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Synthesis and application of modified magnetic nanoparticles for removal of Cyanide from aqueous solutions

ABSTRACT

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Cyanide is one of the major Environmental pollutants in industrial wastewater. Entrance of it to existence environmental contains very health hazardous. The cyanide can be removed from aqueous solutions in many ways, but most of these methods are expensive. In the present study, novel magnetic nanoparticle modified with a polydentate ligand is used to remove cyanide. The procedure is efficient and cost-effective. In this study, novel magnetic nanoparticle (Fe_3O_4-SiO_2 –Met) is used to remove cyanide. Various parameters affecting the removal rate such as pH (9-11), the amount of absorbent (0.01, 0.03, 0.05gr) and contact time (4-12 hr) were evaluated. Data from the experiment were analyzed with a mathematical model of the smallest sum of squares. The relationship between time and pH value on the removal of cyanide are linear. Nevertheless, the amount of the adsorbent and time are effective. Absorbent weight is increased from 0.01 to 0.05 g and removal efficiency reaches from 20% to 60%. With increasing contact time from 4 to 12 hours removal efficiency reaches from 30% to 55%. The finding of this research is introducing modified nanoparticles Fe_3O_4-SiO_2 –Met as an adsorbent for removing cyanide.

Keywords: *Cyanide; Magnetic nanoparticles; Adsorption efficiency; Absorbent weight; Environmental pollution.*

INTRODUCTION

Cyanide is widely used in industries, in a variety of forms, including HCN, salts (such as NaCN or KCN). Hydrogen Cyanide as an inhalation poison and it is used in chemical synthesis. Cyanide salts used on the gold extraction [1], and hardening of metal, metal plating, photography, coal coking. Perhaps one of the most lucrative and important cases of cyanide consumption and most of the mining industry to extract precious metals like gold and silver as well as materials recovery be low grade, The extraction of valuable metals such as copper, nickel, cobalt, molybdenum separation processes is also desirable metals from tailings and concentrate building used to be[2,3].

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Humans are in close contact with cyanide in their daily life through food, drink, smoking, medicines and while using products which contain cyanide [22]. Cyanide inhibits several cellular enzymes including cytochrome oxidase, which is a key enzyme in the cellular respiratory chain. At short-term exposure, cyanide causes rapid breathing, tremors, and other neurological effects Skin contact with liquids containing cyanide may produce irritation and sores [23]. Cyanide is included in the CERCLA priority list of hazardous substances [4]. Therefore, environmental regulations require reducing the cyanide concentration in wastewater to below 0.2 mg/L prior to discharge into the environment. The current U.S. Environmental Protection Agency water quality criterion for cyanide is 5.2g/L for freshwater aquatic life, and 1.0g/L for marine aquatic life and wildlife [5]. According to the United States Environmental Protection Agency (USEPA), the cyanide concentration in electroplating process wastewaters must be reduced to less than 5.0 mg/L for facilities discharging less than 10,000 gal/d or 1.9 mg/L for facilities discharging more than 10,000 gal/d [6].

Cyanide adsorption by waste materials has been reported only rarely; for instance, Yazici et al reported a low cyanide adsorption capacity of 0.401 mg/g onto rice husk [7]. However, this technique is unattractive from both economic and environmental perspectives because it requires the use of chemical compounds and does not degrade the full range of cyanide compounds] 8]. Dash et al. have recently reviewed and compared methods that have been investigated f the removal of cyanide from wastewater [9]. Although biodegradation is usually the preferred technique for treating wastewater due to its cost-effectiveness and environmental friendliness, there is little information on the use of bioprocesses for treatment of cyanide-laden wastewater [10,11].

In a recent publication, Han et al. describe a number of processes such as alkaline chlorination, sulfur oxidation, hydrogen peroxide oxidation, acidification–volatilization– recovery (AVR), activated carbon adsorption, ion exchange, ozonation, photochemical destruction and microbiological degradation[12-13].

Magnetic nanoparticles (MNPs) are receiving increasing interest in recent years owing to their unique properties and potential in various fields such as catalysts industrial [14, 15], magnetic fluid, [16] Biotechnology [17], magnetic resonance imaging contrast agents [18], data storage [19], drug delivery and cellular targeting [20] and spatially eliminate environmental pollution [21].One of the challenges of use particles with diameters of less 100 nm are difficult to separate by filtration techniques and use of expensive ultracentrifugation . In contrast, magnetic nanoparticles can be easily separate by applying an external magnet and these properties make them useful in the chemical industry for the extraction of samples.

