

Application of the column of Fe₃O₄ free nanoparticles to removal of Heavy metals in real and synthetic leachate

ABSTRACT

Background and Aim: landfill leachate is a type of wastewater that contains significant amounts of soluble organic compounds. The aim of this study is determining the efficiency of the column of nanoparticles in removing heavy metals from leachate. In this study; the required leachate was prepared synthetically. Furthermore, the natural leachate's samples were also collected from Isfahan compost factory on which this study was done. The samples used for analysis from the input of the column of free nanoparticles, first the leachate is stirred by 2 g/L of free nanoparticles for 10 min at 130 rpm, followed by collection and analysis all the samples after 2 min of sedimentation. To determine the efficiency of free nanoparticles and iron (III) magnetic column in removing organic compounds, nitrogen, and phosphorus, first the concentration of these parameters was investigated before and after adding the magnetic nanoparticles, where the efficiency of the removal of COD concentration, ammonia nitrogen, and natural leachate's phosphorus was 98.91, 99, and 99.2%, respectively. Iron (III) nanoparticles in free form can efficiently remove COD, ammonia nitrogen and phosphorus from the leachate obtained from solid waste materials. Across all these stages, it was found that the levels of COD, phosphorus, and ammonium of the leachate before and after the column have significant relationships.

Keywords: column, nanoparticles, Fe₃O₄, leachate

1. INTRODUCTION (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

Landfill leachate is a type of wastewater that contains significant amounts of soluble organic compounds. Before discharging wastewater to what resources, the foods and other contaminants present in the wastewater should be removed. This entails using effective treatment processes that can convert typical and hazardous contaminants present in the wastewater into non-toxic materials or less harmful effects [1]. Contamination of soils, surface waters, groundwater, and air with typical pollutants, as well as toxic and hazardous contaminants, can result in significant problems to the human health and the environment [2]. When contaminants such as nitrogen enter water resources, part of it (around 20-30%) is absorbed by plants, while the rest of it remains in water in the form of inorganic nitrogen, where its aggregation in a closed system can bring about toxic and hazardous effects to aquatic species [3]. Moreover, in response to the entrance of it treating the environment, the acidity of the soil, groundwater, and surface waters increases [4]. The considerable attention that has recently been directed towards removing the effects of nutrients in the environment has resulted in the enactment of strict rules for controlling these compounds especially phosphorus in the wastewater obtained from treatment plants [5]. Currently, the wastewater treatment industry uses numerous methods for removing nitrogen, phosphorus, and other contaminants from wastewater [6]. One of the methods employed for separating materials in industries is magnetic separation. This process is usually applied for removing magnetic impurities present in compounds and materials. In the treatment, the wastewater and processes, high gradient, magnetic separators (HGMS) can also be used [7]. Use of magnetic nanoparticles for removing contaminants from aquatic environments has various advantages with practically and theoretically. These particles enjoy a high absorption capacity and are recoverable entirely [2]. The nanoparticles employed when Nanomaterials are used in household and industrial equipment are eventually discharged along with wastes or wastewater. This then enters sludge in the wastewater treatment plant and remains there. The escape of these nanoparticles from the sludge and its entrance to output wastewater can cause contamination of water and soil resources. Therefore, one of the points that should be recognized about applying nanoparticles is the behavior and the effect of these nanoparticles in wastewater and wastewater

sludge [8]. Currently, officials in water and wastewater industries around the world are seeking methods that are able to remove or limit contaminants or wastewater more effectively, while they do not need developing substantial changes in the structure of treatment plants and also do not cause the addition of another contaminant to the environment [9]. One of the most important advantages of using magnetic nanoparticles in the environment is that they are easy to be removed from a sample by an external magnetic field. Magnetic nanoparticles can develop a very large area while preserving their magnetic properties. To recognize whether it is possible to remove contaminants by nanoparticles, their molecular properties and the way they are attached to magnetic nanoparticles should be well understood. For this reason, the nanoparticles that are selected should be superparamagnetic, have a constant powerful magnetic property, and not prevent developing magnetic waste [10]. The significance of magnetic nanoparticles has been shown virtually across all these areas. Recently, iron nanoparticles have been extensively used in various studies [11]. Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are the most common forms of iron magnetic nanoparticles in nature [12, 13]. In the study by Marthius et al used a high magnetic separation for removing phosphorus (eliminating eutrophication). They found that magnetic particles act as absorbents in combination with a magnetic separator to remove phosphorus from wastewaters and waters rich in phosphorus that enter surface waters [14]. Furthermore, in a study by Li et al in this area, successful results were obtained [15].

