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Preparation of Hematite Nano Particles from Galvanizing Effluents for the Applications in Heavy Metal Removal

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ABSTRACT

Due to climate change on earth, governments are pursuing the policy of gradually reducing Greenhouse Effects. For example, country like Germany has The demand for safe drinking water grows day by day together with the increasing world population. Meanwhile water resources become increasingly scarce, and quality of natural water decreases due to a combination of natural and anthropogenic factors. Industry and agriculture have become a premiere source of hazardous constituents, along with natural processes such as rock weathering and volcanic eruptions. The ability to remove hazardous components, particularly heavy metals from water depends on the selected technology and nature of pollutant. Water purification technologies, mostly involved with sorption and ion-exchange processes, often uses natural iron oxides as ion-exchangers for removal of harmful contaminants from water. These technologies are based on the unique cation-exchange behavior of iron oxides, thus making this sorbent limited to cation removal. Arsenic, copper and nickel are commonly found in water supplies and, therefore, are selected for this study to represent heavy metals in water systems. In this work, hematite nanomaterials were synthesized from the galvanizing effluent collected from the LTL Galvanizers at Makola, Sri Lanka. The industry generates approximately 50 m^3 of galvanizing effluent per month and it composes both iron and zinc chlorides. To synthesize pure iron oxide materials, we used the effluents from none re-galvanized chemical baths, which does not contain any zinc chlorides. The synthesized materials were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Sorption behaviors of As(III), Cu(II) and Ni(II) were examined batch-wise as a function of pH, temperature, contact time, adsorbent dosage and initial metal ion concentration. Residual concentrations of As(III), Cu(II) and Ni(II) in the solution were determined by the inductively coupled plasma mass spectroscopy (ICP-MS). The adsorption studies were performed by changing one of the conditions while keeping all others fixed. According to the results, maximum percent removals (%) for all metal ions tested were reached within a short period of 30 minutes. For a given parameter the maximum percent removal (%) of both Cu(II) and As(III) reached more than 95%, while the Ni(II) had percent removal between 35% and 65%.

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Introduction

Water pollution by heavy metals is a global issue and may occur due to several natural or anthropogenic activities such as mining and smelting operations, industrial production and during domestic and agricultural use of metals and metal-containing compounds [1]. Water pollution of arsenic has been reported in many countries all over the world and it has become a major problem associated with agriculture. Arsenic contaminated water is readily absorbed by living organisms and cause life term diseases such as kidney related diseases, cancer, neurological disorder, nausea, and loss of appetite [2]. Acute oral poisoning primarily leads to hemorrhagic gastritis and colitis in human, ultimately causing damage to the kidney. Nickel is a non-biodegradable toxic metal ion present in wastewater, which may cause adverse health effects such as anemia, diarrhea, encephalopathy, hepatitis, lung and kidney damage, gastrointestinal distress, pulmonary fibrosis, renal edema, skin dermatitis, and central nervous system dysfunction [3]. Among these health effects, skin dermatitis is the most prevalent effect of nickel. On the other hand, copper is an essential trace nutrient that is required in 5–20 µg/g by humans but can be toxic if exceeding 20 µg/g. The most bioavailable and therefore the most toxic form of copper is the cupric ion (Cu^{2+}) [4]. Excess exposure to copper in short term causes irritants, dermatitis, and gastrointestinal distress, while long-term exposure causes liver and kidney diseases, Wilson's disease, coma, and eventual death.

Several conventional methods are available for the removal of heavy metals from aqueous solutions such as solvent extraction, chemical precipitation, coagulation, reverse osmosis, distillation, ion-exchange, adsorption, electro-deposition etc [5]. In this study, adsorption of heavy metals in water samples on nano-hematite was chosen as the mode of their removal, which is one of the superior

methods for the removal of heavy metals from wastewater. The method is cost effective, highly efficient, and easy to operate even in an industrial scale [6]. The adsorption is affected by several factors such as contact time, amount of adsorbent, temperature, concentration of adsorbate and pH of solution.

Utilizing nano materials for the heavy metal removal has become a promising avenue due to being able to enter the contamination region where microparticles cannot. And the removal efficiencies increase rapidly in nanomaterial engaging processes, which may be attributed to the greater availability of the exchangeable sites or surface areas of these nanostructures [7]. A variety of nanomaterials have been studied for the removal of heavy metals from water, including metal oxide nanoparticles, carbon nanomaterials and nanocomposites [8-10]. Metal oxide nanoparticles (MONs) are potential heavy metal adsorbents because of their large surface area and high surface activities due to the size-quantization effect. Among various MONs, ferric oxide nanoparticles such as hematite (α- Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) are extensively used in removing heavy metals. They are low-cost materials because of the facileness of resources and ease in synthesis [11].

