Indonesian Physical Review
Volume 6 Issue 2, May 2023
P-ISSN: 2615-1278, E-ISSN: 2614-7904

Review on The Adsorption of Heavy Metals in Water by $MnFe_2O_4$ and Zeolite

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Article Info

Article info:
Received: 07-01-2023
Revised: 09-04-2023
Accepted: 02-05-2023

Keywords:
Heavy metal; MnFe2O4; Zeolite; Coprecipitation; and Characterization

How To Cite:
L. A. Melinia, M. Naibaho, E. Puspita, Ramlan, M. Ginting "Review on the adsorption of heavy metals in water by $MnFe_2O_4$ and Zeolite", Indonesian Physical Review, vol. 6, no. 2, p 196-219, 2023.

DOI:
https://doi.org/10.29303/ipr.v6i2.215.

Abstract

The existence of quality water on earth is essential for life and the consumption of existing living things. The problem of water pollution is a matter of great concern in world researchers' management of water resources. Heavy metals have a toxic effect on humans and the environment. This paper reviews the characteristics and methods of synthesis of $MnFe_2O_4$ and zeolite materials as adsorbents for removing heavy metal ions in water with critical properties such as surface area, magnetic properties, and adsorption capacity. We have collected data regarding the appropriate method for synthesizing $MnFe_2O_4$ and zeolite nano adsorbents. We have accumulated much data on the properties of $MnFe_2O_4$ and zeolite materials and the optimum adsorption capacity for heavy metal ions. Experimental factors such as pH, temperature, adsorption capacity, and ionic strength affecting metal ion removal have also been explored.

Introduction

Water is earth's most essential and indispensable life substance [1]. Water pollution and clean water supply have become significant problems worldwide [2]. Deteriorating water quality due to the expansion of civilization [1], population growth, agriculture, shipping, domestic waste, and industrial activities (such as metallurgy, chemistry, mining, batteries, nuclear energy, textile dyes, tanneries, etc.[3][4]), as well as other ecological and environmental phenomena [5]. Different pollutants are released into the wastewater, such as heavy metal ions, dyes, pesticides, herbicides, drugs, etc. [6]. The presence of heavy metals in water or wastewater can cause serious environmental problems, threatening the lives of all organisms [7] due to their non-biodegradability, bioaccumulation, and high toxicity [8].

Heavy metals are unique environmental elements because most are biogenic (small concentrations needed by nature and humans, respectively). Still, if most are in high concentrations, they can accumulate in humans and biological organisms [9]. The most common heavy metals in industrial waste are Cd, Pb, Ni, Cr, Cu, and Zn. Sources of heavy metal contaminants come from battery manufacturing manure, phosphate fertilizers, alloy manufacturing, textiles, wastewater irrigation, atmospheric sedimentation, solid waste disposal from mining, improper collection of solid waste, coatings, explosives production waste, leather tanneries, pesticides, printing dye waste, metal fabrication waste, steel production waste, and electroplating metal waste, photographic art waste, dye waste, and pickling waste [10]. In addition, excessive consumption of these pollutants in the long term, especially heavy metal ions such as Cr, Cu, Mn, Ni, Pb, and Cd, can damage the kidneys, cancer, liver, brain function, nervous system, or even death [11]. Can be seen in Table 1 presents summary data of common heavy metal ions, their sources, and the harmful effects of heavy metals.

Table 1. Some Heavy Metal Ions, Sources, and Adverse Effects

Heavy metal	source	Harmful effect	References
Cobalt	Mining, processing of cobalt-containing ores, fertilizers, industrial waste, and household waste	Vomiting, nausea, diarrhea, asthma, pneumonia, kidney congestion, skin degeneration, weight loss, cardiomyopathy, and harm to the heart muscle	[12][13][14]
Chromium	Dyeing, electroplating, paint production, leather tanning, steel industry, textiles.	Simple skin irritation and lung cancer	[12][13]
Copper	Copper polishing, mining, paint, plating, pesticides, printing operations, plating industry, steel, electrical cables, insecticides, alloys, and pipelines	Vomiting, diarrhea, stomach cramps, nausea, or even death.	[12][15][13]
Lead	Coal burning, electroplating, insecticides, herbicides, battery manufacturing, mining, paints, and pigments.	Diseases of the brain and nervous system	[12][16]
Manganese	Mining and mineral processing	Nervous system side effects, Dullness, Changes in behavior, Lethargy, and Weakness	[12][13]
Nickel	Car batteries, electroplating, surgical instruments, non-ferrous metals, paints, and porcelain enamel.	Allergic dermatitis and sensitization, lung, and kidney problems	[12][13]
Zinc	Brass manufacturing, mining, oil refineries, plumbing	Depression, lethargy, and neurological signs	[12] [10]
Cadmium	Electronic equipment, such as batteries	Kidney dysfunction, lung disease, tumors in the bones, hypertension, and the shape of the fetal bones have abnormalities	[17][13]

Judging from some of the negative impacts caused by heavy metal waste, it is imperative to carry out water purification to eliminate the pollution of heavy metal waste. Various conventional techniques can be used for wastewater purification, such as the reverse osmosis method [18], ion exchange method [19], chemical precipitation method [20], solvent extraction method [21], and so on. Some of the above methods have advantages and disadvantages, which are explained in Table 2. Some of the above methods are very efficient, and their disposal meets standards; most produce secondary waste [22]. A more effective and economical technology for heavy metal removal of wastewater is the adsorption method [23], which has the advantages of simple operation, low price, high efficiency, and environmental protection [24].

Table 2. Methods that can be used to remove heavy metal ions from water

Method	Advantages	Deficiency	Reference
Chemical precipitation	The simplicity of the process, low capital costs	Sludge contains metals, has high operational costs, and cannot filter out metals	[25]
Membrane filtration	Little solid waste, little use of chemicals, can be done in a small space	Uneconomical membrane fouling flow is limited	[26]
Ion exchange	Able to remove parts per billion (PPB) levels and effectively remove cations or anions while managing relatively large volumes	It is not efficient, and the exchange matrix is easily contaminated	[27]
Adsorption	Effective in terms of economy, high absorption, ease of operation, reusability, and technology using natural materials	Requires a large amount of adsorbent	[28] [29][30]
Reverse Osmosis	Low energy use, ease of scaling up, and ease of operation.	Limited scaling and fouling of the membrane, decreased water flux, and increased operating costs for repeated membrane cleaning.	[31]

