

Removal of Chromium from a Tannery Wastewater by Using a Maghemite Nanoparticles

B. Lkhagvadulam, B. Tsagaantsetseg, D. Tergel, and S. Chuluunkhuyag

Abstract—This study investigates the applicability of maghemite nanoparticles (MNPs) for the removal of total chromium (TCr) from the tannery wastewater (TWW). The MNPs of 122 nm were synthesized using a co-precipitation method and characterized by Nanometer particle size analysis (NANOPHOX), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Batch experiments were carried out for the removal of TCr from the TWW by MNPs. The effects of dosage of MNPs, pH, initial concentration and contact time on TCr removal were investigated. Maximum removal efficiency of TCr in the TWW was achieved 96.7% at optimum condition (pH 2, MNPs dose was 0.5g/L, initial concentration of TCr was 33.2 mg/L, 40minute) at room temperature. It is observed that the best efficiency in removing major physico-chemical parameters (TCr, SS, COD, sulfide and turbidity) in the TWW, which are well below the standard prescribed limits for MNS 6561: 2015. Thus the study suggests that the treatment with MNPs could be promising to reduce pollutants from the other TWW.

Index Terms—Maghemite nanoparticles (MNPs), tannery wastewater (TWW), total chromium (TCr), treatment.

I. INTRODUCTION

Tanning is the chemical process that converts animal hides and skin into leather and other related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater [1]. Treatment of the TWW has been difficult due to their components such as BOD, COD, SS, oil-grease, sulphur, chromium (VI), TCr and pH. These parameters pose a biological risk. Heavy metals which have been an important toxic pollutant group tend to accumulate in soils, plants and animals according to the seasonal condition and the characteristics of soil of the region. Among these metals, Cr(VI) exists especially in leather tanning industries. Also Cr(VI) has been known to have toxic effects on the activated sludge process in the wastewater treatment plant. Chromium exists in Cr (III) form in many biological proteins, nucleic acids and low molecules weighted ligands. Chromium (VI) form is much more toxic than chrome (III) form due to its oxidation potential and its penetration in the tissue [2]. Major Cr(VI) species include, HCrO_4^- , chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). It can

cause severe damages to the human health including, but not limited to, liver and kidney damage, producing lung tumors, severe diarrhea, allergic dermatitis, skin irritation, internal hemorrhage and respiratory problems [3].

Several methods have been developed for the treatment of chromium containing wastewaters, including biological and physicochemical processes. Conventional methods for removing Cr(VI) include chemical reduction to the Cr(III) followed by precipitation under alkaline conditions or removal by ion exchange. Other [1], [3], [4] reported removal methods are as follows; adsorption reverses osmosis, electrochemical precipitation, bio adsorption, foam separation, separation by freezing and evaporation.

Recently, the utilization of nanomaterials for removal of heavy metals from water has arisen as an attractive research direction. This is because, compared to bulk materials, nanomaterials-based adsorbents possess much larger surface area, which can provide a greater number of active sites for interaction or adsorption. Some kinds of nanomaterials, such as carbon nanotubes, iron oxide, aluminum oxide, and titanium oxide have been used as nano-adsorbents in many studies [5]-[9] and have showed excellent adsorption capacity for various heavy metals including chromium.

Among these nano-adsorbents, the utilization of iron oxide nanomaterials has been received much attention due to their unique properties, such as high surface area-to-volume ratio, surface modifiability, excellent magnetic properties, great biocompatibility, ease of separation using external magnetic field, reusability and comparatively low cost [3].