In the search for raw materials for the development of these iron oxide nanomaterials, we were able to identify that hot dip galvanizing plants generate large quantities of $FeCl_3$ as waste. The LTL Galvanizers Pvt. Ltd, located in Makola, Sri Lanka, produces approximately 50 m^3 of $FeCl_3$ per month and dumps as scheduled waste. In this research, this waste material was converted to hematite nanomaterials and applied in the heavy metal removal. We believe that by manufacturing these nanomaterials in bulk amounts would eliminate two major environmental complications; heavy metal accumulation in natural water sources and aggregation of $FeCl_3$ as waste.

Methods and Materials

Characterization of nanostructures as well as the desiring properties of the modified nanomaterials were done using several different techniques. The XRD analysis was performed to identify crystalline phases of nanomaterials synthesized and to calculate average particle size of the crystalline phase. Scanning electron microscopy (SEM) was used to investigate on the morphology of the prepared materials. Residual concentrations of As(III), Cu(II) and Ni(II) in the solution were determined by the ICP-MS.

Material

The $FeCl_3$ liquid sludge obtained from galvanizing effluent, together with NaOH and H_2O_2 were used to synthesize Fe_2O_3 nanostructures. Copper(II), nickel(II), and arsenic(III) stock solutions were prepared using $Cu(NO_3)_2$, $NiCl_2$, and As_2O_3 respectively, which were obtained from Sigma Aldrich in analytical grade.

Methods

Synthesis of Fe_2O_3 Nanoparticles

The nanoparticles were synthesized by chemical precipitation method adding 0.05 M NaOH to a mixture of 0.01 M H_2O_2 in a 0.005 M $FeCl_3$ solution (prepared using the above-mentioned liquid effluent) while stirring vigorously using a magnetic stirrer until the pH of the solution is reached 9. (The ratio of Fe(II) to Fe(III) present in the liquid effluent has been determined separately using a titration method to determine the required amount of H_2O_2 needed to add). The precipitate formed was filtered and washed with distilled water and the pH of the solution was adjusted to 7. Then the solution was heated, and all the water was evaporated at 100°C, and the precipitate obtained was washed again with distilled water and dried. The characterization of the prepared particles was carried out with XRD and SEM techniques.

Preparation of Various Metal Ion Solutions

Stock solutions of arsenic(III) (1 ppm), copper(II) (1 ppm) and nickel(II) (1 ppm) were prepared by dissolving appropriate amounts of arsenic trioxide, (As_2O_3), copper nitrate ($Cu(NO_3)_2$) and nickel chloride ($NiCl_2$) in 1000 mL of distilled water. Working solutions (influent) with different concentrations were prepared by appropriate dilution of the stock solution.

Kinetic Studies

Column studies were carried out in a column made of Pyrex glass with 1.8 cm internal diameter and 20 cm length. The column was fitted with the adsorbent by tapping, so that maximum amount of adsorbent would be packed without gaps. In each trial, 10 ml of artificially contaminated water with a single heavy metal of known concentration was transferred to the column and the effluent solution was collected at regular intervals of time. The concentration of metal ions in the effluent after the adsorption was determined using ICP-MS. The adsorption behavior was studied under five different conditions: different contact time, different pH, different metal ion concentration, different dosage of iron oxide nanoparticles, and different temperature. First, the effect of contact time was examined to determine the optimum contact time at which the nanoparticles are saturated, and the adsorption is at equilibrium. Artificially contaminated water with above mentioned heavy metal solutions (10.00 mL) was treated with 0.350 g of developed iron oxide nanoparticles in each trial at different periods of contact times ranging from 5 min up to 40 min (5, 10, 15, 20, 25, 30, 35 and 40 min), at room temperature (21.5 ± 1°C) and effluent was collected. It was found that after 30 minutes the system reaches the maximum percent removal (%) and therefore decided to retain the influent for 30 min in the column during all the other studies. The pH was adjusted by adding 0.100 M HCl and 0.100 M NaOH solutions into the ultrapure deionized water. Eight solutions of different pH (from pH 3 to pH 10) were prepared. Portions of 10.00 mL of solutions containing 1 ppm of metal ions were treated for 30 min with 0.350 g of nanoparticles at room temperature (21 ± 1°C). The concentration of metal ions in the effluent was measured by ICP-MS and the percent removal (%) of heavy metals was calculated. Three trails for each pH were conducted. For studying the effect of concentration, eight different concentrations were prepared for all the three heavy metals (100, 200, 300, 400, 500, 600, 700 and 800 ppb, respectively). All prepared solutions were treated for 30 min with 0.350 g of nanoparticles at room temperature and at pH ~7. Three trials were carried out for each concentration. To determine the effect of different dosage of iron oxide nanoparticles, five different masses of nanoparticles (0.100, 0.200, 0.300, 0.400 and 0.500 g, respectively) were used to treat 10.00 mL of each metal ion solution (1 ppm) at room temperature, at pH ~7. In the temperature study, the 10 mL solution portions (1 ppm) in PTFE tubes treated with 0.350 g of nanoparticles and kept for 30 min, were tested in eight different temperatures (0, 10, 20, 30, 40, 50, 60 and 70°C, respectively). After the times end, the solutions were centrifuged for 5 min and then filtered using 0.2 ⌈m filters. Finally, the samples were measured using ICP-MS.

