Removal of Nickel from Waste Water Using Graphene Nanocomposite

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Abstract

Nickel (Ni) is frequently responsible for allergic skin reactions i.e. 'Nickel Itch' and also causes asthma, conjunctivitis, inflammatory reactions. Nickel salts act as emetics when swallowed. More than 30 mg of nickel may cause changes in muscle, brain, lungs, liver and kidney and can also cause cancer, tremor, paralysis and even death. Finely divided particles of nickel and nickel compounds from mining, smelting, refining, electroplating can enter the environment .Conventional methods for the removal of Ni(II) from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, adsorption, ion-exchange, reverse osmosis, electro dialysis, membrane separation processes, etc. Adsorption is the most widely used method for removal of Ni from wastewater and is the most cost effective method for very dilute samples. Activated carbon, magnetite, fly ash, calcined phosphorous, metal oxides are the most commonly used out of which metal oxides show higher adsorption characteristics than the rest. MnO₂ is widely used metal oxide owing to its high active surface area and high affinity towards metal cations. But it tends to agglomerate in the aqueous solutions reducing the active area.

The graphene nanosheets (GNS) δ - MnO_2 is the nanocomposite of MnO_2 loaded on graphene nanosheet which is believed to possess greater adsorption capacity than the conventional adsorbents used. In the present study the GNS/ δ - MnO_2 is synthesized in the laboratory and was used for the removal of nickels from the waste water. The batch experiments for nickel removal had been carried out and the parameters affecting the adsorption along with the kinetics and the results obtained from GNS/ δ - MnO_2 in comparison with MnO_2 are also reported.

Introduction

Industrial waste water may contain a large number of heavy metals in it. Nickel, one of them, is a non biodegradable toxic heavy metal ion present in waste water. The main source of nickel pollution in the water derives from processes such as galvanization, smelting, mining, dyeing operations, batteries



manufacturing and metal finishing^[1]. Trace amounts of nickel are beneficial to human organism as an activator of some enzyme systems, but if it is beyond the scope of normal levels, different types of diseases occur such as lung cancer, renal edema and skin dermatitis and gastro intestinal disorder. For this reasons, the Water Sanitation and Hygiene (WSH) under the World Health Organization (WHO) established the toxic limits of permissible concentrations of nickel at a level of Ni (II) and insoluble compounds of 1.0 mg/m³, soluble compounds of 0.1mg/m³, nickel carbonyl of 0.05-0.12 mg/m³ and nickel sulphide of 1.0mg/m^{3 [2]}. The conventional methods of Ni (II) removal from water include chemical oxidation or reduction, chemical precipitation, ion exchange, membrane separation, filtration, electrochemical treatment and adsorption, etc. As an economical and efficient method, adsorption technique has been widely applied to remove heavy metal ions from waste water.

Numerous materials have been used as adsorbents for the removal of Ni (II) processes including activated carbon, silica, ion- exchange resins, rock materials, activated slag, agricultural wastes, microbial and plant derived biomass and chitin, etc. But it remains necessary to develop a low-cost, easily available, high adsorption capacity material for waste water treatment that might remediate the Ni (II) environmental problems.

In recent years, a number of novel metallic oxides have gained a growing interest since they are especially useful in the removal of heavy metal ions from waste water effluents. Several investigations have been undertaken extensively for trace heavy metals removal from waste water using different oxides or composite oxides. MnO₂, Al₂O₃, Fe₂O₃, TiO₂, Fe₃O₄, MnFe₂O₄ and other composite oxides are reported for the removal Cu (II), Ni (II), Co (II), Zn (II), Cr (VI) and Pb (II)^[3-6]. Among them, MnO₂ with different polymorphic phases (α , β , γ , and δ -type) has attracted much attention because of its particular physical and chemical properties. However, it is difficult to be applied independently due to its easy conglomeration and poor dispersion. Graphene nanosheets (GNS) have some significant advantages in the preparation of carrier matrix due to their high surface area and remarkable mechanical stiffness. Graphene, a monolayer of graphite, exhibits a number of intriguing unique properties, such as high surface area of over 2600m²/g, large surface-to-volume ratio, high room temperature (RT) carrier mobility, conductance quantization. Recently, GO based composite materials, such as GO/bentonite, GO/aluminum polycation, GO/iron oxide, GO/iron acetate, GNS/δ-MnO2 have also been studied as the absorbents for heavy metals from waste water, ammonia, nitrogen oxides etc^[7]. Removal of heavy metal ions from aqueous solution by MnO₂ has been reported but the sorption capacity is relatively low in the previous reports ^[7].

The sorption capacity of MnO_2 can increase if it is modified to $GNS/\delta-MnO_2$ composite because GNS as a carrier offers high surface area. The objective of this study was to synthesize $GNS/\delta-MnO_2$ composite and to investigate the $GNS/\delta-MnO_2$ composite for the removal of Ni (II). Batch experiments



were carried out to investigate sorption fundamental mechanisms of Ni (II) onto GNS/δ -MnO₂ composite in comparison with pure MnO₂ and GNS ^[12]. We proposed the adsorption kinetics based on the experimental data.