Several studies have been conducted for aqueous Cr (VI) removal and magnetite NPs, MNPs and mixtures of above two NPs were extensively studied for Cr(VI) removal [3]. Hu, Chen *et al.* [10], [11] studied the performance and mechanism of (Cr(VI) removal from industrial wastewater, using MNPs. In these studies, 17 and 19.2 mg/g adsorption capacity were reported at pH 2.5. In Wenjun Jiang's study [12], 1.62 mg/g adsorption capacity was reported at pH 4. Magnetite nanoparticles with or without functionalization agents have also been widely studied for aqueous Cr (VI) removal. Shen, Pan *et al.* [13] was done a study to remove Cr(VI) from copper and chromium co-existing water system, with amino functionalized nano sized magnetite particles. Maximum Cr(VI) uptake was reported as 370.37 mg/g. In a different study, Jing Hu *et al.* [14] the Cr(VI) adsorption capacity of the -FeOOH-coated -Fe₂O₃, was determined to be 25.8 mg/g, and Thi May Do *et al.* [5] was determined 22.0 mg/g for Cr(VI). Ethylenediamine-functionalized Fe₃O₄ magnetic polymers revealed adsorption capacity of 32.15 to 61.35 mg/g for Cr(VI) [15]. In addition to above mentioned nano-sorbents, Fe₃O₄/carbon nanotube NPs, Fe₃O₄@n-SiO₂

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NPs, $\text{MnO}_2/\text{Fe}_3\text{O}_4/\text{o-MWCNTs}$ [3], [16] of Magnetic Hydrogel [17] were also reported where adsorption capacity ranging from 2.3 mg/g to 205 mg/g.

The Pre-treatment facility of Ulaanbaatar city in Mongolia is the first facility that was established in 1972 from wool scouring wastewater. This facility has the capacity to treat approximately 4,000 m³/day wastewater using mechanical and chemical method. The facility receives and treats wastewater from 27 leather and wool washing plants. After the pretreatment, the industrial wastewater pumped to the central wastewater treatment facility. According to Mongolian standard MNS 6561:2015 (Environment. Water quality. Effluent water for sewerage network. General requirements MNS 6561:2015) [18], the recommended amount of TCr content in the pre-treated industrial wastewater pumped to the central wastewater treatment facility is 1.0 mg/L. However, sometimes the amount of chromium content in the pre-treated water is higher than the recommended standard limit. This creates challenges for the central wastewater treatment facility by reducing the percentage of fully-treated wastewater outputs. Therefore, our main purpose was to remove toxic, TCr quantity from treated industrial wastewater by using iron oxide nanoparticles synthesizing technique.

Most of the researcher reports on aqueous Cr (VI) removal by using iron oxide NPs have focused on characterization of NPs and the effect of some factors for Cr (VI) removal and the adsorption isotherm mechanisms. Thus, in this study, MNPs has been synthesized using a co-precipitation method, characterized, applied for the removal of TCr from TWW. The TWW was characterized and treated by using MNPs. The factors possibly affecting TCr removal performance, including sample pH and the adsorbent dosage, the initial TCr concentration and contact time were examined. The adsorption capability of the synthesized MNPs for TCr and Cr(VI) were evaluated. Furthermore, we evaluated major physico-chemical parameters of TWW before and after the treatment.

II. MATERIALS AND METHODS

A. Synthesis and Characterization of MNPs

MNPs were prepared according to the literature procedures [12]. MNPs were prepared by a co-precipitation method. All solutions were purged with argon for 15 min to remove oxygen prior and during reaction. Iron solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4 g) were diluted to 30 mL with water. The iron mixture was stirred magnetically, gently purged with argon and heated to 80 °C and then 40 mL of 15% diluted ammonium hydroxide solution added dropwise into the mixture over a 20 min time interval. The mixture was aged at 80 °C for an additional 40 min. The product was rinsed with water then ethanol three times. The samples were separated using a magnet and dried in a vacuum oven at 50 °C to a constant weight.

Particle size and size distribution analysis of the MNPs was done on Photon Cross Correlation Spectroscopy (PCCS) (Sympatec GmbH, Germany). The MNPs were characterized by a combination analysis of transmission electron

microscopy (TEM), and X-ray diffraction (XRD). TEM images were performed on a (JEOL, JEM 2011). A typical sample for TEM was prepared by drying of a drop of the solution at room temperature on a carbon-coated copper grid. XRD was recorded on an X-ray powder diffractometer XRD (Enraf Nonius Delft) using Cu K α radiation ($\lambda=1.54$ Å).

