate agricultural pollutants. Herein, MNPs were prepared using a variety of methods including reduction reactions [79], coprecipitation method [76,80], a modified polyol method [81], and MNPs were synthesized by one-step solvothermal method [79], hydrothermal method [75,82], the Stöber method [76,83], a modified Stöber method [84], the thermal decomposition method [85], hydrothermal method [86–89], one-pot polyol method [90], a typical sol-gel method [81], salinization reaction [91], a solvothermal method [92–96], a momentary gelation method [97], silanization and alkylation method [98], magnetization and modification [99], a modification of Hummers's method [100,101] and thermal-initiated polymerization [81]. These MNPs showed important developments in pore volume, pore diameter distribution, specific surface area, high stability, processability, magnetic separation, surface active sites as well as catalytic degradation capacity that affect the pollutants elimination. Although MNPs as an efficient adsorbent for separation and enrichment of pollutants in water, involving pesticides, antibiotics and toxic metals, has been investigated broadly. Few published papers have reviewed and discussed the sorption of agricultural wastewater by using MNPs.

Herein, the critical purposes of this research were to implement a synthetic review of peer-reviewed articles involving the adsorption of agricultural wastewater contaminated with antibiotics, pesticides and toxic metals by MNPs, and to definite the prospective research necessities and challenges. According to different components in agricultural wastewater, the potential mechanisms for the elimination of pollutants as well as influence factors of adsorption are summarized and discussed.

2. Overview of functionalized MNPs based adsorption researches

Most of the MNPs studies have concentrated on three different fields: (i) the synthesis and functionalization of magnetic nanoparticles for diversified applications (e.g. medicine, biology, biomedicine, drug delivery and environment) (ii) the sorption of inorganic and organic contaminants on MNPs for environmental applications and consequences, as well as (iii) the environmental behavior of MNPs. In these applications, this review only concentrate on sorption of antibiotics, pesticides and toxic metals by MNPs, and it has been quickly growing in

the last few years (Tables S1, S2 and S3). It is extraordinary necessary to analyse the mechanisms of pesticides, antibiotics and toxic metals sorption by MNPs, respectively. Simultaneously, analyzing the primary elements affecting adsorption is also important. To precisely evaluate the utilization of MNPs for those pollutants elimination, comprehending the sorption of MNPs on pesticides, antibiotics and toxic metals is indispensable.

The literature redacted in Tables S1, S2 and S3 involves the sorption of pesticides, antibiotics and toxic metals for various types functional materials modified MNPs, containing abundant functional groups (e.g. amino group (-NH₂), hydroxyl (-OH), sulfonic acid group (-SO₃H), carboxyl (-COOH), phenyl (-C₆H₅), cysteine) [7,76,78,87,102,103], functional particles (e.g. SiO₂, MnO, CoO, Pb(II)) [103–106], various clay (e.g. bentonite, zeolite, montmorillonite, clinoptilolite) [107–109], carbon materials (e.g. carbon, grapheme, C₁₈, graphene oxide, carbon nanofibers, MWCNTs graphitic carbon sand composite) [5,7,79,90,104,107,110–113], and other functional nano-materials (e.g. nitrilotriacetic acid, ethylenediamine, cyclodextrin, polyethyleneimine, benzenesulfonic acid, cellulose, chitosan, EDTA, humic acid, ICPTES, piperazine) [1,2,78,79,87,90,102,111,114–120]. Specifically, more than 9 antibiotics (e.g. tetracycline, sulfonamide, oxytetracycline, ampicillin, ciprofloxacin, chloramphenicol, thiamphenicol, florphenicol, sulfamethoxazole), 10 pesticides (e.g. polar acidic herbicides, organophosphorus pesticides, pyrethroid, glyphosate, benzimidazole fungicides, phosalone, diazinon, chlorpyrifos, sulfonyleurea herbicides, pentachlorophenol) and 13 toxic metals (e.g. Hg(II), Pb(II), Cd(II), Ni(II), Cu(II), Zn(II), Co(II), Cr(III), Fe(III), Mn, As(III), U(VI), Cr(VI)) were adsorbed by MNPs. A meteor rain chart was structured to deeply understand the most universal trends for agricultural water pollutants adsorption by MNPs in Fig. 1. It is clear that research on antibiotics and pesticides is less than research on toxic metals until now.

3. Adsorption of agricultural contaminants by functionalized magnetic nanoparticles

To assess the elimination efficiency of MNPs to agricultural contaminants, the potential mechanism of the adsorption process must be clearly illustrated. MNPs have diverse adsorption behaviors for various agricultural pollutants, involving antibiotics, pesticides and toxic metals, which are tightly interrelated with the nature of agricultural pollutants. Furthermore, its natures involving nano-materials, mineral components, specific surface area, as well as surface functional groups could influence the adsorption mechanism. Numerous mechanisms could be contained in the sorption processes, involving electrostatic attraction, electron- π donor-acceptor interactions, hydrogen bonding, surface complexation, chelation, amidation reaction, ion exchange, as well as π - π and cation- π interactions. In recent years, numerous investigators have issued a good deal of researches on the removal of various agricultural pollutants by MNPs (Tables S1, S2 and S3). To eliminate antibiotics, pesticides and toxic metals by using MNPs, countless labors have already been implemented in their abundant works.

