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Removal of Heavy Metals Using Nanostructured Graphite Oxide, Silica Nanoparticles and Silica/ Graphite Oxide Composite

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Abstract

Heavy metals are known to be toxic for living organisms even if they are present at low levels. The presence of heavy metals and other pollutants in water continues to be a major concern and the removal of such contaminant is considered to be a major problem in environmental remediation. In the present study, nanostructured graphite oxide, silica/graphite oxide composites and silica nanoparticles were used for the removal of the heavy metal ions from aqueous solutions by a batch adsorption method and have been modelled using classical Langmuir and Freundlich adsorption isotherms. The results revealed that the adsorption of heavy metals by nanostructured graphite oxide was observed in the following order: nickel > zinc > lead > cadmium > chromium. Langmuir adsorption isotherm results showed that graphite oxide is an effective adsorbent for the removal of Nickel ions from aqueous solutions, while Freundlich data obtained for Cadmium, Chromium, Lead, Nickel and Zinc ions suggest monolayer type of adsorption by graphite oxide. Results showed that silica/graphite oxide composite (2:3) is a highly effective adsorbent material for heavy metal ions and highly recommended to be used in water purification technologies.

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Keywords: Adsorption; Langmuir and Freundlich Isotherms; Heavy metals; Nanostructured graphite oxide, Silica nanoparticles, Silica/graphite oxide composite

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1. Introduction

Water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Moreover, water pollution is considered to be a major environmental problem worldwide, and among the various water pollutants, heavy metals require special attention because of their toxic effect on humans and the environment [1]. Heavy metals are considered to be the most important pollutant in source and treated water. The increased use of heavy metals industrially resulted in an increase in the availability of metallic substances in natural source water [2]. Moreover, heavy metals form a very dangerous category due to their toxic and carcinogenic nature, non-biodegradable and hence, tend to accumulate in the environment for long time. Some of these toxic elements are cadmium, lead, mercury, nickel, chromium and zinc [3].

Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatments [4, 5]. Several studies have addressed nanoparticles, mainly metal oxides, as effective and efficient adsorbents in the cleanup of environmental contaminants, mainly because nanoparticles can penetrate into the contamination zone where microparticles cannot [6]. Conventional techniques for removing heavy metals from water and wastewater include electroplating, evaporating, membrane filtration, oxidation, reduction, ion exchange and adsorption [7]. Among these methods, adsorption is the most effective technique. Various adsorbents such as activated carbon, silica gel, and graphite oxide can be used in the purification of water [2,8]. Historically, graphite oxide and other carbon based nanomaterials have been used as adsorbent for environmental purification and water treatment applications for the removal of inorganic and organic pollutants [6, 9, 10].

Graphite oxide and its composites offers utility in several applications due to its unique two-dimensional nature and associated band structure [11]. Features like large surface area and presence of surface functional groups make single sheets of carbon and their composites an attractive adsorbent candidate for water purification. The present study aimed to test the effect of graphite oxide, silica and silica/graphite oxide composites in the removal of heavy metal ions, using batch adsorption methods and modelled using the classical Langmuir and Freundlich adsorption isotherms.

2. Materials & Methods

In the present investigation, natural graphite powder (<20 micron), Sulfuric acid (H_2SO_4), Potassium persulfate ($K_2S_2O_8$), Phosphorus pentoxide (P_2O_5), Sodium chloride, Hydrogen Peroxide, Silicon Dioxide and 3-aminopropyltriethoxysilane (APS) Coupling agent were all supplied by Sigma-Aldrich. All the chemical compounds and Heavy metals standard reference solutions were of analytical grade and purchased from recognized chemical suppliers. The concentrations of heavy metals under study were determined by the atomic absorption technique type AA-6800, Shimadzu, Japan.