The equilibrium concentrations of heavy metals were determined after different treatments with nanoparticles. And the percent metal removal (%) was calculated using the following equation

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where C_o is the initial concentration and C_e is the concentration at equilibrium, after treatments with nanoparticles.

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} 100\%$$

Results and Discussion

The Study of Applicability of Iron Oxide Nanoparticles for Heavy Metal Removal

Effects of Contact Time

The concentrations of heavy metals have been determined after different times of treatments with nanoparticles, varying between 5 to 40 minutes. The percent metal removal (%) has been calculated using the given equation. According to the fig.1, all metals reached maximum adsorption within 30 minutes, and it was relatively high and above 95% for As and Cu. This indicates that after 30 minutes, the concentration of metals was at equilibrium (Ce), at which the amount of metal desorbed is equal to the amount of metal adsorbed. Compared to As and Cu, Ni(II) showed a lower adsorption around 35%.

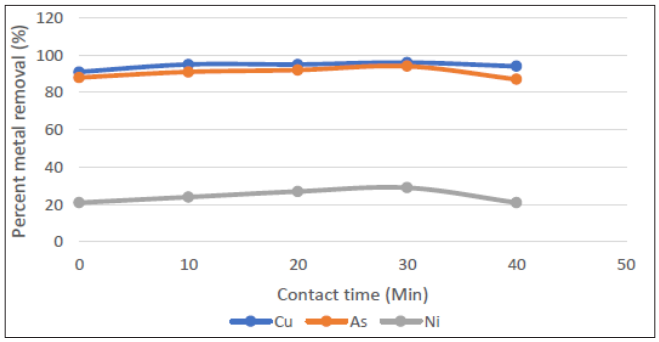

Figure 1: Percent Removal (%) of Metals Versus Contact Time

Effects of pH

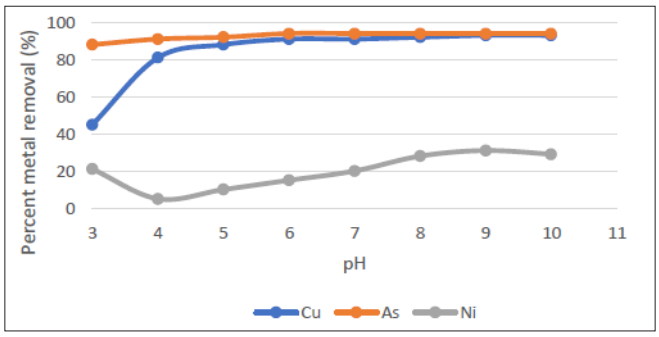

Figure 2: Percent Removal (%) of Cu, As & Ni at Different Ph

The adsorption behavior of metals under different pH shown in fig.2 indicates that there are electrostatic interactions between the adsorbent and the metal (adsorbates). At various pH, the nanoparticles acquire different polarities. They are positively charged at pH below 4.6, and negatively charged at pH above 4.6. This is due to the higher concentration of protons (H^+) that surrounds the nanoparticles at lower pH. Therefore, positive metals will have higher electrostatic repulsion with the adsorbent surface at lower pH and, as a result, the adsorption of positive metals will reduce. Increasing pH will decay the competition between H+ and the positive metals for surface sites and the adsorption of the positive metals with iron oxide nanoparticles will increase. As pH increased, the percent removal for all the metals increased as well reaching a maximum level. At much lower pH (Lower than pH 4) both Cu(II) and Ni(II) removal is comparatively low and the percent removal of Ni (II) decreased back to 5% around pH 4 and 5. After pH 5, the percent removal of both As(III) and Cu(II) are increased more than 95% and the removal of Ni (II) is comparatively low. As(III) and Cu(II) remained positively charged and obtained higher removal percentages in the more alkali solutions.