3.1. Adsorption of antibiotics

The removal of antibiotics by MNPs in agricultural wastewater remediation is the main investigative interests. Table S1 summarizes the adsorption characters of MNPs for diverse antibiotics and those MNPs were modified by various functional materials such as carbon materials, functional groups, clay, complexant, functional particles. Studies on the adsorption of antibiotics on MNPs have been published not less than once involving tetracycline [1,104,111], sulfonamide [5], oxytetracycline [107], ampicillin [107], ciprofloxacin [114], chloramphenicol, thiamphenicol, florfenicol [121], sulfamethoxazole [110], fluoroquinolones [115], doxycycline [111]. And, the most normally

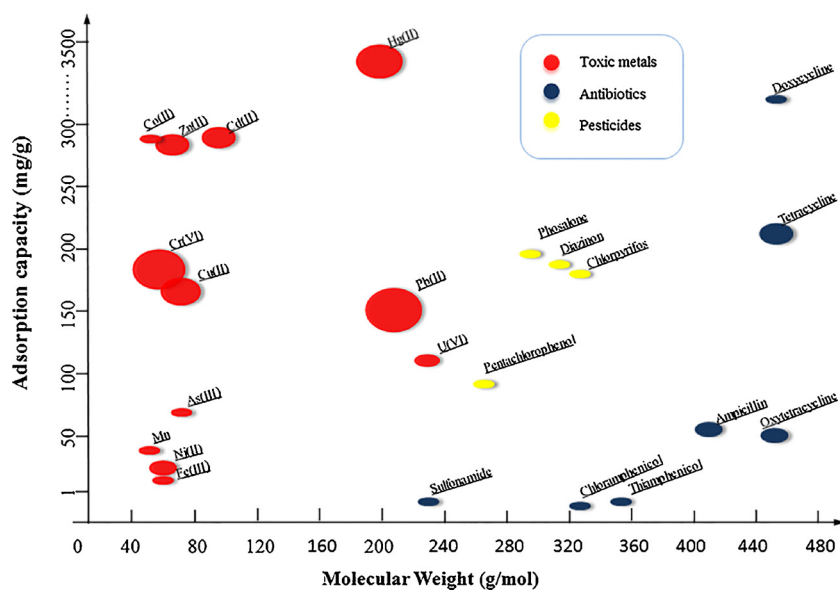


Fig. 1. Meteor rain chart of the literature review detailing the adsorption data of antibiotics, pesticides and toxic metals by functionalized MNPs.

researched antibiotic is tetracycline. The adsorption ability of different MNPs to tetracycline ranged from 39.1 to 666.7 mg g⁻¹ (Table S1), and β -cyclodextrin functionalized magnetic graphene oxide nanoparticles presented the highest sorption capacity [111].

To investigate the adsorption of MNPs on pollutants, some simulating adsorption kinetic models have been used, the most widely and popularly being the pseudo-second-order. Correspondingly, the equilibrium of antibiotics adsorption as well as experimental data onto MNPs has been explained and analyzed by employing some isotherm models: Dual-mode (D-M), Langmuir-Hinshelwood (L-H), and Langmuir-Freundlich (L-F). The summarized data (Table S1) demonstrated that Langmuir, Freundlich as well as Langmuir-Freundlich are frequently employed. The production methods, the target antibiotic as well as properties of MNPs broadly influence the consequences of kinetic and isotherm studies. What's more, numerous mechanisms affect the elimination of antibiotics by different MNPs.

The multi-mechanisms could govern the sorption of antibiotics on the MNPs (Fig. 2). The increase of surface area and surface functional groups of MNPs is two main contributors in the process of antibiotics elimination. As for those different materials modified MNPs, the interactions between antibiotics and MNPs have some mechanisms in the adsorption processes, involving π - π interaction, hydrogen bonding, cation- π interaction, electron- π donor-acceptor interaction, electrostatic attraction as well as amidation reaction. In comparison to magnetic nanoparticles, the modified materials possess large surface area, high electron mobility [107,122,123], and functional groups (e.g. amide group, carboxyl groups, carboxylic groups, formyl groups and hydroxyl groups) [1,5]. Those hydrophilic groups might supply more available active sites to improve the adsorption capability. And the interactions between MNPs and antibiotics were straight facilitated by these functional groups via shaping π - π interactions [1,104,110,111,114], cation- π interaction [1,111], and hydrogen bonding [1,114], which tremendously accelerate the pollutants adsorption. Such as, Li et al. proved that the NDMGO shows greater adsorption capability for TC in water solution than unmodified MNPs owing to abundant amino and oxygen-containing groups and it may play an indispensable part in the TC elimination [1]. In their adsorption experiments, the effects of initial solution pH were conducted at different pH with two different concentrations respectively [1]. Kinetic experiments were performed by increasing the shaking time, combined with adsorption thermodynamic studies were carried out in different concentrations of TC with different temperatures respectively [1]. In