Selection of method

While selecting an effective method for removal of Ni from waste water some factors must be considered such as pH, temperature, chemical properties, concentration and presences of other metals, purpose of application of the treated water etc. Acidity and basicity of sample waste water greatly affects the selection of process to be used. Water having pH at the range 8-9 is considered most suitable for the separation process of Ni. Rate of removal may vary significantly with pH values of samples. Temperature plays important role for adsorption and ion exchange based methods. For bio-based methods, the optimum temperature is needed for proper growth and functioning of biological medium. For chemical treatment based methods, the chemical behaviour of Ni at different temperatures and at different process conditions are needed to be considered. If the water sample contains other heavy metals along with Ni, then extensive study of combined properties of these metals on the separation process or medium is needed. The application of treated water and corresponding threshold limits do affect the selection procedure. Cost is also one important parameter to be considered. The physical separation methods which are primarily used for pre-treatment are cheaper than those involving advanced methods for high degree of purification [^{8]}.

Separation Methods

Attempts to separate from the waste water by using various scientific experiments have been made, which includes conventional methods like Chemical Precipitation, preventing heavy metals from reaching downstream processes and the receiving waters can be accomplished by removing the heavy metals using chemically enhanced primary treatment (CEPT)^[9]. Chemical precipitation by coagulation and flocculation by trivalent metal salts is a century old and proven technology.

Adsorption is the most widely used method for removal of Ni from wastewater. It is the most cost effective method for very dilute samples. The efficiency of this method mainly depends on the properties of the adsorbent used. The primary requirement of an economical adsorption process is selectivity, high adsorption capacity and cost. Activated carbon is one effective but very expensive material being used as an adsorbent. Agricultural Waste, Natural Materials, MnO₂, Nanocomposites are other materials used as an adsorbent. Several studies have been conducted on the potential of industrial by-products for metal removal, and that has surprisingly shown satisfying results^[10].

Other methods include Ion exchange technology, Reverse osmosis method and Electrodialysis. Ion exchange ^[14] is a reversible chemical reaction wherein an ion from a wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are



either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. Reverse osmosis (RO) ^[11] is a separation process that uses pressure to force a solution through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side. More formally, it is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied.

Electrodialysis (ED) is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through. By placing multiple membranes in a row, which alternately allow positively or negatively charged ions to flow through, the ions can be removed from wastewater. In some columns concentration of ions will take place and in other columns ions will be removed. The concentrated saltwater flow is circulated until it has reached a value that enables precipitation. At this point the flow is discharged. This technique can be applied to remove ions from water. Particles that do not carry an electrical charge are not removed. After analysis of all the above different methods, adsorption is found to be an economical and efficient method. Adsorption technique has been widely applied to remove heavy metal ions from wastewater.

Experimental

Chemicals

Graphite, hydrazine solution, EDTA, KMnO₄, HCl, Ethyl Alcohol, All dilutions are made in deionized water.

Synthesis of Adsorbents

Graphite was selected as the starting material. Graphene oxide was synthesized from graphite according to a modification of the Hummers-Offeman method ^[13]. The chemical exfoliation has raised a lot of interest from researchers since it is scalable and versatile. So far, research efforts have been mainly focused on exfoliation of GO since the strongly hydrophilic nature of its layers allow an easy intercalation of water molecules and, consequently, a complete, simple exfoliation to single-layer GO sheets by sonication. The synthesis of GNS using hydrazine reduction of GO was carried out. The synthesis of GNS/δ-MnO₂ composites was prepared by a redox reaction under microwave irradiation. First, 100 mL of

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GNS suspension (1.65 mg mL–1) was subjected to ultrasonic vibration for 1hr. Then KMnO₄ powder (0.9482g) was added into above graphene suspension, and stirred for 10 min. the suspension thus obtained was heated using a household microwave oven for 5 min. Finally, the black deposit was filtered, washed several times with distilled water and alcohol, and dried at 100^oC for 12h in a vacuum oven. For comparison, MnO₂ was prepared by dissolving 18g KMnO₄ in 200 mL deionised water under 80–90^oC. Then 500mL 1:1 (v/v) HCl was added from a fast dripping burette. The black suspension solution was centrifuged, and washed several times with distilled water, dried at 100^oC for 6 hours in a vacuum oven. **Batch Adsorption** ^[14]

Standard solution (0.5N) of 1 liter was prepared by dissolving 59.4275 gm of NiCl₂·6H₂O in 1 liter of water. Two samples were taken each of 250 ml of above solution. 50 mg of GNS/ δ -MnO₂ was added to first beaker and same amount of dry δ -MnO₂ was added to another one in order to carry out adsorption of Ni by using dry δ -MnO₂ and GNS/ δ -MnO₂ separately and to compare their adsorbent activities. Both the samples were subjected to magnetic stirring for 3 hr to ensure adsorption equilibrium. The adsorbents were separated by centrifuge at 4000 rpm for 5 min. The concentration of Ni (II) was analyzed using UV–Visible Spectrophotometer at wavelength 393nm.