B. Characteristic of the TWW before and after the Adsorption Studies

The study was conducted during March 2016 – April 2017, the samples were collected from the two main drains, in particular for sulphide and chrome-containing liquors of TWW pre-treatment facility in Ulaanbaatar city. After collecting the sample in a container it was mixed thoroughly. Test samples were separated for the container to beaker and the settle able suspension were allowed to settle. Supernatant of the sample was taken for determining COD, SS, Sulphide and pH [19], [20]. The pH of the sample was determined by using Mettler Toledo pH meter (MNS ISO 10523:2001) [21]. COD were determined by Closed Reflux, Titrimetric Method (MNS ISO 6060:2001) [22], respectively. A quantitative analysis for the determination of suspended solid (SS) was carried out by simple laboratory method (MNS ISO 11923:2001) [23]. Sulfide was determined by using MNS ISO 5597:2006 [24]. The turbidity of the sample was determined by using 2100P Turbid meter Hach [25]. TCr and Cr(VI) were measured using the spectrophotometer (V-1200 Spectrophotometer) CS 11-0037-2008 [26] and MNS ISO 11083:2001 [27]. Sample dilution was conducted before the spectrophotometer measurement, where necessary. All chemicals were used of analytical grade reagents and the experiments were performed at least three times to minimize analytical error.

C. Adsorption Studies

Batch adsorption studies were performed by mixing 0.5 g of MNPs with 50mL of the sample in 100mL glass vials. The adsorption on MNPs was first studied at pH values of 2 to 11 to investigate the effects of pH values on the TCr adsorption. 0.1MHCl and 0.1MNaOH solutions were used to adjust the pH values of samples. The pH values of samples were stable over the experiment period [28].

For effect of adsorbent dose MNPs studies, between 0.1 -10g/L MNPs was added into 50 mL of the samples. Adsorption equilibrium studies were conducted by varying the initial concentration of 50 mL of samples from 6 to 33.2 mg/L at pH 2, respectively [12], [28], [11].

All the adsorption experiments were carried out at a room temperature of $22 \pm 2^\circ\text{C}$ and were performed in triplicate. The TCr was measured using the spectrophotometer (V-1200 Spectrophotometer). The amount of the TCr and Cr (VI) adsorbed on the MNPs was determined by chromium mass balance, the amount of adsorbed chromium at equilibrium q_e (mg/g) was calculated as follows: [5]

$$q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

where C_o , C_e , are the initial and equilibrium liquid-phase concentrations of chromium respectively (mg/L), V the

volume of the solution (L) and m the weight of the MNPs used (g).

III. RESULTS AND DISCUSSIONS

A. Synthesis and Characterization of MNPs

The commonly used synthetic way of MNPs is a co-precipitation method of the iron mixture ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) using ammonium hydroxide solution [12].

The size of MNPs was investigated using Photon Cross Correlation Spectroscopy (PCCS) (Sympatec GmbH, Germany). Fig. 1 shows the Particle Size Analyzer image of the MNPs that deionized water was used in process. The MNPs have the average size of them was 122 nm and specific surface area was $S_v = 49.42 \text{ m}^2/\text{cm}^3$. Fig. 2 shows TEM images of MNPs. The results show that the shape of them was spherical and diameters around 122 nm and well dispersed with no aggregation.

To investigate the structure of the MNPs, XRD pattern was measured. Fig. 3 shows the spectrum of the XRD pattern included peaks at 3.35, 2.55, 2.27, 1.95, 1.75, 1.64, 1.50, 1.45 and 1.37 that can be assigned to the (1 1 0), (2 1 0), (2 1 1), (2 2 0), (3 1 1), (2 2 2), (400), (422), (511) and (440) planes, respectively, which have a good match with the standard diffraction pattern of JCPDS 39-1346 [29], [30]. The XRD pattern indicated that the MNPs were in the primitive cubic crystal structure in nature [31].