the last step, the effects of ionic strength were adjusted by dissolving different amount of NaCl and four foreign ions were added to TC solutions to assess the influences of background electrolytes on TC adsorption [1]. And their results presented that the absorption of TC by NDMGO is mainly π - π interaction, cation- π bonding, hydrogen bonds and amidation reaction. Additionally, the nitrogen-containing functional groups have a comparatively high reactivity as well as are effortlessly reacted with various chemicals, which might help to enhance adsorption capability [1]. Lan et al. discovered that Ni@CNFs have an outstanding magnetic response and a number of hydrophilic carboxylic groups with a negative charge (RCOO⁻) on the carbon surface, which dominate the adsorption of the sulfamethoxazole antibiotic [110]. Generally, both the nanoparticles and the functional groups could offer the chief reactive sites for antibiotics in water solutions.

3.2. Adsorption of pesticides

Except for antibiotics, the capability of MNPs to eliminate other agricultural pollutants such as polar acidic herbicides [2], organophosphorus pesticides [22], pyrethroid [112], glyphosate [124], benzimidazole fungicides [116], phosalone, diazinon, chlorpyrifos [125], sulfonyleurea herbicides [126] and pentachlorophenol [113] have also been investigated. In which, herbicides are the most commonly studied pesticides (Table S2). Based on a self-assemble way, Fe₃O₄@PEI-RGO can be synthesized through electrostatic interaction between positive charged magnetic polyethyleneimine (Fe₃O₄@PEI) and negative charged GO sheets. As presented in Table S2, pseudo-first-order and pseudo-second-order commendably described the elimination processes of pesticides in most instances. Furthermore, compared with other isotherm models, Freundlich and Langmuir better suited the data and Freundlich equation described the behavior of pentachlorophenol adsorption onto the Fe₃O₄@SiO₂-MWCNTs. During the adsorption process, PCP was adsorbed quickly due to the surface of Fe₃O₄@SiO₂-MWCNTs has a great deal of vacant surface sites and a high affinity of the interacting groups at the initial stage. After a period of time, repulsive forces between the solute molecules on the solid phase and in the bulk liquid phases block the acquisition of the remaining vacant surface sites. The outer surface of the adsorbent was saturated, and the adsorption was reached equilibrium [113].

The mechanisms which MNPs adsorb pesticides were also associated with diverse types of interactions. Generally, electrostatic interaction and π - π interaction, π -stacking interaction, π - π

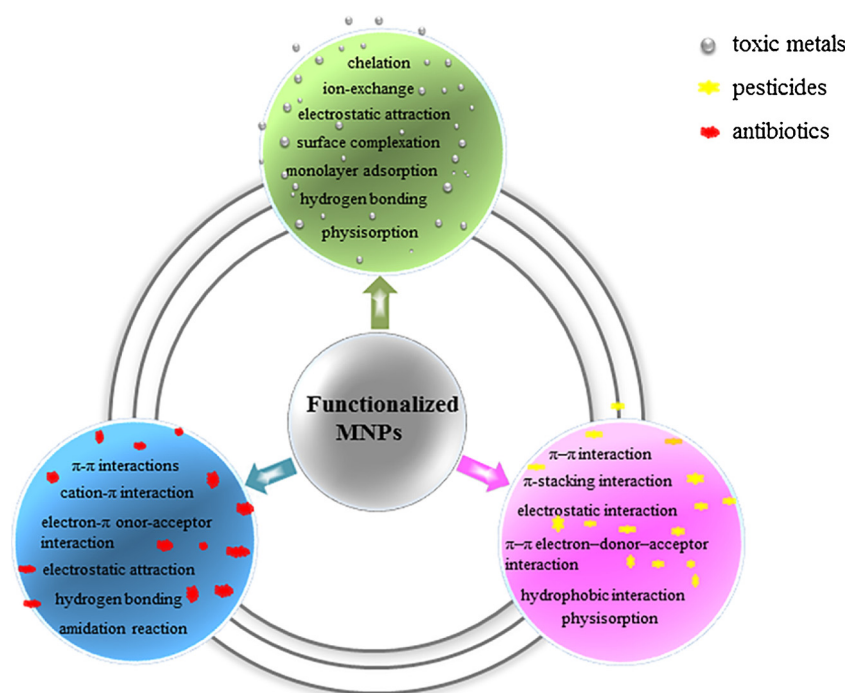


Fig. 2. The mechanisms of functionalized MNPs on the removal of various agricultural contaminants, including antibiotics, pesticides, and toxic metals.