In this study novel magnetic nanoparticle (Fe_3O_4-SiO_2 –Met) is used to remove cyanide. Various parameters affecting the removal rate such as pH, the amount of absorbent and contact time were evaluated.

The Parabolic Trough Collector focuses direct normal irradiance or beam radiation onto a focal line on the collector axis. An absorber tube with water or temperature stable synthetic oil flowing inside absorbs the concentrated solar energy and raises its temperature at the focal line.

EXPERIMENTAL

Chemicals

$FeCl_2.4H_2O$, $FeCl_3.6H_2O$, ammonium hydroxide(28%NH_3 in water), hydrochloric acid (37%), tetraethylorthosilicate (TEOS), 3-chloropropyl trimethoxysilane (CPTS), trisodium citrate, KI, K_2CO_3, NaCN،($AgNO_3$) were purchased all from Merck. NaOH and metformin hydrochloride were purchased all from Aldrich. PH was controlled by the addition of 1M NaOH, if required.

Stock cyanide solution

Cyanide solution was prepared by diluting aliquots of 1g/L stock cyanide solution into distilled water. The stock solution was made by dissolving NaCN in distilled water. All experiments were carried out at a constant room temperature of 24±3◦C.

Preparation of Fe_3O_4/SiO_2-Met

Fe_3O_4/SiO_2-Met were prepared following the procedure of Alizadeh et al.[25]. Briefly, 1 mL

(5 mmol) of CPTS was dissolved in 100 mL of dried toluene, was added to 1 g of Fe_3O_4/ SiO_2 and the solution was stirred for 18 h at 60 ˚C. The chloropropyl-functionalized solid (Fe_3O_4/ SiO_2-Cl) was washed with toluene, separated by a magnet, and dried in vacuum. The obtained magnetic solid was used in the following step to synthesize metformin-modified silica-coated MNPs. The prepared Fe_3O_4/SiO_2-Cl (1 g) and KI (1.66 g, 10 mmol) were added to a solution of metformin hydrochloride (0.21 g, 5 mmol) and K_2CO_3 (10 mmol, 1.38 g) in acetonitrile (50 mL) in a round-bottom flask and the mixture was stirred under reflux condition for 5 hrs. The obtained Fe_3O_4/SiO_2-Met was then magnetically collected from the solution and washed copiously with water/ethanol followed by drying at 80 °C for 6 hrs.

Adsorbent characterization and analytical methods

Transmission electron microscopy (TEM) measurements were performed using a Philips CM10 operated at 100 kV electron beams accelerating voltage and equipped with a CCD camera. One drop of the sample solution was deposited onto a copper grid and the excess of the droplet was blotted off the grids with filter paper; then the sample was dried under ambient conditions. The sizes of the magnetic nanoparticle cores were determined by photo enlarging the micrographs and measuring at least 150 individual cores manually. Fourier transform infrared (FTIR) spectra were collected between 450 and 4000cm−1 using a Nicolet spectrometer.

The concentration of cyanide ions in solution was measured by the titrimetric method as described in section 4500-CN− D. of the Standard Methods [24]. The pH of wastewater was adjusted to the desired level using a 0.1N NaOH.

Cyanide removal from water with MNPs (Fe_3O_4-SiO_2 –Met)

Because of the potential hazards associated with cyanide, control and remediation of cyanide-contaminated water is usually desired.

The cyanide adsorption capacity of the media was evaluated in batch cyanide adsorption experiments at three final pH values, 9.1 ±0.1 and 10.0±0.1and 11 in 0.01, 0.03, 0.05gr Fe_3O_4-SiO_2 –Met with an initial cyanide concentration of C_0 ≈1000 ppm. These pH values were selected because (1) most natural waters exhibit pH in this range; and (2) the cyanide adsorption capacity is affected by pH due to the speciation of cyanide and change in the surface charge of the adsorbent. Adsorption of cyanide was modeled using with a mathematical model of the smallest sum of squares. The pH of the solution was adjusted to desired values by using dilute NaOH before the addition of adsorbent. The concentrations of residual cyanide, after magnetic separation of MNPs, were computed by measuring the absorbance at the concentration of cyanide ions in solution was measured by the titrimetric method.