B. Characteristic of the TWW before the Adsorption Studies

The study was conducted during the March 2016 – April 2017 and the wastewater of the pre-treatment facility in Ulaanbaatar city was collected several times. From these samples, only two samples were determined considerable result of TWW. The analysis results of the samples before adsorption studies are shown in TABLE I. The pH values were 11.8 and 12.4, which were relatively high compared to those in technical requirements for MNS 5582:2006 standard [32]. The TCr in the samples was 15.2 and 33.2 mg/L. In addition, TCr of TWW, was measured, varied from 6 mg/L to 33 mg/L during the study. Average value of TCr of these samples was 15.2 mg/L and maximum value was 33.2 mg/L during the study. And the COD in the sample were 5599 and 5078 mg/L and the SS of the sample were 3900 mg/L and 1840 mg/L, respectively. The sulfide in the sample was 121.0 and 44.8 mg/L, respectively. And the turbidity of the samples was 1560 and 1452 NTU, respectively. The TCr, COD, SS and Sulfide values except of the pH values of these samples were below compared to the technical requirements for MNS 5582:2006 standard [32].

C. Adsorption Studies

Several factors can be affected to the adsorption process, such as solution pH, adsorbent dosage and contact time. In addition to these factors, the NPs size and shape also affect to the adsorption performance [3]. Several researchers Wenjun Jiang *et al.* [12], Jing Hu *et al.* [10], [11] and Thi May Do *et al.* [5] have used the synthetically prepared wastewater for the study.

Because our objective was the wastewater treatment of the

pre-treatment facility by using the MNPs, higher adsorption capacities can be obtained by optimizing above parameters in the sample. The effect some of these factors are discussed below.

1) Effect of solution pH

The pH of the solution is an important parameter which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surface charges of the adsorbent. Therefore, investigating the effect of pH on the adsorption is essential in adsorption experiments [3].

The experiments were carried out to find the optimum pH on the adsorption of TCr onto MNPs using different pH values of 2 to 11.

Fig. 4 shows the effects of pH on the adsorption of TCr as compared to MnSO_4 . As observed in the graph, when pH of the sample was increased from 2 to 11, the removal efficiency of TCr of MNPs was decreased from 98.4 to 86.6%, but MnSO_4 was increased from 69.7% to 82.4 %. The highest adsorption efficiency of MnSO_4 was obtained at pH 9. Previous study by Ozdemir *et al.* [2] using 530 mg/L MnSO_4 dose at pH value 9 in the wastewater sample showed about 96% removal of Cr (VI). In this case, because initial concentration TCr of the wastewater sample was relatively lower 15mg/L and was added 10 g/L of MNPs into it, the removal efficiency of TCr was relatively high than other studies [3], [11], [12]. From that graph, the highest adsorption efficiency of MNPs was obtained 98.4 % at pH 2.

Wenjun Jiang *et al.* [12] observed the removal efficiency of Cr(VI) increases with the decrease of pH to 4 at 60 minute. Jing Hu, *et al.* (2005, 2006) [10],[11] studied the removal efficiency of Cr(VI) decreased gradually with an increase in pH and the maximum removal of TCr occurred at about pH 2.5. The result was qualitatively similar to our result.

This indicated that a water sample with a lower pH value was favorable for the protonation of sorbent surface [3], [11]. Increased protonation could result in the increase of positively charged sites, which enhanced the attractive forces between the sorbent surface and the anions with chromium. Therefore, it will result in the increase in the adsorption capacity. On the other hand, in a water sample with higher pH, the negatively charged sites dominate and this could enhance the repulsion forces existing between the sorbent surface and the anions with chromium and therefore decrease the adsorption of anions with chromium [3].

2) Effect of the adsorbent dosage

The adsorbent dosage is another significant parameter in the examination of the adsorption capacity of an adsorbent. The determination of effect of adsorbent dosage gives an idea about the minimum amount of adsorbent need to be used for adsorption process. This value is useful in the viewpoint of cost [3].