electron-donor-acceptor interaction, hydrophobic interaction, and physisorption might be the primary mechanisms. The different mechanisms explained the interaction between MNPs and pesticides described in Fig. 2. The properties of MNPs contribute to various particular mechanisms of reaction with different pesticides. The surface area of MNPs is enhanced by using impregnated functional materials, which could notably enlarge the adsorption of pesticides. For example, the as-prepared $\text{Fe}_3\text{O}_4\text{-@-PEI-RGO}$ demonstrated greater sorption performance for polar acidic herbicides than $\text{Fe}_3\text{O}_4\text{-@-PEI}$, $\text{Fe}_3\text{O}_4\text{-@-RGO}$ as well as $\text{Fe}_3\text{O}_4\text{-@-PEI-GO}$, owing to the presence of many amino groups and C=C double bonds or benzene rings adsorbed on the surface of RGO, which increases the surface area and adsorption sites [2]. Shokouh et al. were successfully synthesized $\text{Fe}_3\text{O}_4\text{-@-SiO}_2\text{-@-GO-PEA}$ nanostructure which possesses a large delocalized π -electron system on the surfaces of GO, and the multi-layers of GO around the microspheres supply abundant sites for adsorption of organophosphorus pesticides [22]. Wang et al. were also issued this mechanism. The improved physico-chemical characteristics of MG-MS-Ph like large specific surface area, adsorption sites, high pore volume as well as hierarchical “bridge-pore” structure contribute to adsorbing capacity toward eight pesticides. It shows that MG-MS-Ph composites are an inexpensive and effective adsorbent for the elimination of toxic pesticides from complex wastewater [7].

3.3. Adsorption of toxic metals

Ecological systems and human health are faced with a serious danger due to the pollution of toxic metal in agricultural wastewater [119,127]. Therefore, the elimination of toxic metals has caused great concern in the research of wastewater treatment using MNPs. The Table S3 showed special adsorption characteristics of MNPs contacting numerous toxic metals. The concerned toxic metals include Cr(III, VI) [77,79,102,128–131], Hg(II) [117,120,129,132], Pb(II) [90,108,117,123,129,133–136], Cd(II) [129,130,134], Ni(II) [129,134], Cu(II) [87,117,134,136,137], Mn(0) [109], Zn(II) [119,134,136], Ni(II) [134], U (0, VI) [118], Co(II) [130]. Among them, Pb(II) and Cr(VI) are two most frequently researched metal pollutants (Table S3). The adsorption capability of diverse biochar-based functional materials to Pb(II) ranged from 27.95 to 508.4 mg g^{-1} ,

as well as the MNPs synthesized by modified mGO and EDTA, demonstrating the maximum adsorption capability [117]. The adsorption capability of various MNPs to Cr(VI) ranged from 17.09 to 284.1 mg g^{-1} . The MNPs have the best performance, obtained by the silica/CTAB composites and amine groups coated on the surface of the magnetite nanoparticles [77].

As presented in Table S3, Freundlich and Langmuir model can better describe the data, representing the equilibrium adsorption of MNPs to toxic metals, and indicating that the natures of toxic metals and MNPs can broadly change the consequences. The Langmuir isotherm indicates that the adsorption process of adsorbent to target analytes may be monolayer adsorption [85]. The information relating the heterogeneous adsorption was disclosed by the Freundlich isotherm and was assumed to be owing to the variety of adsorption sites [129]. In the study of removing Cd(II) and Pb(II) metal ions by $\text{Fe}_3\text{O}_4\text{-@-TAS}$, Langmuir and Freundlich isotherm models were tried to explain the adsorption isotherms. The consequences exhibited that Langmuir equations preferably fit the adsorption behavior of Cd(II) [130]. However, Pb(II) adsorption isotherm was discovered to preferably fit with Freundlich equations [129]. Besides, adsorption kinetics explained the adsorption mechanism by describing an important relationship of the chemical and physical peculiarities of MNPs and it may include chemical reaction as well as mass transport processes. The adsorption of toxic metals by MNPs was researched using the kinetic models of pseudo-second-order (Table S3). The pseudo-second-order kinetic model is according to the supposition that the rate-limiting procedure could be chemisorption involving valence forces via the sharing or exchange of electrons between adsorbent and adsorbate rather than the intraparticle diffusion [79]. The pseudo-second-order model better suits the adsorption kinetics of adsorption of Cr(VI) by diverse MNPs. [128].

And the possible adsorption mechanisms of toxic metals commonly include synthetical results of multiple interactions, involving electrostatic attraction, ion-exchange, chelation, physisorption, surface complexation, hydrogen bonding, monolayer adsorption. Fig. 2 summarized the multiple mechanisms referring to the interaction of MNPs with toxic metals. Generally, chelation, ion-exchange, electrostatic attraction, surface complexation, monolayer adsorption, hydrogen bonding and physisorption might be the primary mechanisms. Compared to