From the explanation in Table 2, the application of sorbents is one of the best methods for removing various pollutants, including heavy metals, in water [32]. Some advantages of surface assimilation applications are high absorption, energy saving, and environmental friendliness [4]. The adsorption process occurs on the pore surface of the adsorbent material, and the metal (adsorbate) in the liquid undergoes a mass transfer process from the liquid to the adsorbent surface [33]. Several heavy metals in the environment have been successfully analyzed and removed using various materials such as chitosan-based hybrid adsorbents [34], chitosan-silica beads [35], coal fly ash [36][37], lignin-based magnetic [38], bentonite [39], Zeolite [40], manganese ferrite-biochar [41], activated carbon [42], and dextran-chitosan composite macromolecular resin [43]. Manganese ferrite adsorbents continue to grow year to be used to remove heavy metal waste[44]. The advantage of the $MnFe_2O_4$ adsorbent is its magnetic properties that facilitate separation from Solution and adsorption ability to remove heavy metal ion waste [45]. In addition, the $MnFe_2O_4$ adsorbent has a larger surface area, saturation magnetization, and high stability than other spinel ferrites, which are very suitable for adsorbent materials. Zeolite has a large surface area with more active sites and high porosity, which can increase adsorption efficiency. It has exchangeable cations, so Zeolite is a permanent material to become an adsorbent material because it has high efficiency and capacity to remove heavy metal ions [46]. Based on theory and in-depth literature review, we are interested in further discussing $MnFe_2O_4$ and zeolite materials.

Research development of manganese ferrite adsorbent ($MnFe_2O_4$)

Magnetic adsorbents are considered appropriate adsorbents for the removal of heavy metals and organic pollutants because they are easily separated from aqueous solutions using an external magnetic field, in addition to their advantages such as non-toxicity, small dispersion, resistance, and large surface area [47]. Combining the properties of magnetism and adsorption allows these adsorbents to have better effectiveness with magnetic separation. Efficient magnetic adsorption method and automatic separation [48]. In recent years there have been many studies on magnetic adsorbents to remove heavy metals in water, such as manganese ferrite ($MnFe_2O_4$) nanoparticles [49], magnetic Fe_3O_4-chitosan@bentonite [50], $\alpha -$ Fe_3O_4 nanoparticles [51], $MgFe_2O_4$ adsorbents [52], nanoparticles magnetic cobalt ferrite ($CoFe_2O_4$) [53], adsorbent $ZnFe_2O_4$ [54]. Recently, it has been fascinating to remove metals with various magnetic adsorbent ferrite particles [45].

Manganese ferrite ($MnFe_2O_4$) adsorbent is one of the advanced research materials that continues to develop in dealing with water pollution by heavy metals. In removing heavy metals, using $MnFe_2O_4$ adsorbents with the advantages of nanotechnology and magnetic separation is the right choice [44]. Manganese ferrite has a fairly good level of stability against the influence of external fields and temperatures. This causes manganese ferrite not to rust easily and has strong mechanical properties [55]. Among the magnetic oxides, spinel ferrite MFe_2O_4 (M = Mn, Co, Zn, Ni, Mg, etc.) known as spinel ferrite, has a cubic spinel material that has oxygen atoms located at each corner and center throughout the cubic faces (fcc) and M^{2+} and Fe^{3+} occupy tetrahedral or octahedral sites. $MnFe_2O_4$ adsorption capacity, biocompatibility, and high magnetic sensitivity compared to $NiFe_2O_4$, $CoFe_2O_4$, and $CuFe_2O_4$ nanoparticles [56].

The magnetization of $MnFe_2O_4$ is equal to 2, 3, 4, and 5 μB for M = Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}. Therefore, the magnetization of $MnFe_2O_4$ is greater than that of other ferrite magnets, which is 5 μB. Moreover, its surface area can be modified by divalent cation exchange, and $MnFe_2O_4$ is reported to have a larger surface area than other spinel ferrites. Therefore, because of the saturation magnetization, stability, and high surface area, $MnFe_2O_4$ is one of the most suitable spinel ferrites to adsorb metal ions [57]. Another advantage of manganese ferrite compared to cobalt and nickel ferrites is its higher magnetic susceptibility, low resistivity, and consistent magnetic moments with Neel's coupling scheme [58]. Several studies have developed the development of manganese ferrite ($MnFe_2O_4$) adsorbents for heavy metal removal (Table 3)

Table 3. Some of the adsorbents used to remove metal ions from water

Adsorbent	Method	Heavy Metal	Adsorption Capacity (mg/g)	pH	References
$MnFe_2O_4$-biochar	Adsorption	Thallium (Ti)	170,55	6	[59]
Biochar- $MnFe_2O_4$	Adsorption	Uranium (U)	27,61	4	[60]
$MnFe_2O_4$@C–NS	Adsorption	Mercury (Hg)	108.56	7	[61]
bentonite clay $MnFe_2O_4$	Adsorption	Cr(III) , Cr(VI)	175,4, 178,6	6 and 3	[62]

Although the $MnFe_2O_4$ sorbent has magnetic properties that can be used to remove heavy metal ions, however, $MnFe_2O_4$ tends to aggregate in the liquid phase, which can reduce its surface area so that the adsorption capacity is low, so modification of $MnFe_2O_4$ seems important. Modification of $MnFe_2O_4$ can be carried out with materials that have a large surface area and can adsorb heavy metal ions, as research conducted by M. Ghobadi et al. carried out the synthesis of $MnFe_2O_4$ adsorbents with the addition of graphene oxide (GO) [57].

Zeolite as Heavy Metal Adsorbent

Zeolite with a hollow structure can absorb many smaller molecules from the cavity or, according to the cavity [62]. The three-dimensional tetrahedral structure of the Zeolite. Zeolite with a hollow structure can absorb many smaller molecules from the cavity or, according to the cavity [63]. The three-dimensional tetrahedral structure of Zeolite has aluminosilicate crystals in which oxygen atoms bound the Si and Al components. The Al element in the zeolite framework produces a partial negative charge, so it has the potential to be used as a cation exchanger. Zeolite has a porous microstructure, high surface area, and relatively good adsorption and catalytic properties [64]. Because of its advantages, Zeolite can be used not only for adsorption but also for ion exchange and as a catalyst [65].

Furthermore, the crystal shape is very regular, with cavities connected in all directions, making the surface area of the Zeolite very large [66]. Based on research by Setiawan et al., the surface area of the Zeolite, the pore diameter of the Zeolite, and the pore volume of 100 mesh of Zeolite were 439,48 m^2/g, 94,11 nm, dan 9,01 cc/g, respectively. The surface area is affected by the particle/pore size, the shape of the pores, and how the pores are arranged within the particle [64].

Many studies have been carried out for heavy metal removal using zeolite adsorbents, such as Cu(II) heavy metal removal using zeolite adsorbents made from bagasse ash. The results showed that the best adsorbent for Cu(II) metal adsorption was Zeolite, with a reduced rate of 41,57% [64]. Then Zeolite adsorbents were used to absorb metal iron (Fe), and the optimum absorption percentage obtained was 47.6074% [63]. The removal of Pb metal using a zeolite adsorbent synthesized using the hydrothermal method was 70,194 % [67]. The percentage of reduction of heavy metal Fe (III) was 97,46 % [68]. The development of zeolite adsorbents has been widely carried out by combining adsorption and magnetic properties for heavy metal removal, such as research conducted by Yunita on zeolite-magnetite adsorbents for chloride ion removal [65].