2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY (ARIAL, BOLD, 11 FONT, LEFT ALIGNED, CAPS)

In this study, the required leachate was repaired synthetically using the compounds employed in papers in the laboratory. Furthermore, natural leachate samples were also collected from compost factory on which this study was done. The utilized samples were collected for analysis from the input of the column of magnetic nanoparticles and its output after 10 min of retention time and concentration of 2 g/L. considering the application of free nanoparticles, first, the leachate with a concentration of 2 g/L of free nanoparticles was stirred for 10 min at 130 rpm, followed by a collection of samples after two minutes of sedimentation and then analysis of the samples. The number of samples required in this study was determined by the formula. The largest sample number with a confidence of 95% was obtained as 20 for COD with an acceptable error level [10] and variance of 22. Therefore, to determine the properties of the developed initial samples, 20 samples should be analyzed. For investigation under conditions before the column and after it, 40 samples should also be analyzed along with 20 samples to examining the effect of free magnetic nanoparticles of Fe_3O_4 . In addition, to study the effect of the magnetic column and free nanoparticles of iron on natural leachate, 60 samples are also required, amounting to 120 samples in total.

Fabrication of iron (III) magnetic nanoparticles: To fabricate single-domain magnetite iron (III) magnetic nanoparticles, chemical deposition method was used [6]. These nanoparticles were synthesized out of ferric chloride (FeCl_3) and ferrous chloride (FeCl_2) salts in a molar ratio of 2:1. The utilized molar ratio of the ferric and ferrous chloride salts can reduce 1 mol magnetic nanoparticles Stoichiometry. Ammonium solution was also used as depositor under atmospheric and the vigorous agitation conditions. The temperature of the experiment was kept within the ambient temperature. The potential reaction taking place in this state is as the (1-3) reaction [7].

The procedure of fabricating iron (III) magnetic nanoparticles: In order to synthesize magnetic nanoparticles, the following steps were taken:

1. Preparation of 2 Molar solutions of hydrogen chloride acid (HCl): 168 ml of HCl with a purity of 36.5% was dissolved in 1 L of distilled water.

2. Preparation of 2 Molar solutions of FeCl_2 : 199.9 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powder was dissolved in HCl 2 M. this solution reacts with oxygen, and thus should be synthesized on a daily basis.

3. Preparation of FeCl_3 1M: 135.25 g of $\text{FeCl}_3(\text{H}_2\text{O})_6$ powder was dissolved in 500 cc HCl 2M. This solution is dissolved slowly.

4. Preparation of ammonium 1M solution: 74.88 ml of ammonium 25% should be taken out and then dissolved in 1 L of distilled water so that ammonium 1M solution is obtained.

In order to fabricate the utilized nanoparticles, 4 ml of FeCl_3 1M was stirred with 1 mL of FeCl_2 2M in a 100-mL beaker. Next, during the stirring, 50 ml of ammonium 1M is added to it such that its addition time is not over 5 min. For this situation, a Burette can be used. The stirrer was then turned off and the beaker was quickly placed on a powerful magnet. The magnetic nanoparticles deposit in the bottom of the beaker. The dish's supernatant was discharged, followed by three times of drainage. Eventually, by placing the magnet in the bottom of the dish, its water content was removed as much as possible, followed by addition of 2-1ml tetra methyl ammonium hydroxide 25%. The stirring is done at least for 1 min and then its supernatant is discharged. What remains in the bottom of the dish are magnetic nanoparticles totally crystallized by approaching it to the magnet. If these nanoparticles are not crystallized, the dish containing the nanoparticles should be shaken several times around the magnet so that the fabricated nanoparticles find magnetic properties. Finally, the synthesized magnetic nanoparticles were dried at 60°C for 8 h and then used.

1. COD experiment: In this research, the total COD was measured. Considering the high concentration of COD in synthetic leachate as well as the natural leachate, the first dilution was done on the leachate such that the synthetic leachate and natural leachate were diluted 4 and 150 times, respectively. In order to measure COD, HACH method was used, where its prepared vials were used for concentrations of 15-150 mg/L with the code of LCK314 and concentrations of 150-1000 mg/L with the code of LCK114.