The TCr adsorption by MNPs was performed with continuous mixing on an orbit shaker at room temperature. The TCr remaining in the sample was monitored as a function of MNPs concentration and pH 2, 5, 7. Experiments were run with the initial concentration of TCr in the sample at 15.2 g/L, and dosage of MNPs from 0.1 to 10.0 g /L. The effect of the dosage of MNPs on TCr adsorption is shown in the Fig. 5. The adsorption efficiency increased from 96.7 to 99.7% at

pH 2, from 63.5 to 96.8% at pH 5, from 32.7 to 96.4 % at pH 7, with increasing the amount of MNPs from 0.1g/L to 10g/L. This is due to increase in surface area where the adsorption takes places [12]. At MNPs dosage 0.5 g/ L, the removal efficiency of TCr in the sample was effectively increased to 98.2, 75.4, 44.4 at pH 2, 5,7, respectively. In this case, about 0.5 g/ L MNPs was enough to remove about 98.2% of TCr at initial concentration equal 15.2 g/L wastewater sample at pH 2. Further, based on the adsorption studies, a concentration of 0.5 g/ L MNPs was employed for studying the initial TCr concentration and contact time.

Although a direct comparison of MNPs with other adsorbents dosage difficult, due to the different applied experiment conditions; especially initial concentration of Cr (VI), it was found, in general, that the dosage of MNPs for Cr (VI) using equilibrium experiments at pH of 2-4 and room temperature of 22-25 °C, determined to be 0.5g/L of MNPs is higher than those of 0.3g/L (initial concentration of Cr (VI) was 500ppb) by Wenjun Jiang *et al.* [12]. And it is lower than 5g/L of MNPs (initial concentration of Cr (VI) was 50mg/L and the removal efficiency was found 97.3% by Jing Hu, *et al.* 2005 [10] and [11], respectively. And the above dosage 0.5 g/ L is higher than 150mg/L of FeCl₃ coagulant (initial concentration of Cr (VI) was 9.8mg/L and the removal efficiency was found 96% by Manjushree Chowdhury *et al.* [20].

3) Effect of the initial TCr concentration and contact time on TCr adsorption

The study was conducted during 2016-2017 and at that time TCr concentration of TWW incoming the pre-treatment facility was between 6.3-33.2mg/l. Maximum concentration of TCr was 33.2mg/l. Therefore, our main purpose was to find an optimum solution for the wastewater outputs from the pre-treatment facility. Previously, other researchers conducted this experiment in the synthetic solutions Cr(VI) [5], [10], [11], [12].

The concentration of TCr in the wastewater samples vs. the adsorption time at various initial concentrations of TCr is illustrated in Fig. 6. Experiments were run with the initial concentration of TCr from 6.3- 33.2 mg/L, while varying the contact time from 0 to 120 min, and dosage of MNPs 0.5 g/ L at pH 2. The adsorption of TCr by MNPs was rapid in the first 10 min followed by a slow TCr adsorption stage at longer contact times as illustrated in Fig. 6.

The concentration of TCr in the samples at equilibrium gradually increases with increases in the initial concentration of TCr. After 10 minute, the observed removal efficiency of TCr by MNPs at initial TCr concentration of 6.3, 10.8, 15.2, 22.5, 28.5 and 33.2 mg/l were 98.6%, 98.4%, 98.2%, 90.3%, 84.3% and 77.4%, respectively. Under these experimental conditions, the removal efficiency of TCr modestly decreased as a function of the increase in initial concentrations of TCr. Chromium ions were adsorbed onto MNPs rapidly, and equilibrium was established at 40 minutes. After 40 minute, the observed removal efficiency of TCr by MNPs at initial TCr concentration of 6.3, 10.8, 15.2, 22.5, 28.5 and 33.2 mg/l were 99.7%, 99.5%, 99.3%, 97.5%, 96.1% and 96.7%, respectively.

The results shown in Fig. 6 and Table II indicate that the

TCr adsorption capacity reached 62.4 mg/g within 40min at TCr concentrations of 33.2mg/L. And the Cr(VI) adsorption capacity reached 8.04 mg/g within 40min at Cr(VI) concentrations of 4.6 mg/L. This might be due to the fixed amount of MNPs, meaning that the number of available active sites for adsorption was kept constant. Thus, no more increase in the adsorption efficiency was observed above 33.2 mg/L.