Synthesis Method of $MnFe_2O_4$ and Zeolite

Various strategies have been developed for the synthesis of $MnFe_2O_4$ and zeolite adsorbents. These include vapor deposition synthesis, microemulsions, solvothermal conditions, and coprecipitation. In a study conducted by Mashadi et al., they synthesized $MnFe_2O_4$ using the solid-state method using a milling technique for 10 hours. It is known that the single-phase form of $MnFe_2O_4$ is formed at compositions x = 0 and 0.5. The results of the IR spectra showed that the two absorbances in the range of ~446 and ~557 cm^{-1} peaks were associated with the octahedral site and the tetrahedral site of $MnFe_2O_4$ [69]. In A. Almahri's research, $MnFe_2O_4$ was synthesized using the solid-state method. The results showed a uniform morphology of Mn having spherical particles with a diameter of 40 nm and a high porosity ratio. It can be seen that the total pore volume is about 2.48 x10-2 cm^3/g surface area is about 57.46 m^2/g [70]. Solvothermal methods generally synthesize metal elements, metal oxide materials, polymer composites, etc., in various forms, such as polycrystalline in nanopowder, including single crystals. Based on the research of H Qin et al., high pressure during the preparation of the solvothermal method in an autoclave produces nanoparticle-sized samples in the form of uniform balls with a diameter of 40 nm[61].

Just like $MnFe_2O_4$, Zeolite can be synthesized by various methods, such as the research conducted by R. Panek et al., who synthesized Zeolite Na from fly ash using the hydrothermal method with 3 M sodium hydroxide solution for 48 hours at 80°C. The results obtained by the zeolite adsorbent have a swollen surface, a much higher specific surface area (728 m^2/g), and a large microporous content in its structure (about 87%). The Na zeolite obtained can adsorb Zn^{2+} ions very quickly and efficiently, as evidenced by the achievement of equilibrium after 10 minutes due to the large specific surface area of Na-X [71]. In the study of M. Bayat et al., synthesizing clinoptilolite zeolite using the coprecipitation method showed results with many pores on the surface [72]. The coprecipitation method is also good for synthesizing $MnFe_2O_4$, as research has been done by M. Hassan et al., they obtained mn with a smooth surface with a particle size of 10 nm with a surface area of 145 m^2/g mn, high purity level, and for the ability to good adsorption for removing Pb ions with 100% efficiency with a capacity of 75.75 mg/g [45]. Therefore a further review was carried out on the coprecipitation method.

Coprecipitation Method

Based on the research development of manganese ferrite and Zeolite as heavy metal removal, good crystallinity and uniform structure of manganese ferrite and Zeolite were successfully synthesized by the coprecipitation method [45][73]. Coprecipitation is an effective and efficient method with the advantage of mixing the reagents at the molecular level, thereby having stoichiometric monitoring, high purity and homogeneity, and good morphology [74]. Not only that but because this method is a bottom-up synthesis method, the result is in the form of nanoscale particles[75]. While other methods, such as the sonochemical method, only provide nanoparticle morphology[76]. Not only coprecipitation and sonochemical methods can synthesize nano-sized particles. However, many other methods can synthesize nanoparticles with advantages and disadvantages, as seen in Table 4.

Table 4. The advantages and disadvantages of the nanoparticle synthesis method

Metode	Advantages	Deficiency	Reference
Hydrothermal	Adjustable Crystal growth is adjustable under high temperature and pressure conditions	processes difficult to control, limiting reliability and reproducibility	[77][78]
Sol-Gel	The low-cost operation, low temperature, controllable composition, and the resulting structure, easy to upgrade	Long-time and complex Toxic solvents limit large-scale production	[79]
solid state	A simple method for forming thin films	high operating costs, low material volume, and high throughput on an industrial scale	[78]

	at low cost are required for the successful implementation of this method

Of the many methods that can be used to synthesize adsorbent nanoparticles in Table 4, The coprecipitation method has the advantages of low temperature, small particles, high porosity, short processing time, high purity, strong purity chemical uniformity, good crystallinity, and simple process. It is a suitable method for synthesizing adsorbent nanoparticles[80]. In addition, this method is a method of deposition of fabrication techniques by chemical means which brings a solute down so that the desired precipitate forms [81][81]. This method uses a low reaction temperature (<100 °C) or room temperature and a short time, making it known as a simple method [82]. The coprecipitation method produces materials with good material properties and characteristics, high levels of purity, and nano-sized particles.

Characterization of $MnFe_2O_4$ and Zeolite

The advantages of the coprecipitation method, such as crystal structure and magnetic properties, can be optimized by controlling the experimental parameters: temperature, contact time, and pH [65]. Many studies have been carried out by synthesizing $MnFe_2O_4$ using the coprecipitation method. Based on the research of M. R. Hassan and M. I. Aly [52] the $MnFe_2O_4$ adsorbent has been successfully synthesized using the coprecipitation method, the absorption of the obtained lead ion is 88%, and the distributed ferrite particles have a uniform structure.