magnetic nanoparticles, the surface of modified magnetic nanoparticles has luxuriant functional groups (e.g. sulfonic acid group ($-\text{SO}_3\text{H}$), carboxyl ($-\text{COOH}$), amino group ($-\text{NH}_2$), hydroxyl ($-\text{OH}$), cysteine) [76,78,87,102,103], functional particles (e.g. SiO_2 , CoO , Pb(II)) [103,105,106] or other functional nano-materials (e.g. zeolite, chitosan, cellulose, CNTs, graphene, clinoptilolite, montmorillonite, humic acid, LDHs, EDTA) [90,102,108,109,118,129,132,138]. Herein, for other functional nano-materials, for example, chitosan has higher potentials of adsorbing toxic metals, primarily owing to the presence of hydroxyl and amine groups. Nevertheless, the hydrophilic property of chitosan is poor in practical application. Then carboxymethyl chitosan (CMC), a chemical modification of chitosan, was required, which contains hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$) and amine ($-\text{NH}_2$) groups in the molecule. These functional groups have better hydrophilic property of CMC and plenty adsorption sites, increasing the adsorption capacity of magnetic nanoparticles for toxic metals [123]. In addition, silica have high adsorption capacity, high binding strength with iron-oxide core, great resistance to organic solvents, ease of attachment, easy availability, ease of functionalization and rather economic cost. Silica coatings possess stability, inertness and accelerate the grafting of other ligands [76]. What's more, multiple functional materials synergistically influence the elimination of toxic metals by concurrently coating dissimilar functional particles onto single magnetic nanoparticles. $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -Amine were successfully prepared by immobilizing silica, metformin and amine, which displayed the highest elimination efficiency of Cu(II) (about 92%) because of high affinity in Cu(II) adsorption (Fig. 3). The increase of Cu(II) elimination in FeSi membranes compared to Fe series could attribute to the higher hydrophilicity of SiO_2 . And owing to the greater hydrophilicity of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles, a higher dispersion of nanoparticles results in an increase in the number of attainable adsorption sites on the membrane surface. What's more, the functional groups play an indispensable role in the enhancement of Cu^{2+} adsorption [139].

3.4. The effect of background solution properties

Background solution chemistry can impact the adsorption of MNPs on agricultural waste water pollutants, which has been showed in recent peer-reviewed publications. While the influences of pH, ionic strength as well as natural organic matter (NOM) were debated in this review.

3.4.1. The effect of pH

The pH of the background solution is one of the primary elements affecting the adsorption of MNPs on agricultural wastewater pollutants. pH plays a significant parameter for the adsorption of the analytes by influencing both the present systems of the goal compounds and the restraining species and density on the adsorbent external. Solution pH should be changed to confirm that the analyte is electrically neutral so as to it can be effectively adsorbed and the adsorption unaltered by controlling the surface of adsorbents [140]. The acidity of the water solution shows a thoughtful effect on the adsorption development, which can attribute to it disturb the solution chemistry of pollutants and the form of functional groups on the external of adsorbents [141].

3.4.1.1. The effect of pH on antibiotic sorption. Solution pH has significant effect to remove the target compounds by changing the speciation of adsorbate, the surface properties of the adsorbent as well as the degree of ionization [100,101,142,143]. For example, as the pH increased from 2.0 to 4.0, the adsorption ability of TC on NDMGO was improved. Nevertheless, the adsorption ability was weakened when the pH values exceeded 4.0. It can be inferred that pH obviously influenced the adsorption performance of TC by NDMGO. This may be attributed to all kinds of functional groups on the NDMGO surface and the molecular structural characteristics of TC [100]. Li et al. also investigated the effect of the solution pH values to sorption of CIP on NDMGO at pH 3.0–11.0. At $\text{pH} < 6.0$, CIP^+ is the primary species of CIP, and the electrostatic repulsion that exists between CIP^+ and positively charged material surface prevented further sorption. As the pH was increased from 6.0 to 9.0, CIP elimination efficiency improved and the highest removal efficiency of CIP was happened at pH about 9.0. CIP^\pm is the dominating species, and it can be more effortlessly adsorbed on the negatively charged NDMGO surfaces in this pH range. CIP started to form at $\text{pH} > 9.0$, but it is difficultly to be adsorbed, leading to a decrease in the amount of adsorption [101]. For the magnetic porous adsorbent prepared in Lu's group, the number of the primary adsorption groups $-\text{SO}_3\text{H}$ and $-\text{SO}_3^-$ as a function of pH in the adsorbent is an essential factor in regulating the characteristic of the adsorbent. When the solution pH values increased, the $-\text{SO}_3\text{H}$ were transformed as $-\text{SO}_3^-$ groups and the prime varieties of existing TC and CTC were all changed. And, it showed that the electrostatic attraction of between SO_3^- and CTC as well as the change of amount of Fe_3O_4 -MNPs-M can adjust the porous structure of the adsorbent, and TC was the primary adsorption driving force [143]. Similar trend was