Results and discussion

In the batch adsorption experiment the samples were taken out from adsorption mixture at the interval of 20 minutes. The effects of contact time on the $GNS/\delta-MnO_2$ and MnO_2 adsorption from the solution are given in Fig. 2.



Figure 1 Absorbance Vs Wavelength (λ) for Determination of λ_{max}





Figure 2 Contact Time Effect of Ni(II) Removal onto GNS/δ-MnO2 and MnO2

It can be observed that the adsorption of Ni (II) increases with increase of contact time, and very rapid adsorption is observed in first 60 min for both the samples. The ascending curve after around 60 min is found to be transformed into slow increasing curve which indicates the dynamic equilibrium process must be established. Comparing with other adsorbent, GNS/δ-MnO₂ exhibits higher adsorption capacity and speed probably due to its abundant availability of active sites from smaller MnO₂ growth on graphene nanosheet. The curve shows that after 120-140 min both the curves show no increase in extent of adsorption. It suggests that all the active sites might be occupied. Based on these observations, a shaking period of 3h was assumed to be suitable for equilibrium to attain for the further sorption experiments.

The pseudo-first order and pseudo-second order reactions kinetics were studied in order to investigate the adsorption kinetics. The relating equations are as follows:

$$\log (q_e - q_t) = \log q_e - (k_1 t) / 2.303$$
⁽¹⁾

$$(t/q_t) = 1/(k_2 q_e^2) + (1/q_e) *t$$
(2)

Where, q_e and q_t are the amount of Ni (II) adsorbed per unit weight of adsorbent at equilibrium and any time t (mg g⁻¹), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are rate constants for first and second order equations.

Both the equations were approximated to line. From the fig.3 it can be seen that for the pseudofirst order kinetics it gives a curve rather than a straight line. However, the pseudo-second-order kinetics gives a perfect linear plot (fig. 4). Further the pseudo-second order model provides a near-perfect match between the theoretical and experimental q_e values.

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Figure 3 Pseudo-First Order Reaction Kinetics Analysis



Figure 4 Linearized Adsorption of Ni(II) by Pseudo-Second Order Reaction Kinetic Analysis
 The equilibrium constant k₂ (0.0197 g mg⁻¹ min⁻¹) for pure MnO₂ is higher than that for GNS/δ-MnO₂ (0.00893 g mg⁻¹ min⁻¹). However, the uptake percentages after equilibrium are 77.04% and 47.17%

 for GNS/δ-MnO₂ and MnO₂. Based on above discussion, the pseudo-second-order adsorption mechanism is predominant, meaning that chemical sorption takes part in the adsorption process.

Sr. No.	Adsorbent	$(q_e)_{exp} (mg g^{-1})$	$(q_e)_{cal} (mg g^{-1})$	$k_2(g mg^{-1} min^{-1})$
1.	GNS/δ-MnO ₂	770.8	769.23	0.00893
2.	MnO ₂	471.93	495.06	0.0197

Table 1 The Kinetic Constants of the Ni (II) adsorption onto GNS/δ-MnO₂ and MnO₂



Conclusions

 $GNS/\delta-MnO_2$ composite used as adsorbent for the removal of Ni (II) ions from aqueous solution was prepared by a microwave-assisted method. The adsorption capacity of Ni (II) for $GNS/\delta-MnO_2$ is 1.5 times higher than that for MnO_2 which mainly comes from MnO_2 nanoparticles growth on the surfaces of GNS. The adsorption data are fit well by the second-order reaction kinetics equation model.

References:

- 1. Z. Al-Qodah, Desalination, 2006, 196, 164–176.
- 2. http://www.who.int/water_sanitation_health/gdwqrevision/nickel2ndadd.pdf
 - A. K. Mishra, S. Ramprabhu, *Desalination*, 2011, 282, 39-45
- 3. Y. Zhu, S. Murali, Adv. Mater, 2010, 22, 3906-3924
- 4. H. HongKun, G. Chao, Sci. China Chemistry, 2011, 54, 397-404
- 5. M. Compel, Polish J. of Environ. Stud., 2006, 15, 375-382.
- N. Jovi, D. Dudi, A. Montone, M. A. Vittori, M. Mitri, V. Djokovi, , *Ultramicroscopy*, 2008, 108,885–892.
- 7. Rudolf Amann, Hilde Lemmer, Michael Wagner, FEMS Microbiology Ecology, 1998, 25, 205-215
- P. D. Johnson, P. Girinathannair, K. N. Ohlinger, S. Ritchie, L. Teuber, J. Kirby, *Water Environ.*, 2008, 80, 472-479

A. Radenvoic, J. Malina, A. Strkalj, *The Holistic Approach to Environment*, 2011, **3**, 109-120

- 9. T. Bakalár1, M. Búgel, L. Gajdošová, Acta Montanistica Slovaca Ročník, 2009, 3, 250-253.
- 10. P. Senthilkumar, K. Ramakrishnan, R. Gayatri, J. Engg. Sci. Tech., 2010, 5, 232 243
- 11. W.S. Hummers, R.E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339-1341
- 12. Y. Ren, N. Yan, Q.Wen, Z. Fan, T. Wei, M. Zhang, J. Ma, Chem. Engg. J., 2010, 15, 1-7