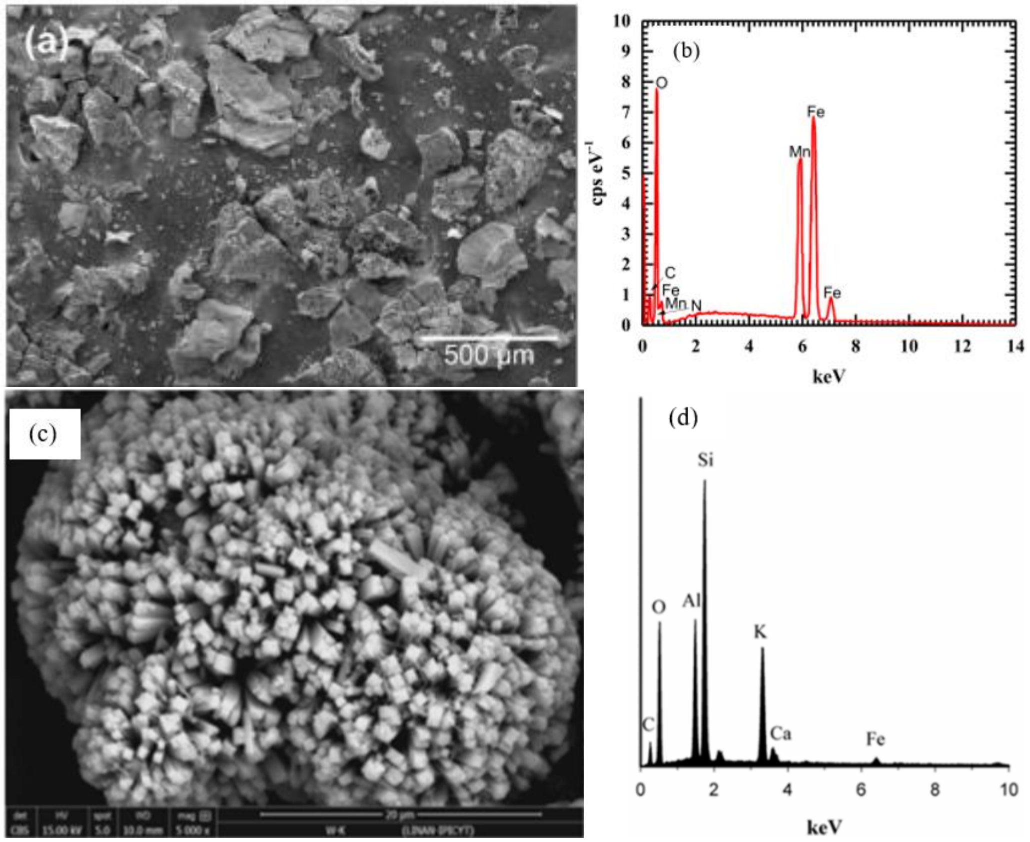


Figure 1. SEM and EDS characterization of (a-b) $MnFe_2O_4$ nanoparticles [83] (c-d) Zeolite W [84] reuse and clearance from MDPI.

The characteristics of a good adsorbent $MnFe_2O_4$ and Zeolite, can also be analyzed through the surface morphology and the content of any elements contained therein, as illustrated in Figure 1. Figure 1a shows the Scanning electron microscopy (SEM) results used to analyze the morphology of the synthesized $MnFe_2O_4$ adsorbent. Figure 1a, taken at 100x magnification, shows a rough surface with deep cracks. It can be seen from the morphology of the $MnFe_2O_4$ adsorbent that agglomeration occurs. The agglomerated morphology is mainly due to the magnetic characteristics of the sample [85]. The qualitative EDS spectra for $MnFe_2O_4$ (Fig. 1b) confirm the predominant presence of Fe, Mn, and O, indicating successful synthesis of the adsorbent $MnFe_2O_4$ [86]. $MnFe_2O_4$, synthesized using the combustion method at low temperatures, resulted in an average particle size of 172 nm [83]. Meanwhile, $MnFe_2O_4$, synthesized by the coprecipitation method, produced fine particles with a particle diameter of 10 nm [45]. According to Figure 1c, the W zeolite has a pseudo-spherical aggregate morphology of long needle-like and elongated crystals. In the results of the EDS spectrum (figure 1d) from zeolite W there are elements Al, Si, K, Ca, Ti, O, and Fe. In addition, the samples were analyzed by XRF where the chemical composition of the pure W zeolite was: SiO_2 (43.43%), Al_2O_3 (17.92%), K_2O (15.09%), Na_2O (0.20%); Fe_2O_3 (3.97%), CaO (2.61%), TiO_2 (0.72%), LOI (16.06%) [84].

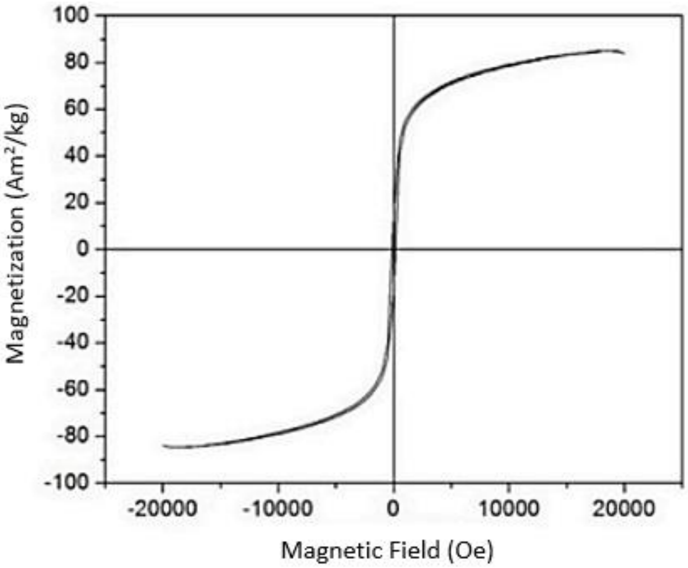


Figure 2. VSM characterization of the $MnFe_2O_4$ loop hysteresis curve [87] reuse and clearance of MDPI.

In addition, the magnetic properties of calcined $MnFe_2O_4$ synthesized by the sol-gel self-combustion method are illustrated in Figure 2. The hysteresis loop of the $MnFe_2O_4$ adsorbent shows that the material is ferromagnetic with a saturation magnetization (Ms) of 85 Am^2/kg, a coercivity (Hc) of 148.7 Oe, and a remanent magnetization (Mr) as low as 16. 68 Am^2/kg [87]. Meanwhile, $MnFe_2O_4$ synthesized by the coprecipitation method produces $MnFe_2O_4$ with a saturation magnetization (Ms) of 60.1 emu/g, coercivity (Hc) of 220 Oe, and remanent magnetization (Mr) as low as 5.6 emu/g [49]. The coercivity (Hc) value of $MnFe_2O_4$ synthesized by the coprecipitation method was higher than the $MnFe_2O_4$ nanoparticles synthesized by the sol-gel self-combustion method. These results are related to the size of the $MnFe_2O_4$ particles, the shape of the particles, the crystallinity, and the large magnetic moment of Mn^{2+} (5 μB) [49].

Meanwhile, the magnetization saturation of 16.3 emu/g can be used for magnetic separation in Solution with the help of an external magnet [24]. The area of the formed $MnFe_2O_4$ hysteresis curve is narrow, so the sample is included in the category of soft magnetic materials [88]. The synthesis of $MnFe_2O_4$ involves a coprecipitation reaction, which can be seen in equation 1, which is described below:

$$2Fe^{3+} + \tfrac{1}{4}\, Fe^{2+} + \tfrac{3}{4}\, Mn^{2+} + 8OH^{-} \rightarrow Mn_{3/4}Fe_{9/4} + 4H_2O \qquad (1)$$