Few studies have been conducted for aqueous Cr (VI) removal and adsorption capacities of some of the MNPs. Hu, Chen *et al.* [10], [11] and Wenjun Jiang *et al.* [12] studied the performance and mechanism of different heavy metals (Cr(VI), Cu(II), and Ni(II)) removal from industrial wastewater and Cr (VI) from drinking water using MNPs. When comparison with other MNPs adsorbents capacity, that the adsorption capacity of MNPs our prepared is higher than those of 1.62mg/g at pH 4 for Cr (VI) by Wenjun Jiang *et al.* [12] and it is below than 17 mg/g and 19.2 mg/g by Jing Hu *et al.* [10], [11] for Cr (VI), respectively.

The rapid adsorption of metals is perhaps due to external surface adsorption. Since nearly all of the adsorption sites of MNPs exist on the exterior of the adsorbent compared to the porous adsorbent, it is easy for the adsorbent to access the active sites; hence, a rapid approach to equilibrium. This result is encouraging, as the equilibrium time is one of the important engineering parameters for an economical wastewater treatment plant [11].

D. Characteristic of the TWW after the Adsorption Studies

Turbidity, odor and appearance: The color appearance of untreated wastewater was found bluish green. The odor was found very pungent smell in untreated effluent and unobjectionable odor was observed after the treatment with MNPs. In Fig. 7 and TABLE III, the reduction in turbidity of the TWW was showed. Initially the turbidity of the wastewater was found to be 1452 NTU, which was higher than the previous studies [33], [34]. After treating the wastewater with MNPs the turbidity was reduced to 9.5 NTU, which was 152 times below than the untreated wastewater value.

TCr: The TCr value of the untreated and treated wastewater were 33.2 and 1.09 mg/l, respectively (TABLE III), which the TCr value of the untreated wastewater was higher than the previous studies [12], [20], [33] and which was lower than the other previous studies same with MNPs [10], [35], [11]. The results shown in Fig. 7. and TABLE III indicate that after 40 minute, the removal efficiency of TCr by MNPs was 96.7% (1.09 mg/L) and the value was well below the standards permissible limits of MNS 6561:2015. If initial concentration TCr in the untreated wastewater was increased to higher 33 mg/l, in the treatment by MNPs the value of TCr may be higher than the standard MNS 6561:2015 [18].

pH: The pH value of the untreated and treated wastewater were 12.4 and 2.85, respectively (TABLE III). Before the treatment, pH value of the untreated wastewater was highly alkali, which was similar to the previous studies [36] and also was higher than the other previous studies [20], [33], [35]. After treatment by MNPs, pH value of the treated wastewater was highly acidic. Similar observation was reported by

Wenjun Jiang *et al.* [12] that the maximum removal of TCr occurred at pH 4 and Jing Hu *et al.* [10], [11] the maximum removal of TCr occurred at about pH 2.5. Therefore, after the treatment, the treated wastewater must be neutralized.

SS: The SS value of the untreated and treated wastewater were 1840 and 51.0 mg/L, respectively. Before the treatment, SS value of the untreated wastewater was similar to the previous studies [33] and which was lower than the other previous studies [20], [36]. After 40 minutes, the removal efficiency of SS by MNPs was 97.2%, which were well below the recommended standard limits of MNS 6561:2015 [18].

COD: The COD value of the untreated and treated wastewater were 5078 and 564 mg/L, respectively (TABLE III). Before the treatment, COD value of the untreated wastewater was similar to the previous studies [20] and which was higher than the other previous studies [33]. After 40 minutes, the removal efficiency of COD by MNPs was 88.9%, which were well below the recommended standard limits of MNS 6561:2015 [18].

Sulfide: The sulfide value of the untreated and treated wastewater were 44.8 and 3.4 mg/L, respectively. Before the treatment, sulfide value of the untreated wastewater was lower than the other previous studies [33], [36]. After 40 minutes, the removal efficiency of sulfide by MNPs was 92.4%, which were well below the recommended standard limits of MNS 6561:2015 [18].