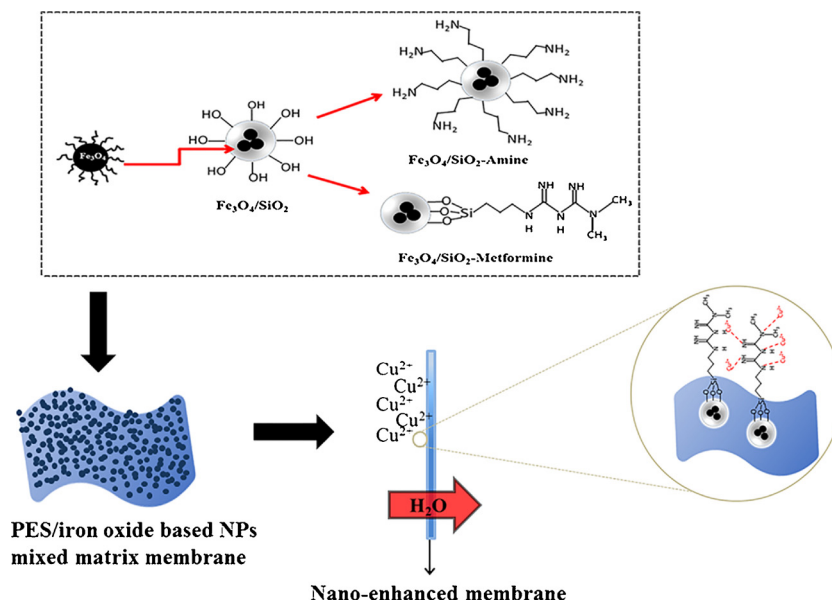


Fig. 3. Polyethersulfone (PES) membranes were enhanced by embedding modified Fe_3O_4 based nanoparticles (NPs) for copper removal from water [139].

reflected in Okoli's experiments, the molecular structure of TC contains three ionizable functional groups that ionize differently to form cations, zwitterions and anions in aqueous solution depending on solution pH [144]. As the pH increases, the monodispersed starch-stabilized magnetite nanocomposite (MSM) surface changes from positively charged to negatively charged [144]. The adsorption interaction deteriorates owing to repulsive forces of surface negative charge of MSM and TC anions, confirmed that π -cation interaction is the leading adsorption interaction [144]. Bao et al. also found that the solution pH could affect the adsorption ability of carbon-coated magnetic nanocomposite ($\text{Fe}_3\text{O}_4@\text{C}$) by influencing the speciation of sulfonamides (SAs) and the surface charge of $\text{Fe}_3\text{O}_4@\text{C}$ [89]. However, the results of Lin et al. study demonstrated that the solution pH had little effect on the interaction between TC and graphene oxide functionalized magnetic particles (GO-MPs) [145]. Consequently, it is very necessary to study the effect of the solution pH, which is helpful to deeply understand the MNPs sorption of antibiotics and obtain greater adsorption efficiency.

3.4.1.2. The effect of pH on pesticide sorption. The value of pH is an essential element influencing the properties of pesticide and adsorbent in the adsorption process. For example, the adsorption amount of 2,4-dichlorophenoxyacetic acid (2,4-D) was reduced when pH was increased from 3.0 to 11.0, and the maximum adsorption was acquired at pH 3.0. In acid solution, the solubility of 2,4-D is even worse, which may result in high removal efficiency of 2,4-D. Meanwhile, the Fe/OMC surface is positively charged when pH lower than 5.3. Therefore, the adsorbing capability to 2,4-D is more higher in acid condition on account of the electrostatic attraction [146]. Deng et al. found the similar phenomenon that the pH values alter the charge properties of adsorbate and the functional groups on the adsorbent [92]. Their study distinctly demonstrated that the recoveries decreased quickly with a pH above 3 due to the diverse ionization degrees related to their acidic dissociation constants. Under lower pH conditions, the benzimidazole fungicides were merely positively charged. And, the benzenesulfonic acid groups on the adsorbents were completely ionized and negatively charged in the pH range researched. The deprotonation of amino groups decreased the electrostatic attraction between adsorbates and adsorbents at $\text{pH} > 7.0$, leading to reduced recoveries [116]. At the same time, Zhou et al. also found a similar conclusion. The degree of deprotonation of PCP increasingly enhances with increasing pH, and the PCP^- is the main species of PCP at $\text{pH} > 6.0$. Electrostatic repulsion force existing between the PCP^- and the adsorbent surface reduces absorption capability. As the pH increases, $-\text{NH}_2$ is the primary form of amine groups and it facilitates the formation of hydrogen bond between adsorbent and PCP instead of PCP^- , reducing absorption ability [147]. Nevertheless, Wanjeri et al. have found that the pH adjustment was not affected the interaction of organophosphorus pesticides (OPPs) on the adsorbent via hydrogen bonding and π - π interaction [148]. This is because the modification of graphene oxide with 2-phenylethyl amine (PEA) that the isoelectric point for $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO-PEA}$ nanocomposites were 6.6 [148]. Mahpishanian et al. also found the same conclusion that the charge of adsorbent is not obviously affected by altering the pH value due to the modification of GO surfaces with PEA groups [149]. This may demonstrate that various surface groups may be affected differently at different pH values.