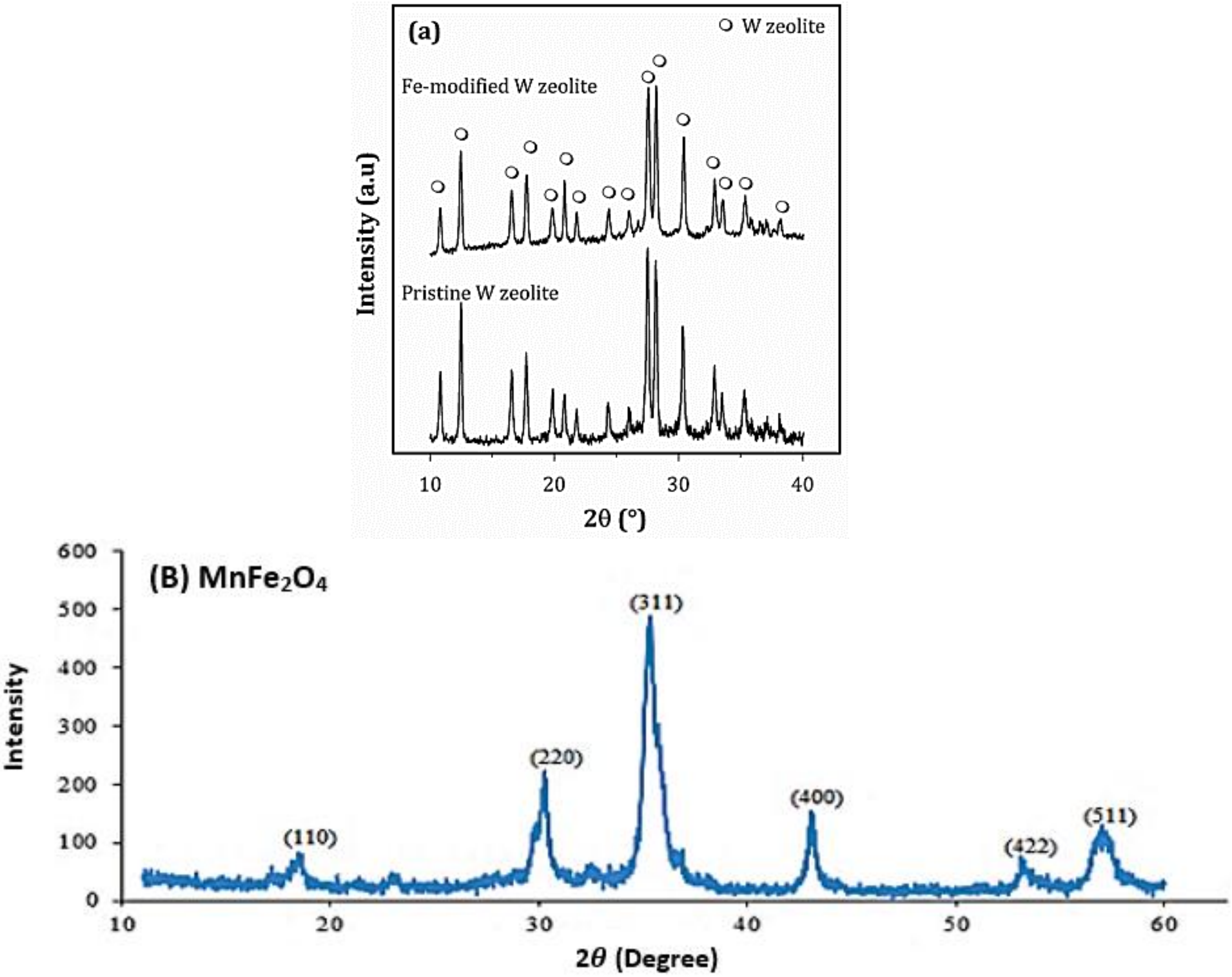


Figure 3. XRD characterization a) Pure W Zeolite and Fe-modified Zeolite [84] b) $MnFe_2O_4$ nanoparticles [89] reuse and clearance from MDPI.

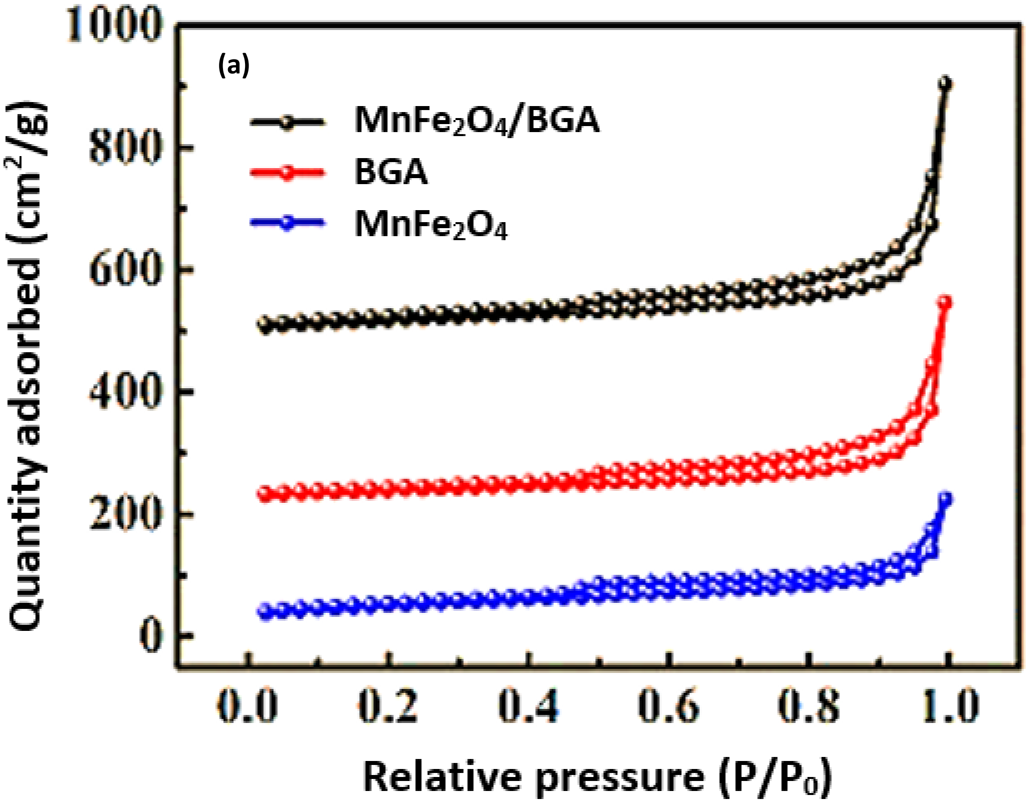
Figure 3a shows the characteristic diffraction patterns of pure W zeolite and Fe-modified W zeolite, which identified unique crystalline phases corresponding to Lynde W (JCPDS 86-1110), with no significant changes as a consequence of the ion exchange treatment. The Si/Al ratio of the Fe-modified W zeolite was 2.04[84]. On the XRD characterization of $MnFe_2O_4$ (Fig. 3b) synthesized using the coprecipitation method with an inverted spinel cubic structure (cubic, space group: Fd3m; JCPDS No. 73-1964) at 18.66° (110), 30.32° (220), 35.38° (311), 43.12° (400), 52.12° (422), and 57.12° (511) [89]. According to the research of M. R. Hassan and M. I. Aly [45], this copy has succeeded in synthesizing $MnFe_2O_4$ with the coprecipitation method. The crystal