IV. CONCLUSION

Magnetic MNPs were synthesized by a co-precipitation method, characterized and employed for TCr removal. The adsorption studies illustrated that the MNPs were very effective for the removal of TCr from TWW. Maximum removal efficiency of TCr in the TWW was achieved 96.7% at an optimum condition (pH 2, MNPs dose was 0.5g/L, initial concentration of TCr was 33.2 mg/L, 40 minutes) at room temperature. It is observed that the best efficiency in removing major physico-chemical parameters (TCr, SS, COD, sulfide and turbidity) in the TWW, which are well below the recommended standard limits for MNS 6561:2015. Thus the study suggests that the treatment with MNPs could be promising in order to reduce pollutants from the other TWW.

TABLE I: CHARACTERISTICS OF UNTREATED WASTEWATER AND COMPARE WITH STANDARD TECHNICAL REQUIREMENTS

| Parameters | Units | Sample 1 | Sample 2 | MNS 5582:2006[32]. |
|------------|-------|----------|----------|--------------------|
| pH | - | 11.8 | 12.4 | 9 |
| TCr | mg/l | 15.2 | 33.2 | 100 |
| COD | mg/l | 5599 | 5078 | 6200 |
| SS | mg/l | 3900 | 1840 | 5500 |
| Sulfide | mg/l | 121.0 | 44.8 | 150 |
| Turbidity | mg/l | 1560 | 1452 | - |

TABLE II: ADSORPTION CAPACITY AND INITIAL CONCENTRATION OF TWW

| Co,TCr (mg/l) | Co,Cr(VI) (mg/l) | Qe,TCr (mg/g) | Qe,Cr(VI) (mg/g) |
|---------------|------------------|---------------|------------------|
| 6.3 | 1.2 | 12.56 | 2.36 |
| 10.8 | 3.6 | 21.49 | 7.18 |
| 15.2 | 3.2 | 30.18 | 6.26 |
| 22.5 | 3.7 | 43.87 | 4.84 |
| 28.8 | 4.3 | 55.35 | 7.86 |
| 33.2 | 4.6 | 62.21 | 8.04 |

TABLE III: CHARACTERISTICS OF TWW AND TREATED WASTEWATER COMPARED WITH STANDARD PERMISSIBLE LIMITS

| Parameters | Units | Untreated Sample 2 | Treated Sample 2* | MNS 6561:2015[18] |
|------------|-------|--------------------|-------------------|-------------------|
| pH | - | 12.4 | 2.85 | 6-9 |
| TCr | mg/l | 33.2 | 1.09 | 1 |
| COD | mg/l | 5078 | 564 | 800 |
| SS | mg/l | 1840 | 51.0 | 400 |
| Sulfide | mg/l | 44.8 | 3.4 | 5 |
| Turbidity | mg/l | 1452 | 9.5 | - |

*(0.5 g/L MNPs, pH 2, 40 minute)

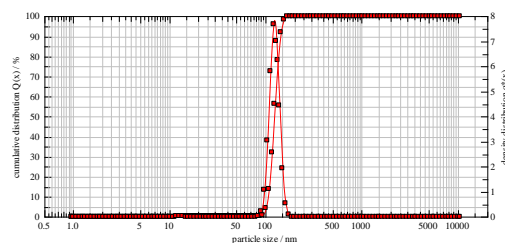


Fig. 1. Particle size analyzer image of MNPs.

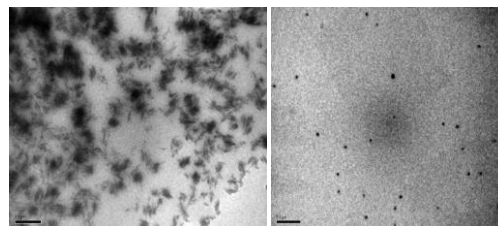


Fig. 2. TEM image of MNPs in deionized water.