Effect of Heavy Metal Concentration

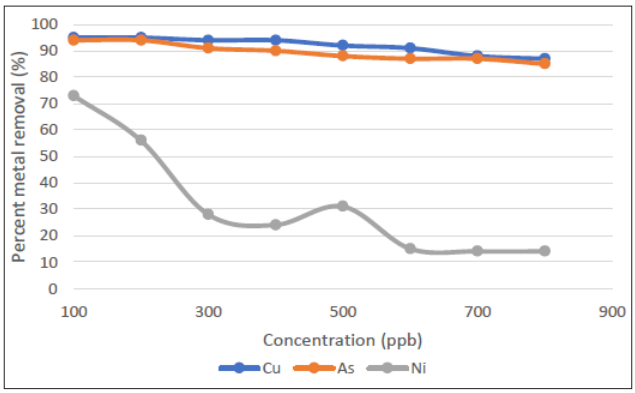

Figure 3: Percent Removal (%) of Metal Versus Concentrations of Cu, As & Ni. 10ml of Aqueous Solution were Treated with 0.35 g $\langle Fe_2O_3$ nanoparticles at room temperature and at Ph~7.

The increasing concentration of the metal did not significantly affect the adsorption of the metals such as As(III) and Cu(II). The percent removal remained around 95% for both. Studies on the effect of initial concentration were conducted by varying it from 0.1 mg/L to 0.8 mg/L and keeping adsorbent dosage of 0.35 g at neutral pH (7) and contact time of 30 minutes. In the case of arsenic when the initial concentration is 0.1 mg/L, the efficiency of removal was increased to 95%, which decreased to 85.0 % at 0.8 mg/L. Same behavior can be observed for Cu (II) as well. It is observed that there was a distinguishable decrease in the percentage of removal of Ni^{2+} and Co^{2+} corresponding to an increased initial concentration.

Effect of Iron Oxide Nanoparticles Dosage

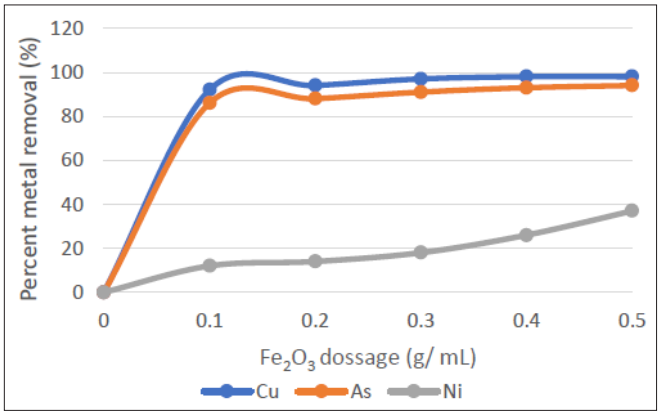

Figure 4: Percent Removal (%) Versus $\langle$-Fe_2O_3 Dosages. 10ml of Aqueous Solution (1ppm) were Treated at Room Temperature and at Ph~7. Contact time = 30 minutes.

The adsorption efficiency increased with the increasing dosage of nanoparticles (Fig. 4). This is due to increase in surface area where the adsorption takes place. About 0.3 g of the iron oxide nanoparticles was enough to remove about 95% of As(III) and 100% of Cu(II) at concentration equal to 1 ppm in 10 mL aqueous solution. The removal is more for higher adsorbent dose. This

may be due to the availability of more adsorption sites. Removal efficiency was found to increase proportionally with the amount of the adsorbent until a certain value was reached (0.4 g); afterwards, the removal efficiency is maintained constant even if adsorbent is added. Still, Ni (II) removal is comparatively low which is similar with previous cases.