2. Phosphorus experiment: To analyze phosphorus in this study, the DR5000 device instruction was used. As DR5000 can measure phosphorus within the range of 0.3-45 mg/L, first the leachate was diluted such that the synthetic and natural leachates were diluted 20 and 150 times, respectively. Since the phosphorus available in the leachate is in the form of orthophosphate, Vanadium molybdate method (Method 8114) was employed.

3. Nitrogen experiment: To analyze nitrogen in this study, DR5000 device instruction was utilized. As the nitrogen available in the leachate is mainly in the form of ammonia nitrogen, Nesler method (Method 8038) was used. According to this instruction, DR5000 can measure nitrogen within the range of 0.02-2.5 mg/L. Therefore, first, the leachate was diluted, where the synthetic and natural leachates were diluted 40 and 150 times, respectively.

4. Iron experiment: In order to analyze the iron, atomic absorption device of Perkin Elmer, Model 2380 was employed, where the synthetic leachate sample was not diluted, while the natural leachate sample was diluted 150 times. In order to prepare to samples, nitric acid was used with the pH of the samples being brought down below 2. The concentration of the iron in the samples was then analyzed by the device

3. RESULTS AND DISCUSSION

The mean percentage of removal of COD of the synthetic and natural leachate before and after Fe_3O_4 free nanoparticles was observed to be 97.5% and 98.91%, respectively. The percentage of the removal of the synthetic and natural leachate's ammonium before and after Fe_2O_3 free nanoparticles was observed to be 94.9 and 99%, respectively. The removal efficiency of the synthetic and natural leachate's phosphorus before and after Fe_3O_4 free nanoparticles was 98.6 and 99.2%, respectively. The efficiency of removal of the synthetic and real leachate's iron before and after the treatment with iron (III) free magnetic nanoparticles was achieved to be 80.23 and 92.24%, respectively.

1. Comparing the removal of the leachate by the column of Fe_3O_4 free nanoparticles in the real and synthetic samples:

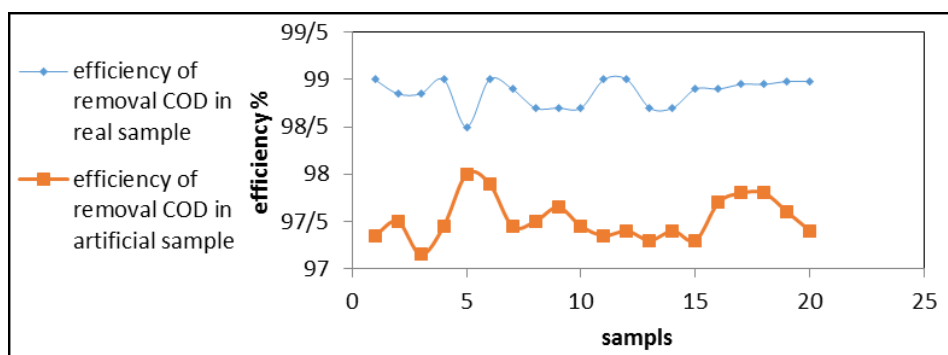


Fig. 1. The comparison of the COD removal from the leachate by the free column in the real and synthetic samples

2. Comparing removal of ammonium by the column of Fe₃O₄ free nanoparticles in the real and synthetic samples:

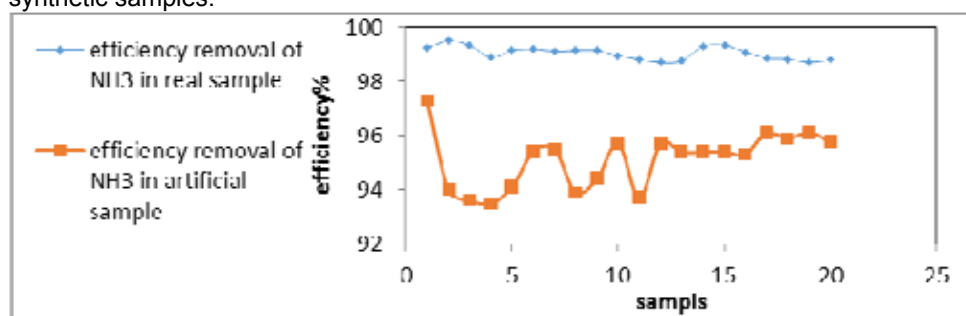


Fig. 2. Comparing removal of ammonium by the column of Fe₃O₄ free nanoparticles in the real and synthetic samples