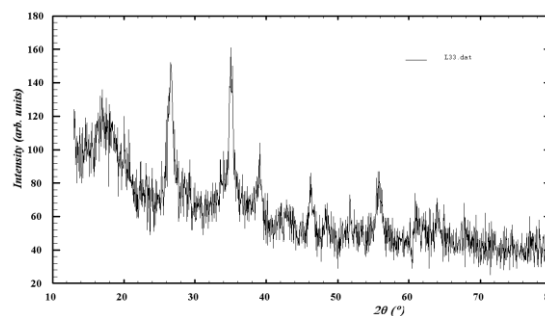


Fig. 3. XRD patterns of MNPs.

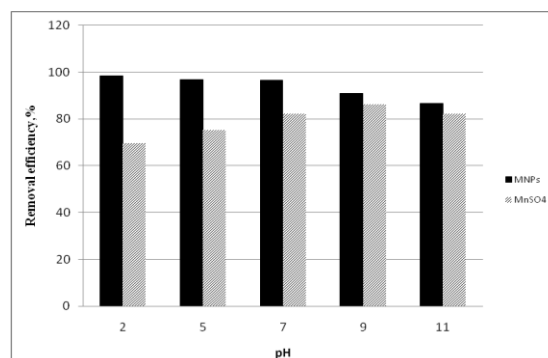


Fig. 4. Effect of pH on TCr adsorption (MNPs, MnSO₄ 10g/l, initial concentration TCr was 15mg/l, 10 minute)

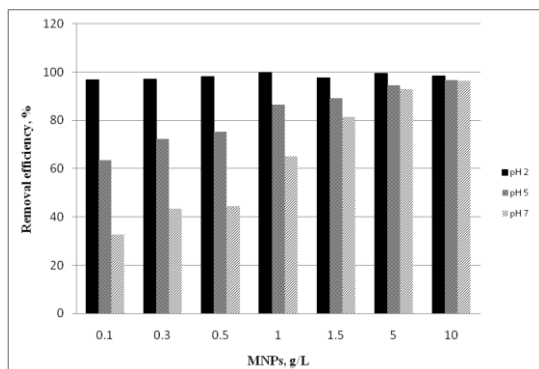


Fig. 5. Effect of the dosage of MNPs on TCr adsorption (initial concentration TCr was 15mg/l, 10 minute).

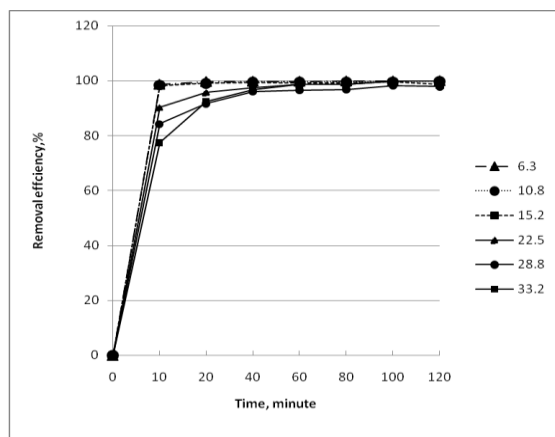


Fig. 6. Effect of the initial concentration TCr (mg/l) and contact time on TCr adsorption.

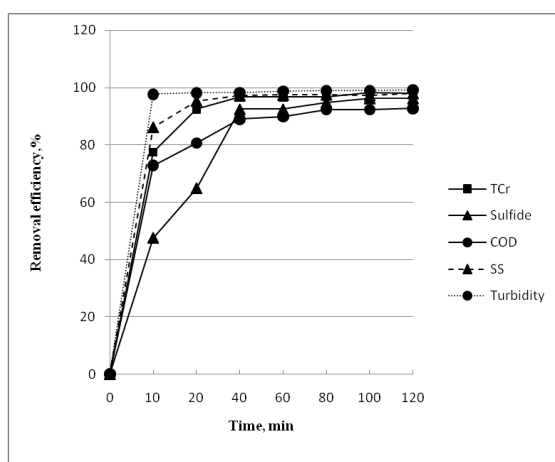


Fig. 7. Effect of time on removal percentage (%) of some physico-chemical parameters (Sample 2, pH 2, MNPs 0.5 g/L).

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