Effect of Temperature

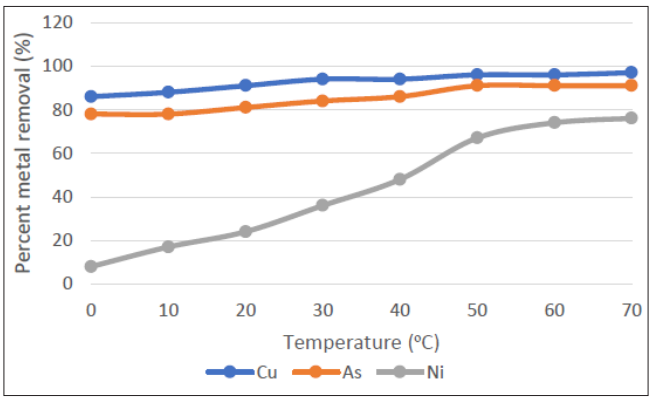

Figure 5: Percent Removal (%) Versus Different Temperature (°C). 10ml of Aqueous Solution (1ppm) were Treated with 0.35g at Ph~7. Contact Time = 30 minutes.

According to the Fig. 5 the adsorption of As(III) and Cu(II) did not change noticeably as a function of temperature. Removal efficiencies of both metals maintained above 90% after 50°C. Ni(II) did not show a reproducible results until 30 °C, but removal of the metal similarly increased as temperature increased and the efficiency reached almost 75% at 70 °C showing the highest removal obtained.

Figure 6: Physical Appearance of Prepared Hematite (Fe_2O_3) Nanomaterials.

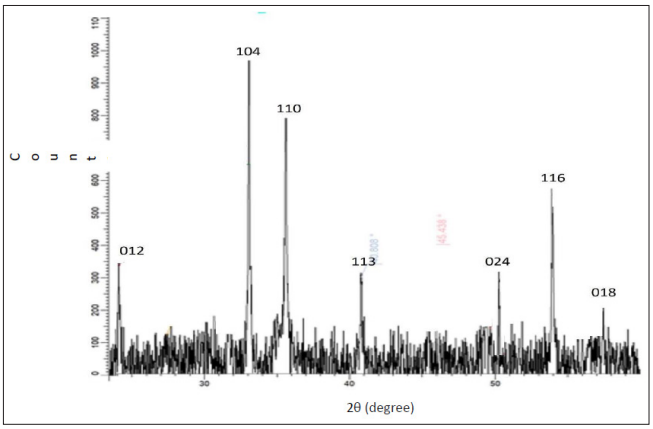

Figure 7: XRD Pattern of Developed Iron Oxide Nanomaterials

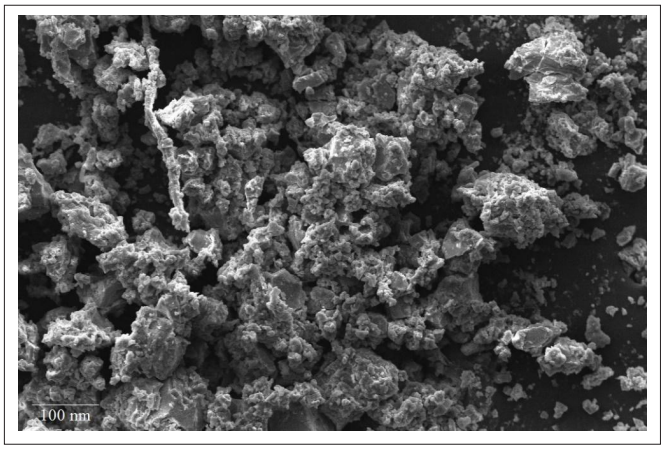

Figure 8: SEM of Developed Iron Oxide Nanomaterials

Prepared iron oxide nanomaterials were red brown in color (Fig. 6) and readily dispersed in water. As shown in Fig.7, the diffraction peaks at 2θ values of 24.36° (012), 32.48° (104), 36.62° (110), 42.46° (113), 51.23°(024), 53.98° (116) and 57.46° (018) correspond to the hematite (α Fe_2O_3) structure of iron oxide [12]. These results, therefore, indicate the successful formation of hematite (α Fe_2O_3) by the chemical precipitation method. The crystallite size of the hematite was calculated from its highest intense peak in the XRD patterns using Debye Scherer's equation and the estimated average crystallite size was 88.32 nm. According to the SEM image, particles are well within the nano-range (below 100 nm) and have sharp flake-like morphologies (Fig. 8). These smaller sheet-like structures can provide much larger surfaces to absorb the heavy metals in a considerably efficient manner.