3.4.1.3. The effect of pH on toxic metal sorption. In the adsorption process, the pH is a significant running parameter affecting the surface charge of the adsorbents and the degree of ionization and speciation of the toxic metals. For example, Alqadami et al. found that the solution pH has strongly affected the adsorption of heavy metals onto magnetic nanocomposite (MBBC) due to it influences the MBBC surface charge and the degree of ionization and speciation of the heavy metals in aqueous medium [26]. The excessive protonation passivate

the MBBC adsorption sites, hindering metal cations binding under strong acidic conditions. Besides, the hydrolysis of metal ions was restrained at relative low pH, which decreases the possibility of metal ions complex formation with the MBBC [26]. As the pH increases, deprotonation of the MBBC adsorption sites with an improved hydrolysis of metals in the aqueous solution contributed to larger adsorption [26]. Badruddoza et al. found that the negatively charged carboxylate ions (COO^-) have powerful coordinative affinity towards positively charged metal ions at pH above the ZPC. Through surface complexation, the electrostatic forces of attraction permit the carboxylate ions to arrest the M^{2+} to form chelate complexes, which improves with increasing pH [150]. Ge et al. also found that the carboxyls were changed into carboxylate anions as well as the adsorption was enhanced with increasing the pH until $\text{pH} > \text{pHpzc}$ [151]. Simultaneously, Zhang et al. found that the chitosan coating was more appealing to long carbon-chain PFCs owing to their lower pK_a . Besides, since the chitosan coating was positively charged at $\text{pH} < 6.0$, better abstraction efficiency was attained. However, at pH 9.0, the low retrievals of all analytes were caused by the electrostatic repulsion among the adsorbent with the target molecules [152].

3.4.2. The effect of ionic strength of pesticides, antibiotic and heavy metals

Owing to their high surface area, independence from ionic strength, thermal stability, quick kinetics, immovability in different pH values and possessing diverse functional group, magnetic solid-phase extraction (MSPE) adsorbents have a robust sorption attraction for the strength of modified magnetic nanoparticles and are suitable for various analytes [153]. With enhancing the addition of salt, the ionic strength increases and the solubility of analytes decreases in the aqueous solution owing to the salting-out influence. Further, the viscosity of the solution would be improved due to the gradual addition of salt. Since the diminution of diffusion factor, it has adverse influences on the extraction efficiency. The influence of ionic strength on the extraction efficiency was researched by altering the sodium chloride (NaCl) concentration from 0 to 30% (w/v) [154].

To see the consequence of contact time on the abstraction efficiency, it was altered from 5 to 240 min. The consequences showed that abstraction of all studied organochlorine pesticides (OCPs) improved with contact time and touched equilibrium at the end of 60 min, at which time retrievals of OCPs ranged from 46 to 100%. Furthermore, the abstraction of OCPs was researched in diverse ionic strengths: no salt addition and 0.1, 0.5, and 1.0 M supported with NaCl. But, further increasing the ionic strength of the example had an undesirable influence on the abstraction of all OCPs. Depending on the target analytes, former research showed that growth in the ionic strength of the water solution may have unlike effect on the abstraction: it may increase, not be an effect, or even be decreased. Consequently, the ionic strength of the sample was selected as 0.1 M NaCl [155]. The adding of salt can reduce the solubility of the aim analytes in solution, facilitating the adsorption of analytes onto the polypyrrole nanowires. For the rest pesticides, the abstraction efficiencies were slightly declined after adding the salt [156]. The sorption of heavy metals on Hydrous ferric oxide (HFO) looks poorly susceptible to the change of ionic strength. For example, Swallow et al. described that diverse ionic strength between 0.005 and 0.5 M NaClO_4 , or altering the properties of the backdrop electrolyte from NaClO_4 to a complicated reproduction seawater mixture can not affect the sorption Cu^{2+} and Pb^{2+} on HFO [157]. The ionic strength influences the binding affinity to the adsorbed species, because it can affect the thickness and interface potential of the electrical double layer. For the moment, the outer layer complexes are more susceptible to the ionic strength changes than internal layer complexes, in that the background electrolyte ions are located in the similar plane for internal layer surface complexes [158].

3.4.3. The effect of natural organic matter (NOM)

From a large number of phenomena, the existence of NOM in the

water could be considered as the formation of odor, taste, and poor color. Besides, NOM increases the solubility of these metals in the water by making complexes with heavy metals; moreover, it promotes procreation of bacteria, which could threaten the health of people. Additionally, NOM stabilizes the dispersion of some possibly dangerous nanoparticles in solutions which could possess a latent danger to human health being and ecosystem [159].

It is universally acknowledged that NOM plays a significant character in the adsorption of heavy metals and other toxic contaminants [160]. The benefits of dissolved organic matter (DOM) exceed traditional surface modifiers. DOM is unaffectedly plentiful in the environment, cheap, non-toxic and easily adsorbed onto the surface of metal oxide nanoparticles. In Chekli et al. research, humic acid (HA) as well as Suwannee River natural organic matter (SRNOM) were examined and used as surface changers for Fe₂O₃ nanoparticles (NPs). Then, the DOM-coated Fe₂O₃ NPs were analyzed by different analytical ways containing: high-performance size exclusion chromatography (HPSEC), flow field-flow fractionation (FIFFF) and Fourier transform infrared spectroscopy (FTIR). The steadiness of the coated NPs was then estimated by evaluating their aggregation and disaggregation performance over time [161]. Therefore, the improved stabilization of the coated maghemite NPs may accelerate their transport in the groundwater, effectively removing pollutants [162]. Many studies have shown that NOM can change magnetic nanoparticles toxicity by altering the bioavailability of metal ions dissolved from magnetic nanoparticles, suspension stabilization of magnetic nanoparticles, steric repulsion and electrostatic interactions between magnetic nanoparticles and organisms, and magnetic nanoparticles stimulated reactive oxygen species generation [163]. And, some research have evaluated the effect of NOM on the bioavailability and following ecological risk for CeO₂ MNPs. These discoveries contain an abridged aggregation of CeO₂ MNPs (resulting from a diesel fuel catalyst) in the occurrence of HA, a steadied hydroponic exposure of CeO₂ MNPs to sets in the occurrence of two kinds of NOM (with no toxic response discovered), and a better level of bioaccumulation of CeO₂ MNPs in the occurrence of NOM in *Caenorhabditis elegans* [164].