(2)

size (D) is calculated based on the full width at the half peak (FWHM) of the highest intensity on the hkl (311) $MnFe_2O_4$ nanoparticle using the Scherrer formula in equation 2 below:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

Where D is the crystal size (nm), k is a constant (0.94), β is the half-peak width (FWHM), λ is the X-ray wavelength (0.154056 nm for Cu Kα), and θ is the peak angle at Bragg (°) [90]. In the research of M. R. Hassan and M. I. Aly [45], the average particle size of $MnFe_2O_4$ nanoparticles was ≈8.7 nm. The specific surface area of $MnFe_2O_4$ obtained by the coprecipitation method is shown in Figure 4.



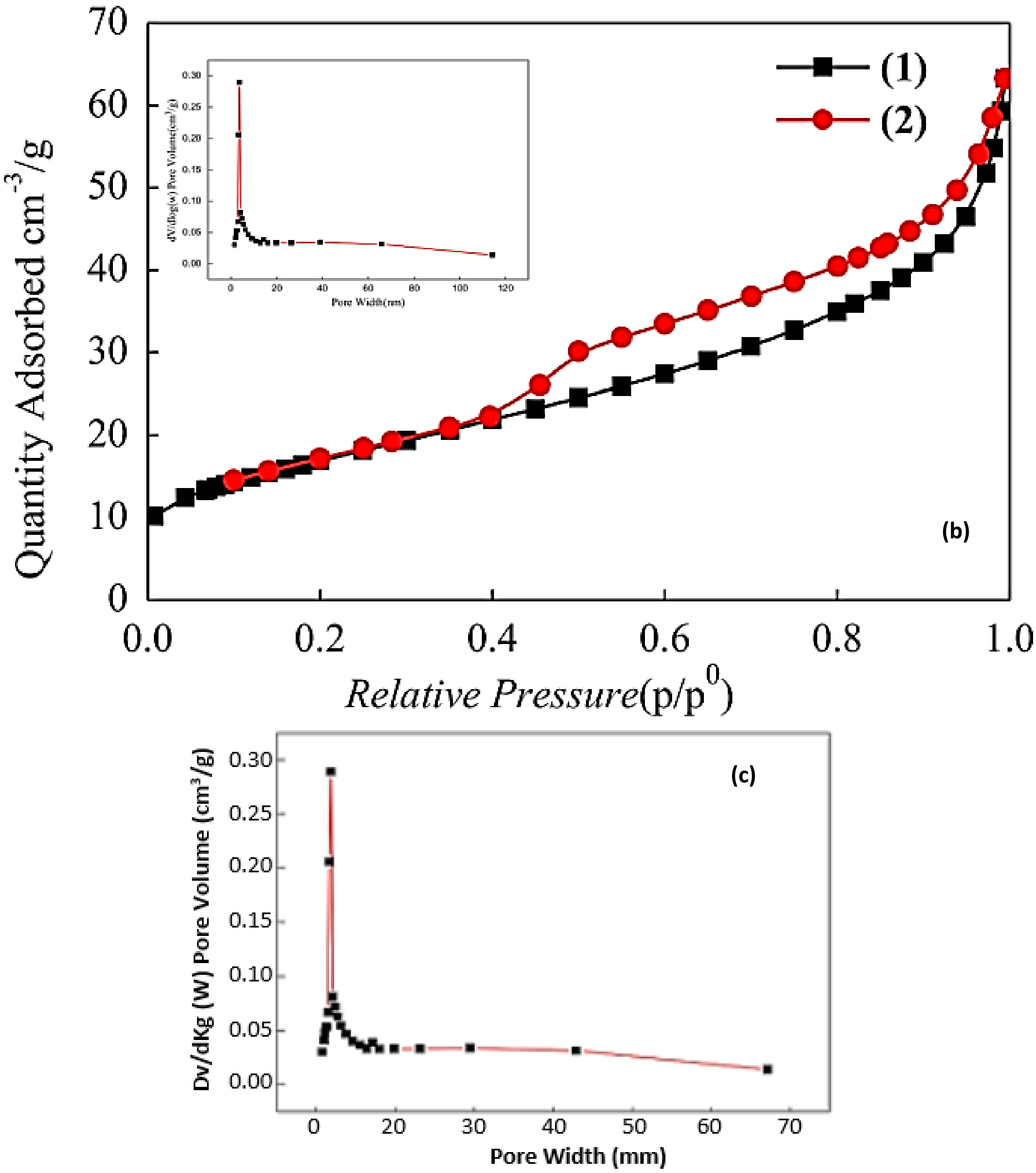


Figure 4. BET characterization for a) MnFe2O4 [91] b-c) Zeolite [92] reuse and clearance from MDPI.

Shown in Figure 4 reveals the N_2 adsorption/desorption isotherms of $MnFe_2O_4$, BGA (boron-doped graphene aerogel), and $MnFe_2O_4$/BGA. It can be seen that all of them are typical type IV isotherms with hysteretic features between the desorption and adsorption curves at higher relative pressures, indicating the presence of a moderate amount of mesopores with flaky or fractured granular pores with flat gaps and very few micropores. In addition, the surface area of $MnFe_2O_4$ was 57.9 m^2/g, while the surface area of the $MnFe_2O_4$/BGA composite was 136.7 m^2/g. Thus, it can be seen that the surface area increases after combining MnFe2O4 and BGA which form the composite [91]. The surface area of the Zeolite can be seen in (Figure 4b) the N2 adsorption/desorption isotherm of the solid phase synthetic zeolite. The synthesized product's specific surface area and total pore volume were 61.1 m^2/g and 0.09 cm^3/g, respectively, and the average adsorption pore diameter was 6.01 nm [92]. However, based on research by A. Setiawan et al. [64] zeolite has a surface area of 439.48 m^2/g, a pore volume of 9.01 cm^3/g, and a pore size of 94.11 nm [64]. Apart from the type of material that has a large surface area, another factor that can affect the surface area of the adsorbent is the particle size, where the smaller the particle size, the greater the surface area.

Furthermore, a reduction in particle size increases pore volume and pore size, increasing the adsorption capacity [64]. Due to the increase in pore volume and diameter, the porosity increases, and thus the adsorption capacity can be increased [46]. Therefore, one of the important factors in the adsorption of heavy metals is the surface area and the amount of pore volume in the adsorbent [93]. Factors affecting adsorption include the characteristics and properties of the adsorbent, the presence of other pollutants, and the parameters of the adsorption test (pH, pollutant concentration, and particle size of the adsorbent [27].