Calculation of cyanide adsorption efficiency (RE)

Cyanide adsorption efficiency (RE) was calculated from Eqs. (1). where C_0 and C_t (mg/L) are initial (t =0) and equilibrium cyanide concentrations.

$$R\%=100\times\frac{C_0-C_t}{C_0} \qquad (1)$$

RESULTS AND DISCUSSION

Adsorbent characteristics

A TEM micrograph of surface MNPs particles is shown in Figure 1 which displays the silica-modification process of MNPs leads to the formation of magnetic/silica composite particles with typical core-shell structure. These observations confirmed the formation of a silica layer around the Fe_3O_4 nanoparticles.

Figure 2a shows the FT-IR spectrum of Fe_3O_4 modified with trisodium citrate and its band characteristics. The signal observed at 579 cm^{-1} is attributed to the Fe-O bond vibration. In addition, two bands observed at 1617 and 1385 cm^{-1}, which are due to the COO-Fe bond and confirm the complexation between the carboxylate moiety of citrate groups and iron ions on the magnetite nanoparticles surface. In the case of Fe_3O_4/SiO_2 nanoparticles (Fig.2b), the sharp band at 1090 cm^{-1} is corresponding to Si-O-Si anti-symmetric stretching vibration, being indicative of the existence of a SiO_2 layer around the Fe_3O_4 nanoparticles. Because the specific surface area of nano particles is low, the functional groups likely have a more pronounced role than particle surface area in adsorbing cyanide ions from liquid (Fig.2c).

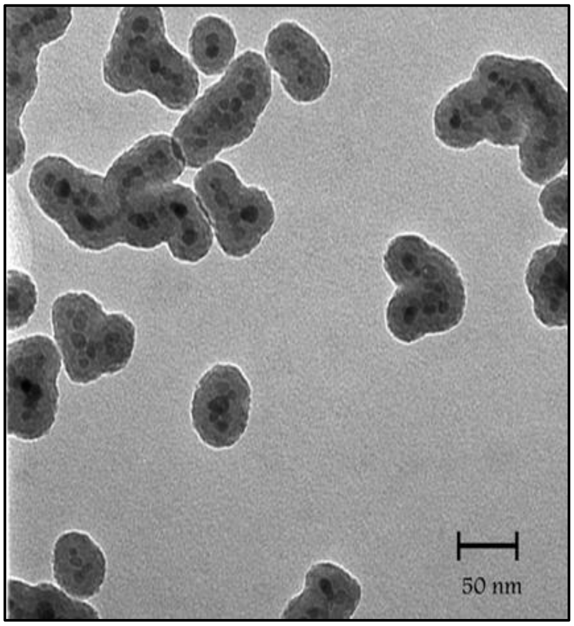

Fig. 1. TEM images of solutions containing coreshell Fe_3O_4/SiO_2 nanoparticles.

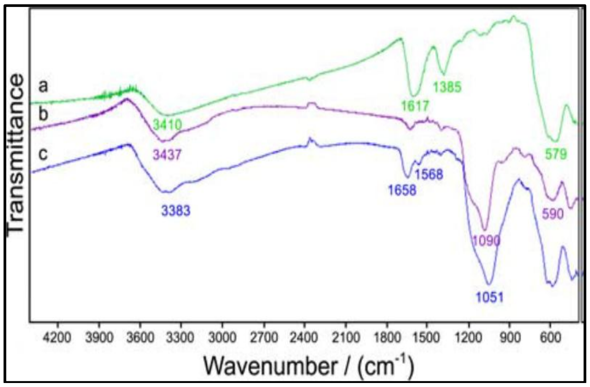

Fig. 2. FT-IR spectra of (a) trisodium citrate-treated magnetite nanoparticles, (b) Fe_3O_4/SiO_2 and (c) Fe_3O_4/SiO_2-Met.

Cyanide adsorption

Figure 3 shows changes in removal efficiency with respect to changes in pH (9, 10, 11) and changes in the amount of nanoparticles (Fe_3O_4/SiO_2-Met) used (0.01, 0.03, 0.05g) and variation of contact time (4-12hr) Concentration of cyanide in solution was determined by silver nitrate titration in the presence of p-dimethylamino benzyl rhodanine (0.02%, w/w in acetone) as indicator.