Considering the normality of data distribution, paired samples t-test was used for comparing iron (III) free magnetic nanoparticles in removing ammonia nitrogen from the synthetic and natural leachates. As can be observed, iron (III) magnetic nanoparticles removed 99.35 and 95.9% of the leachate's ammonia from the real and synthetic samples, respectively. According to the statistical test, there is a significant difference between the percentage of the removal of ammonia nitrogen from the synthetic and natural leachate by the iron (III) free magnetic nanoparticles (p -value=0.000). Therefore, with a probability of 95%, it can be stated that the ammonia free column removes the natural sample more than the synthetic sample.

3. The comparison of the removal of phosphorus by the iron (III) free magnetic nanoparticles in the real and synthetic samples:

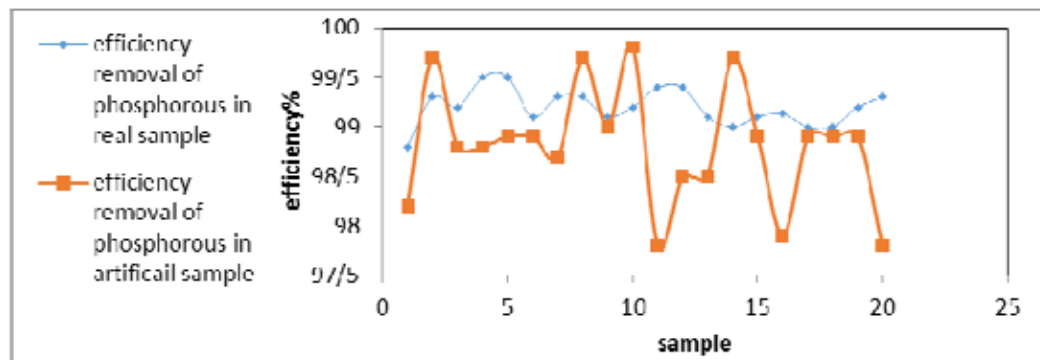


Fig. 3. The comparison of the removal of phosphorus by the iron (III) free magnetic nanoparticles in the real and synthetic samples

4. Comparing the concentration of iron in the output wastewater of the Fe₃O₄ free nanoparticles

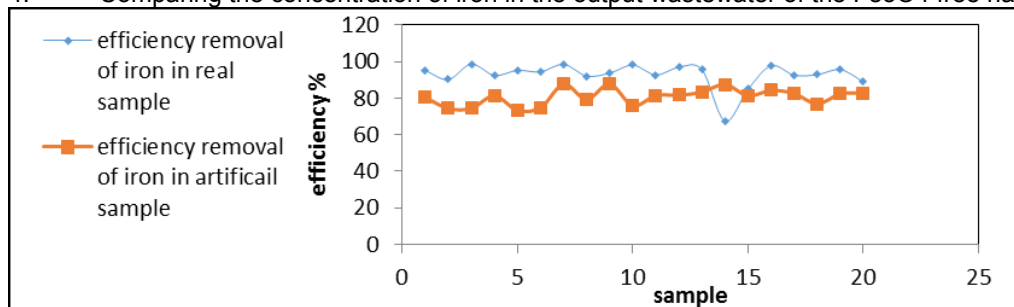


Fig. 4. Comparing the concentration of iron in the output wastewater of the Fe₃O₄ free nanoparticles

Since iron nanoparticles were used for treating the leachate, it should have been recognized that how much iron would remain in the treated wastewater. For this purpose, the iron concentration was analyzed in the synthetic and natural leachate in the input and output of the column of iron (III) magnetic nanoparticles. Considering the normality of data distribution, paired samples t-test was utilized for comparing the iron (III) free magnetic nanoparticles in removing iron from the synthetic and natural leachate. As can be seen from the diagram, iron-free nanoparticles can remove the iron of the natural and synthetic sample's leachate by 98.6 and 84.7%, respectively. According to the statistical test, there is a significant difference between the mean percentage of iron removal from the synthetic and natural leachates by the iron (III) free magnetic nanoparticles (p -value=0.000). Therefore, with a probability of 95%, it can be said that the column of iron (III) free magnetic nanoparticles in removing iron is more effective for the real sample, rather than the synthetic sample, thereby removing larger amounts of iron.