The interactions of NOM with NPs can affect particle dispersion changing fate, transport, bioavailability and toxicity. By adsorbing onto the surface and forming of surface coating, NOM will modify nanoparticle properties. It has found that such a surface coating improve the nanoparticle stability in the diffusion of water and reduce the aggregation rate [165]. HA is the chief component of NOM containing hydrophilic groups, which has extraordinary capabilities to adjust environmental behaviors and toxicity of nanomaterials [166]. HA interact with silver nanoparticles (AgNPs), increasing colloidal stability and affecting toxicity by toxic chelating ions freed from nanoparticles [167]. Beyond the scope of the DLVO theory, NOM can increase a level of complexity that can counteract the tendency of engineered nanoparticles to shape larger aggregates in aquatic environments. By coating and steric repulsion, NOM can improve engineered nanoparticles stability or reduce stability by multitudinous mechanisms, involving bridging and pearls-on-a-string formation [168].

The influences of NOM on nanomaterial toxicity are complicated. NOM can coordinate metals, change their adsorption behavior, and transfer negative surface charges to NPs. Furthermore, NOM can affect nanotoxicity via altering the aggregation/deposition, surface characteristics of nanoparticles and toxic chelating ions freed from nanoparticles [160,167,169]. In a word, it is very indispensable to research the particular effects of NOM on particular MNPs.

4. Future research needs and conclusions

Agricultural water pollution by inorganic and organic compounds for instance pesticides, antibiotic and toxic metals have become a troublesome problem owing to their awfully dangerous influences on humans and the ecological environment. Because of MNPs superior

physicochemical properties in comparison to traditional materials, their use as adsorbent materials for environmental remediation has an enormous prospect. Magnetic nanoparticles allow various specific functional groups anchor their surface to complete the selective removal of various pollutants. The physicochemical characteristics of MNPs (e.g. specific surface area, pore volume as well as functional groups), the components of agricultural wastewater (e.g. pesticides, antibiotic and toxic metals), and the background water natures (e.g. pH, ionic strength and NOM) can affect highly elimination capacity of MNPs in water.

MNPs have numerous advantages containing greater adsorption capabilities and quicker removal rates in comparison to conventional sorbent materials for pesticides, antibiotic and toxic metals removal. Additionally, the magnetic separation alternatives show the benefits and restrictions of traditional separators. Moreover, the adsorption capacity of MNPs for further reuse can be successfully achieved by repeated adsorption-desorption cycles of regeneration. The effect and character of individual mechanisms containing electrostatic interaction, π - π interaction, hydrogen bonds, chelation and ion exchange, which requires further research. The molecular configuration involving pore volume, specific surface area and various functional groups of MNPs is all likely contributors to adsorption.

It is vital problems that the toxicity and environmental fate of materials about select for water purification. In water treatment, nanotechnology is visibly better than other techniques. However the knowledge about the environmental fate, transport, bioavailability as well as toxicity of nanomaterials is still immature today.

To acquire MNPs, the classical means based on physical and chemical techniques are dangerous and high-priced chemicals with high energy input and damaging influences on the environment. Besides, the existence of NOM can increase nanotoxicity of NPs and limit their adsorption.

The main challenges about green procedure to be conquered are restrictions related to optimizing the syntheses processes. The mechanisms of nanoparticle formation need to be entirely explicated, the running of nanoparticle size and allocation needs to be improved, and the reproducibility of biogenic procedures is not whole perfectly upgraded. Moreover, the latent toxicities of these nanomaterials are not completely addressed. Lastly, the toxicity of NPs will change lie with the experimental way of use. It is necessary to consider the influence of pH, ionic strength and NOM for further studies. It is often essential to adjust the draft to attain trustworthy consequence to meet the requirements of research owing to nanoparticles themselves affecting many experiments, a long-range study of nanoparticle toxicity, regularization of toxicity drafts, and the fate of these nanomaterials in the human matter and in the environment.

Concluding, there is an increasing attraction in the use of MNPs for treating wastewater. Although such abundant works, the usage of MNPs in the early stage is still restricted to clean water and still desires plenty of work to establish nanotechnologies which is suitable for use in the area of agricultural wastewater treatment. Meanwhile, the health influences and environmental fate of these MNPs, indetermination, must not be evaded before their extensive use. Subsequently, research about MNPs impacts and fate in the environment is a key challenge for researchers. To make feasibility of MNPs at large scale application, abundant research needs to be accomplished in this field.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jece.2018.10.014>.

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