2.1. Preparation of Graphite Oxide

Graphite Oxide (GO) was prepared according to the modified Hummers Method as reported previously [12]. Concentrated H_2SO_4 (50 mL), $K_2S_2O_8$ (10 g), and P_2O_5 (10 g) were mixed in a 3 L Erlenmeyer flask and heated to 80°C using a hot plate. Twelve grams of graphite powder was added to the mixture under strong magnetic stirring for 4.5 hrs. Afterward, 2 L of deionized (DI) water was added to the suspension. After dilution, the mixture was left overnight and then filtered through a 0.1 μm Teflon Millipore membrane; the filter cake was left overnight for air drying. The filter cake was slowly dispersed into 0.46 L of concentrated H_2SO_4 in a 5 L Erlenmeyer flask in an ice bath with continuous stirring. The temperature of the mixture was carefully controlled to exactly 10°C. The dispersion was kept at 35°C for 2 hrs and then diluted with 900 mL of DI water. During the entire process, the temperature was kept below 50°C. Subsequently 2.8 L of DI water was added over 2 hr with continuous stirring, giving a brownish dispersion. Immediately after diluting 50 mL of 30% H_2O_2 was slowly added to the dispersion, leading to tremendous bubbling as well as an obvious color change from brown to bright yellow. The mixture was left at room temperature for at least 2 days and then washed with 10% HCl and 5 L DI water sequentially. The final filter cake was air dried and kept in desiccators over P_2O_5 . The graphite oxide product can be easily dispersed in water by mild sonication [6].

2.2. Graphite oxide coated silica composites

The surface modification of SiO₂ with APS coupling agent was carried out in liquid phase. SiO₂ powder (10 g) was mixed with 150 mL ethanol, premixed and stirred for 30 min to get well dispersed SiO₂ suspension. After the addition of another 150 mL ethanol, 0.5 mL APS was added into the suspension. The mixture was stirred, heated up to 50°C for 12 hrs, the obtained particles were filtered from the mixture, washed with ethanol and deionized water five times and dried under vacuum [13]. Silica/ GO composites (SiO₂/GO) were prepared in (2:3) (w/w) ratio. Under mild magnetic stirring for 1 hr with continuous addition of SiO₂-NH₂ for the precipitation of GO and the solutions became transparent. The precipitates (SiO₂- GO) were collected and washed with water for several times to remove the unbound GO and dried at 60°C and ground before use [13].

2.3. Batch Adsorption Test on nanostructured graphite oxide

Batch adsorption experiments were performed to investigate the adsorption process of different heavy metals by different adsorbents. Twenty milligrams of the graphite oxide were added to 20 ml of different concentrations of heavy metal standard solutions (200, 100, 50 and 30 ppm), while the pH of the solution was adjusted to 3.0. Mildly sonicate the solution for 20 min, then allowed to cool at room temperature, and finally it was left for 24 hrs at room temperature for equilibration. Solids were allowed to settle down and were removed using syringe filtration. The residual heavy metals were determined by AAS analysis. The adsorption isotherm of GO was obtained by increasing the concentration of heavy metal solutions in the range of 50 up to 200 ppm.

The quantity of adsorbed heavy metal ions was calculated in percentage from the difference between concentrations of metal ions before and after adsorption [8, 14] as follows:

$$\% \text{Adsorption (Removal)} = \frac{C_i - C_e}{C_e} \times 100 \quad (1)$$

Where C_i is the initial heavy metal concentration (ppm), C_e is the heavy metal concentration at final equilibrium (ppm). Adsorption data for adsorbate concentrations are described by Langmuir and Freundlich adsorption isotherms.

2.4. Removal of Nickel by GO, Silica and Silica/GO composite

Removal of nickel by GO, silica and silica/ GO composite were tested using the batch adsorption method, 20 mg of the adsorbent under test were supplemented to Erlenmeyer flasks fortified with 20 ml of 30 and 200 ppm Ni²⁺ one at a time. The solutions were mildly sonicated for 20 min, and then allowed to cool followed by equilibration at room temperature for 24hrs. Solids were allowed to settle down and were removed using syringe filtration. The residual nickel ions were determined by atomic absorption spectrophotometer (AAS) analysis.