1. The efficiency of removing the leachate's COD by Fe₃O₄ free nanoparticles:

The obtained results indicate that iron (III) free magnetic nanoparticles are able to remove $97.5 \pm 0.2\%$ and $98.91 \pm 8.16\%$ of the COD of the synthetic and natural leachate respectively obtained from Isfahan compost factory. These nanoparticles are able to decrease the synthetic leachate's COD from 19.120 ± 4.3376 to 17.5 ± 3.84 mg. They can also reduce the natural leachate's COD (natural leachate has higher levels of contamination) from $83/11147 \pm 160545$ to $32/36 \pm 4/1744$. The results of the statistical analysis reveal that there is a significant difference between the mean concentration of the COD of the synthetic leachate and the raw and treated natural leachate (p -value=0.000). As on average $mg/l/3292$ of the synthetic leachate's COD has been removed by iron (III) free magnetic nanoparticles, the removal capacity for organic compounds by these magnetic nanoparticles is about 1646 mg/g. In 2009, AbasAfkhani et al employed the magnetic nanoparticles of hematite (γ -Fe₂O₃) for removing Congo red dye from the wastewater of textile industries. The absorption capacity of these in particles was around $mg/l/33/208$ [16]. In 2009, Qadri et al studied the removal of acridine dye by magnetic nanoparticles. They observed that Fe₂O₃ nanoparticles were able to remove about 98% of the dye within a 20-min contact, such that the absorption capacity of these nanoparticles for acridine dye was achieved to be 59 mg/g [17].

2. The removal efficiency of the leachate's ammonium by Fe₃O₄ free nanoparticles:

In order to investigate the efficiency of iron (III) free magnetic nanoparticles in removing ammonium, the concentration of ammonium in the synthetic leachate and the raw natural and treated leachate was analyzed with the mentioned nanoparticles in 20 samples. The results of this analysis indicate that the free magnetic nanoparticles are able to decrease the concentration of ammonium in the synthetic leachate from $mg/l/17/1 \pm 28/41$ to mg to $mg/l/41/0 \pm 11/2$, removing $94.88 \pm 1.04\%$ of the synthetic leachate's ammonium. These nanoparticles also decline the mean concentration of ammonium in the natural leachate from $mg/l/2/6 \pm 3/55$ to $mg/l/1/0 \pm 53/0$, reducing the ammonia

concentration $99 \pm 0.22\%$ of the natural leachate. According to the statistical analyses, there is a significant difference between the mean concentration of ammonium of the raw and treated leachate (p -value=0.000). There is also a significant difference between the ammonia concentration of the raw natural leachate with that of the leachate treated by free magnetic nanoparticles (p -value=0.000). As, on average, mg/l17/39 of the synthetic leachate's ammonium has been removed by the iron (III) free magnetic nanoparticles, with the removal capacity of the ammonia nitrogen compounds of about 58.19 mg/g. In 2009, Abas Afkhami et al used γ -Fe₂O₃ magnetic nanoparticles (size=50 nm) for removing and recovering MOVI from water and wastewater. The maximum removal capacity of the nanoparticles achieved to be 4.33 mg/g [18].