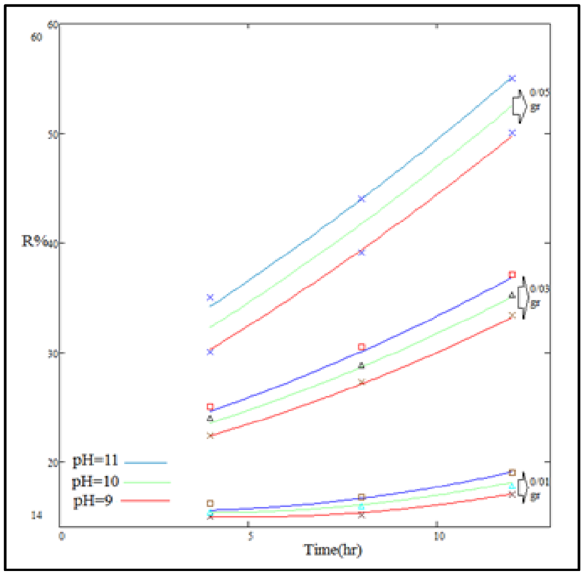

Fig. 3. Influence of adsorbent dosage (Fe_3O_4/SiO_2-Met.) and contact time on 1000ppm Cyanide adsorption efficiency.

Influence of solution pH and the mechanism of adsorption

In the first run of adsorption experiments cyanide adsorption onto MNPs (Fe_3O_4/SiO_2-Met) was studied as a function of pH; results are given in Figure 3. As shown in Figure 3, the highest cyanide removal of 58% obtained at pH 11. Peak cyanide adsorption at pH 11 can be explained by considering the fact that the pH of the solution influences both the surface charge of the MNPs particles (Fe_3O_4/SiO_2-Met) and the dominant species of cyanide in the solution. Because CN^- is a nucleophilic ion, when in contact with the negatively charged adsorbent, it binds with the anionic functional groups present on the surface of adsorbent (Figure 2) and thereby improves adsorption [9]. Therefore, chemical ion exchange is determined to be the prevailing mechanism for the adsorption of cyanide ions onto MNPs. Moreover, some removal may occur through surface precipitations and chemical reactions with surface sites, complexation of CN^- with functional groups, and physical adsorption. According to information, most researchers have similarly reported attaining maximum cyanide adsorption onto different adsorbents in the pH range of 9-11.

Influence of MNPs dosage and contact time

Because adsorption is mainly a surface phenomenon, the amount of surface available for adsorption and thus the mass of adsorbent can significantly affect adsorption efficiency. Therefore, the effect of MNPs dosage on cyanide removal was investigated at pH of 9-11 under the conditions given in Figure 3 represents the removal percentages of cyanide as a function of MNPs dosage. As illustrated in Figure 3 the removal of cyanide at a dose of 0.01g/L was 20%; removal improved to 58% when the MNPs dosage was increased to 0.05 g/L and remained almost unchanged thereafter. Achievement of a high cyanide removal percentage with a relatively low adsorbent dose indicates the high affinity and suitability of MNPs for removal of cyanide from wastewater. The increasing adsorption efficiency with increasing MNPs dose can be attributed to the increase in surface area and by extension the greater number of exchangeable sites available for interaction with cyanide ions. In comparison, for instance, Ref. [26] reported 14.3, 35.4 and 92.3% removal of 100 mg/L cyanide for 4.5 g/L plain, copper- and silver-impregnated GAC, respectively, after around 24 h contact time. Considering the low adsorption capacity of GAC (plain and modified), which is the most conventional industrial adsorbent, as well as its high production cost, MNPs is certainly much more efficient and cost effective and is therefore a promising adsorbent for treating cyanide-laden wastewaters.

A further increasing in the mixing time led to improved removal percentages for 1000 ppm cyanide concentration, which attained equilibrium times of 4, 12 hours increasing adsorption efficiency.

CONCLUSIONS

Adsorption is one of the most widely used treatment methods for removing contaminants from water and wastewater. This work introduced a new adsorbent, novel magnetic nanoparticle (Fe_3O_4-SiO_2 –Met), which is available as a material at no cost. The experimental evaluation revealed that MNPs was capable of removing a high concentration of cyanide ions (1000 mg/L) in a relatively short contact time with a low amount of adsorbent. This study establishes furthermore that the effect of increase of the MNPs concentration is beneficial for the cyanide removal.

Therefore, MNPs (Fe_3O_4-SiO_2–Met) is an efficient, cost effective and thus promising adsorbent for treating cyanide-containing liquid streams.

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