Adsorption of heavy metals by $MnFe_2O_4$ and Zeolite adsorbents

Scientific investigations have examined the effect of pH, adsorbent dosage, contact time, temperature, and initial ion concentration on the adsorption of heavy metal ions on the NP surface. The pH value is also an important factor in the adsorption process because it affects the availability of active sites on the surface of the adsorbent and ions in the air [62]. Therefore, it is necessary to cover its effect on metal ion removal. So here we explain the impact of the pH factor on the adsorptive removal of heavy metal ions by $MnFe_2O_4$ and Zeolite adsorbents, as illustrated in Figure 5 below. Obtaining the proportion of metal ion removal and the capacity or quantity of metal ion removal can be calculated by the following equations 3 and 4:

$$R\,\% = \frac{C_i - C_e}{C_i} \times 100 \tag{3}$$

$$Q_e = \frac{V(C_i - C_e)}{M} \tag{4}$$

where Ci (mg/L) and Ce (mg/L) represent the initial and final concentrations of heavy metal ions, respectively. Qe (mg/g) means the amount of MnFe2O4 nanoparticles removed at the equilibrium concentration, M (g) is the mass of $MnFe_2O_4$ nanoparticles, and V (L) is the volume of heavy metal ion solution [45].

Based on the research of M. Alaqarbeh et al. [94], U(VI) ion removal was influenced by pH, with variations in pH (1–7) with an initial concentration of 50 ppm U(VI) ion solution and a dose of 5.0000 mg $MnFe_2O_4$ adsorbent at 25 °C for 12 hours. The results are shown in Figure 5a, where the maximum U(VI) uptake of 50% is in the pH range (3–5). The pH of the Solution affects the hydrolysis of U(VI), at pH >3 UO_2^{2+} produces $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^{3+}$, and $(UO_2)_2(OH)_2$, which reduces the absorption efficiency of UO_2^{2+}

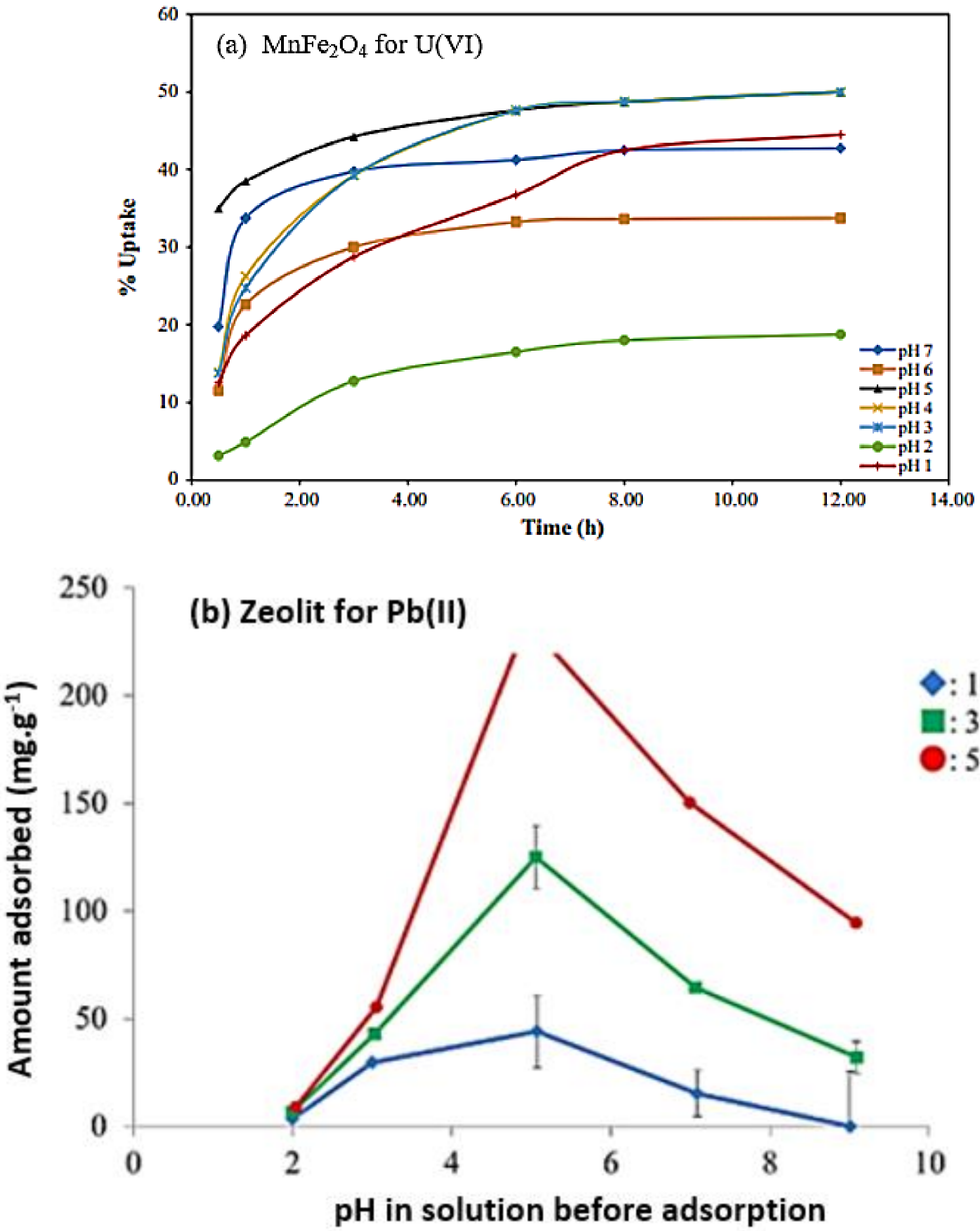


Figure 5. a) Effect of pH on U(VI) by adsorbent $MnFe_2O_4$ [94] b) Effect of pH on Pb^{2+} adsorption by type K zeolite with initial concentrations of 10, 30, and 50 mg/L [95] reuse and permission from MDPI.

In addition, pH affects the chemical stability and surface charge of $MnFe_2O_4$, where the positive charge decreases and changes to a negative charge when the pH increases to 6 because the surface charge is neutral at pHpzc, which is 6.5 for manganese ferrite [96].

Figure 5b shows pH's effect on Pb^{2+} adsorption by K-type Zeolite. The quantity adsorbed increased when the pH was increased from 2 to 5. The adsorption capacity decreased sharply for the optimum pH obtained at pH 5 and more than pH 5. Under acidic conditions, the surface of the Zeolite will be covered by protons (H^+), with which Pb^{2+} competes for adsorption sites.