Conclusion

Hematite iron oxide (Fe_2O_3) nanoparticles synthesized by chemical precipitation method using a galvanizing effluent as iron supply, demonstrate excellent practical applicability for As(III) and Cu(II) removal from aqueous solutions. More than 95% removal efficiency for As(III) and Cu(II) was obtained by hematite iron oxide nanoparticles from aqueous solutions at a low adsorbent dose, and very short time in a wide range of pH. The results indicate that the prepared iron oxide nano-materials were more efficient to remove As(III) and Cu(II) than Ni(II).

Prepared iron oxide nanomaterials were flakes like and well within the nano-range. They were dark brownish red in color which is characteristic for the hematite form of iron oxide. XRD data obtained confirms the crystal structure of hematite and estimated average crystallite size calculated using Debye Scherer's equation was 88.32 nm.

The influences of the initial pH, temperature, contact time and dosage of the adsorbent on adsorption performance have been experimentally verified by column method. For all the metals tested, maximum adsorption was reached in 30 minutes. According to the pH effect on the adsorption behaviors, it was verified that there was electrostatic interaction between the hematite nanoparticles and the metals tested. Fe_2O_3 nanoparticles are positively charged (coated by H^+) at low pH and negatively charged at relatively high pH therefore it undergoes electrostatic repulsion with the positively charged particles at low pH. This maybe the reason to have lower absorption values at low pH. It could be concluded that the absorption ability was increased with increasing temperature and Fe_2O_3 dosage but decreased with increasing metal concentration.

The explained method of preparing hematite Fe_2O_3 nanomaterials from galvanizing effluent is much simpler and effective. This method can be utilized to convert an industrial waste to a much convenient value-added material for removing heavy metals such as As (III) and Cu (II) from aqueous solutions.

References

1. Kumar A, Ali M, Kumar R, Rahman MS, Srivastava A, et al. (2020) High Arsenic Concentration in Blood Samples of People of Village Gyaspur Mahaji, Patna, Bihar Drinking Arsenic-Contaminated Water. Exposure and Health 12: 131-140.2.
2. Hashemzadeh M, Nilchi A, Hassani AH (2019) Synthesis of novel surface-modified hematite nanoparticles for lead ions removal from aqueous solution. Materials Chemistry and Physics 227: 279-290.
3. Gunawardhana BP, Gunathilake CA, Dayananda KE, Dissanayake DM, Mantilaka MM et al. (2020) Synthesis of Hematite Nanodiscs from Natural Laterites and Investigating Their Adsorption Capability of Removing Ni2+ and Cd2+ Ions from Aqueous Solutions. Journal of Composites Science 4: 57.
4. Al-Saad Khalid, Amr MA, Hadi DT, Arar SR, Al-Sulaiti, et al. (2012) Iron oxide nanoparticles: applicability for heavy metal removal from contaminated water. Journal of Nuclear Sciences and Applications 45: 335-346.
5. Nizamuddin S, Siddiqui MT, Mubarak NM, Baloch HA, Abdullah EC et al. (2019) Iron oxide nanomaterials for the removal of heavy metals and dyes from wastewater. Nanoscale materials in water purification 1: 447-472.
6. Wilschefski SC, Baxter MR (2019) inductively coupled plasma mass spectrometry: introduction to analytical aspects. The Clinical Biochemist Reviews 40: 115.
7. Bhateria R, Singh R (2019) A review on nanotechnological application of magnetic iron oxides for heavy metal removal. Journal of Water Process Engineering 31: 100845.
8. Sahu UK, Mahapatra SS, Patel RK (2017) Synthesis and characterization of an eco-friendly composite of jute fiber and Fe2O3 nanoparticles and its application as an adsorbent for removal of As (V) from water. Journal of Molecular Liquids 237: 313-321.
9. Bradl HB (2005) Chapter 1 Sources and origins of heavy metals. Interface Science and Technology 6: 1-27.
10. Oremland RS, Stolz JF (2003) The ecology of arsenic. Science 300: 939-944.
11. Masironi R, Koirtyohann SR,Pierce JO(1977) Zinc, copper, cadmium and chromium in polished and unpolished rice. Science of the Total Environment 7: 27-43.
12. Hjiri M(2020) Highly sensitive NO2 gas sensor based on hematite nanoparticles synthesized by sol–gel technique. Journal of Materials Science: Materials in Electronics 31: 5025-5031.

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