3. The efficiency of removing the leachate's phosphorus by the Fe₃O₄ free nanoparticles:

In order to investigate the efficiency of iron (III) free magnetic nanoparticles in removing phosphorus, the concentration of phosphorus in the synthetic leachate and the raw natural and treated leachate was analyzed with the mentioned nanoparticles in 20 samples. The results of this analysis indicate that the free magnetic nanoparticles are able to decrease the concentration of phosphorus in the synthetic leachate from mg/l73/1 $\pm$ 34/37 to mg/l24/0 $\pm$ 51/0, removing $98.6 \pm 0.66\%$ of the synthetic leachate's phosphorus. These nanoparticles also decline the mean concentration of phosphorus in the natural leachate from mg/l5/5 $\pm$ 6/51 to mg/l1/0 $\pm$ 41/0, reducing the phosphorus concentration by $99.2 \pm 0.18\%$ in the natural leachate. According to the statistical analyses, there is a significant difference between the mean concentration of phosphorus of the synthetic raw and treated leachate (p -value=0.000). There is also a significant difference between the phosphorus concentration of the raw natural leachate with that of the leachate treated by free magnetic nanoparticles (p -value=0.000). As, on average, 183.36 mg of the synthetic leachate's phosphorus has been removed by the iron (III) free magnetic nanoparticles, the removal capacity for the phosphorus by the magnetic nanoparticles is about 41.18 mg/g. In a study by Chang et al in 2009, it was found that the magnetic combinational absorbent of gel cell had the highest absorption level for fluoride at 38 kg/g [17]. In 2009, Gang Pan et al examined the removal of phosphorus scattered in soil using magnetic nanoparticles stabilized on sodium carboxyl methyl cellulose. They concluded that the absorption capacity for phosphorus within 24 hours was about 1.2 mg/g, removing the 73% of the soil phosphorus [19].

4. The efficiency of removing the leachate's iron by the Fe₃O₄ free nanoparticles:

Since iron (III) magnetic nanoparticles for treating the leachate and there was a possibility of liberation of iron in the output waste (considered as a potential environmental pollutant), the concentration of iron was analyzed in 20 samples in the raw leachate and the leachate treated by iron (III) free magnetic nanoparticles individually in the natural and synthetic leachates. At first, the synthetic leachate synthesized by these nanoparticles was treated, followed by treatment of the leachate obtained from compost factory by the mentioned nanoparticles. The results indicate that the free magnetic nanoparticles are able to remove $80.23 \pm 3.98\%$ of the synthetic leachate's iron and $92.24 \pm 6.8\%$ of the natural leachate's iron obtained from Isfahan compost factory. They declined the synthetic leachate's iron from mg/l4/1 $\pm$ 55/22 to mg/l8/0 $\pm$ 43/4 and in the natural leachate, which has a higher degree of contamination; these nanoparticles are able to decrease the mean concentration of iron from mg/l01/21 $\pm$ 03/55 to mg/l84/1 $\pm$ 55/3. According to the statistical analyses, there is a significant difference between the mean concentration of iron of the synthetic raw leachate and the treated synthetic leachate (p -value=0.000). There is also a significant difference between the iron concentration of the raw natural leachate with that of the leachate treated by free magnetic nanoparticles (p -value=0.000). On average, mg/l1/18 of the synthetic leachate's iron has been removed by the iron (III) free magnetic nanoparticles. The removal capacity for the iron by the magnetic nanoparticles is about 9.1 mg/g. In a study by Shen et al in 2009, it was found that Fe₂O₃ nanoparticles with a size of 8 nm were able to remove metal ions from water within 24 hours, with the maximum absorption capacity of them at 46.35 mg/g. In this research, Fe₃O₄ magnetic nanoparticles

were able to remove 99.8% of copper, 97.6% of chromium, 84.7% of cadmium, and 88.5% of nickel [20]. The very small size of the Fe₃O₄ magnetic nanoparticles results in the development of a very large area. Further, the functional groups present on the magnetic nanoparticles lead to increased rate of these reactions such that the metal ions inside the pores of these nanoparticles move critically and randomly. This causes increased absorption capacity of nanoparticles [19, 20]. removal capacity of the nanoparticles achieved to be 4.33 mg/g [18].

CONCLUSION:

Iron (III) nanoparticles in their free form can effectively remove COD, ammonia nitrogen, and phosphorus from the leachate produced by solid waste materials. The removal efficiency of iron (III) magnetic nanoparticles in their free form is 98.91±8.16% for the natural leachate's COD, 99±0.22% for the ammonia nitrogen of the natural leachate, 99.2±0.18 for the natural leachate's phosphorus, and 92.24% for the iron present in the leachate. In the natural leachate, iron (III) free magnetic nanoparticles have a high efficiency in removing ammonium and phosphorus. The removal capacity for the organic compounds and ammonia nitrogen compounds, phosphorus, and iron by the iron (III) free magnetic nanoparticles is 1646 mg/g, 19.58 mg/g, 18.41 mg/g, and 9.1 mg/g, respectively.

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