The positively charged edge groups (Al-OH_2^+ and Si-OH_2^+) on the zeolite surface are described below.

$$\text{-AlOH} + H_2O\ (H^+ + OH^-) \rightarrow AlOH_2^+ + OH^- \tag{5}$$

$$\text{-SiOH} + H_2O\ (H^+ + OH^-) \rightarrow SiOH_2^+ + OH^- \tag{6}$$

Thus, electrostatic repulsion quickly occurs between the two, and it is also challenging to exchange ions between Pb^{2+} and K^+ in aqueous media. With increasing pH, the deprotonation of hydroxyl groups increased, indicating that the number of anionic sites (adsorption sites) on the Zeolite increased, thereby contributing to Pb^{2+} adsorption. However, at a pH greater than 6.0, the metal ion Pb^{2+} form (Pb(II) ion) will precipitate in the hydroxide form or $Pb(OH)_2$, $Pb(OH)_3^-$, dan $Pb(OH)_4^{2-}$ [45][62]. Thus complexion between free Pb^{2+} and the zeolite surface does not occur. In addition, there is electron repulsion occurring between the dissolved negatively charged Pb species and the negatively charged surface of the Zeolite. Thus, the adsorption capacity of Pb^{2+} decreases under alkaline conditions [95]. So based on research conducted by Y. Kobayashi et al. [95], the optimum pH for removing Pb metal ions by zeolite adsorbents is pH 5. Several heavy metals in the environment have been successfully adsorbed using $MnFe_2O_4$ and Zeolite adsorbents, as shown in Table 5.

Table 5. Performance of $MnFe_2O_4$ and Zeolite adsorbents for the removal of some heavy metals

Heavy metal	**adsorbent**	**Optimum Parameters**			**Results Review**	**Ref**
		pH	**Q_e (mg/g)**	**T (℃)**		
U(VI) and Th(IV)	Chitosan nanocomposite /($MnFe_2O_4$)	3	500 and 29	25 and 35	The (Qe) value of U(VI) adsorption on CCsMFO nanocomposites decreased with increasing temperature, reflecting exothermic adsorption. The maximum adsorption capacity (Qe) of Langmuir and D-R of Th(IV) was not affected by temperature.	[89]
Cu(II) and Pb(II)	$MnFe_2O_4$/ Chitosan Nanoadsorbent	4,5	14,86 and 15,36	45	The adsorbent exhibits superior binding and absorption for Pb(II) than Cu(II). Thermodynamic studies revealed that the uptake of Pb(II) or Cu(II) by magnetic chitosan-manganese ferrite is spontaneous and endothermic.	[83]
Cu(II) and Pb(II)	$MnFe_2O_4$	4,5	2,59 and 13,52	45		
Fe (III)	Zeolite	*	10,19	25	The amount of Fe adsorbed in the surface layer and the bulk differed depending on the initial concentration of Fe, namely only 45% was adsorbed on the surface layer of the Zeolite, and in the case of a low initial concentration, 95% of Fe was adsorbed on the surface layer of the Zeolite.	[97]
Pb	faujasite zeolite from vermiculite-kaolinite (VK) clay	*	100,15	25	On Pb adsorption, FAU zeolite adsorbent made from clay (ZVK-FAU) had the highest adsorbed amount (Qmax). The three adsorbed divalent metals (PB, Cu, and CD) are the most	[98]
Cu		*	46,71	25		
Cd		*	41,92	25		
Zn		*	n/a	25		
Co		*	n/a	25		

					and best, while the least adsorbed (Zn and Co) are best explained by Fritz-Schlunder's four isotherm parameters.	
Ni (II)	Zeolite Synthesized from Coal Fly Ash Produced by Gasification Process	5	15,94	30	More than 90% of Ni^{2+} in the air can be removed with Zeolite, indicating that coal fly ash from the gasification process has great potential to be used as an alternative and inexpensive source in producing adsorbents.	[99]
Pb(II)	$MnFe_2O_4$	5,3	75,75	25	$MnFe_2O_4$ nanoparticles are effective adsorbents for removing lead(II) ions from aqueous media, with an adsorption capacity of 75.75 (mg/g) and an adsorption efficiency of 88%.	[45]

* No pH adjustment

Adsorption applications have several advantages of simple technology (simple equipment). They can be adapted to many treatment formats, a wide range of commercial products, and target contaminants (adsorption). But on the other hand, there are drawbacks such as material costs, requiring large amounts of adsorbent, and some of the materials used as adsorbents are difficult to separate from aqueous media. While the application of $MnFe_2O_4$ has magnetic properties that can be easily separated from aqueous media with the help of permanent magnets. And Zeolite, which has a large surface area and several process advantages (adsorption), is very effective and can also be used for ion exchange. The environmental quality of heavy metal waste treated with $MnFe_2O_4$ and zeolite adsorbents is excellent. The combination of magnetic properties and adsorption capabilities can provide adsorption efficiency of heavy metal waste with ease of separation from aqueous media, which does not leave new contaminants in the air.

Conclusion

Based on the studies that have been done, it is concluded that the coprecipitation method has advantages over other methods, such as relatively low cost, high purity, low temperature, homogeneity, simple procedure, optimal crystal structure, and magnetic properties. The $MnFe_2O_4$ adsorbent has a surface area of 57.9 m^2/g and a saturation magnetization value (Ms) of 60.1 emu/g. In contrast, a saturation magnetization value of 16.3 emu/g can already be used for magnetic separation in Solution with the help of an external magnet. The adsorption capacity of Pb(II) ions was 75.75 mg/g $MnFe_2O_4$ adsorbent with an adsorption efficiency of 88%. The zeolite material has a high surface area of 439.48 m^2/g and an adsorption capacity of Pb(II) ions of 100.15 mg/g. Good adsorption results are also influenced by adsorption process parameters such as pH, capacity, and temperature. pH was identified as a significant factor in removing ions from the Solution. The observed removal of metal ions is maximum at moderate pH values rather than at very low or high pH, which will affect the adsorption capacity of a material. Temperature also affects the adsorption process significantly. For the exothermic adsorption process, the adsorption rate decreases with increasing temperature, while the endothermic adsorption process causes an increase in adsorption capacity at high temperatures. The advantages possessed by $MnFe_2O_4$ and zeolite materials as adsorbents make these two adsorbents very attractive because they are easy to synthesize and can be easily synthesized from aqueous media with the help of permanent magnets. Mandatory characterization is XRD, SEM-EDX, VSM, and BET. XRD for identifying and analyzing the phase of a material and finding out the crystal size of a material. SEM-EDX provides sample surface and composition data and VSM to determine the magnetism of a material. BET measures specific surface area, pore volume, and pore diameter. It is hoped that there will be a lot of integration of further research to develop $MnFe_2O_4$ and zeolite materials with suitable characteristics to overcome heavy metal ion pollution in water in the environment.

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