2.5. Characterization of the adsorbents under test

Fourier Transform Infrared Spectrophotometer (FT-IR) analysis (Shimadzu ,FTIR-8400), was used to measure the wave numbers ($\bar{\nu}$, cm⁻¹) for the pure metals (Cd²⁺, Zn²⁺ & Ni²⁺) in comparison with these metals adsorbed on graphite oxide, in the range of 750– 4000 cm⁻¹, by applying an optical resolution of 4 cm⁻¹. The samples under test were investigated by using the KBr pellet technique. Moreover, the microstructure and morphology of the adsorbents under test were characterized using a scanning electron microscope (SEM, TESCAN-INCA) at an acceleration voltage of 20 kV.

3. Results and discussions

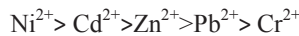
3.1. Removal of heavy metals using graphite oxide

The effect of graphite oxide on the removal percentage of the heavy metal ions (cadmium, lead, chromium, zinc and nickel) are shown in table 1. The optimum concentration of the adsorbent was chosen as 20 mg per 20 ml of heavy metal solutions. Adsorption experiments were conducted with different concentrations of heavy metal solutions and at acidic pH (pH=3). It can be clearly noticed from Table (1) that the percentage removal decreases with the

increase in initial heavy metal concentration. At low heavy metal concentration, the removal percentage was high and gradually decreased with the increase of heavy metal concentration. At 30 ppm of cadmium, lead, chromium, nickel & zinc, the removal percentages were 88.33, 85.0, 63.0, 89.90 & 85.60 %, respectively. However, the highest heavy metal concentration (200 ppm) leads to the lowest removal percentage of the heavy metals under test (71.60, 80.71, 25.90, 78.00 and 75.10 % for cadmium, lead, chromium, nickel & zinc respectively). The obtained results in the present investigation concerning lead, zinc and cadmium differed from that obtained by Sitko et al. who noticed the high affinity of GO toward lead than cadmium and zinc at acidic pH [15].

At low concentrations of initial metal ions, sufficient adsorption sites are available for the heavy metals ions and as the initial concentration of metal ions increases, more and more surface sites are covered and at high concentration of the metal ions, the capacity of the adsorbent get exhausted due to the non-availability of the surface sites [16]. Therefore, the removal percentage of heavy metals depends on the initial metal ions concentration [17].

Moreover, Table (1) showed the removal percentages of all heavy metals under test, at low concentration, were in the following order:



Therefore, the difference in the removal percentage of different heavy metal ions at constant initial concentrations, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional groups on the surface of the adsorbent. Moreover, the chemical structure of the adsorbents is of vital importance in increasing the adsorption capacity [18]. Chemically, there are plenty of oxygen atoms on graphite oxide in the form of epoxy, hydroxyl and carboxyl groups. These oxygen atoms are highly amiable to positively charged ions because of strong electrostatic interaction and considered to be the most important structure that influences the surface characteristic and surface behaviour of adsorbents [18].

The FT-IR spectroscopic characteristics of the pure and adsorbed metals are shown in Table (2). IR spectra of the free metal salts and those adsorbed on GO surfaces supports slight adsorption of the metal cations on the surface, this is reflected in the shifts in wave numbers from 825.53 to 863.70 cm^{-1} for cadmium ions after adsorption with graphite oxide; from 1066.64 to 1097.50 cm^{-1} for zinc ions and 796.6 to 877.61 cm^{-1} for nickel ions. Therefore, the results of the present investigation demonstrated that, after adsorption with nanostructured graphite oxide, there was an increasing shift for zinc, followed by cadmium then nickel ions (30.86, 38.17 & 81.01 cm^{-1} $\Delta \bar{\nu}$ for Zn^{2+} , Cd^{2+} & Ni^{2+} respectively). Hence, these shifts indicated that there were a strong binding processes taking place on the surface of graphite oxide and the greater the shift in wave numbers ($\Delta \bar{\nu}$), the stronger the bond between graphite oxide and adsorbed metal [19]. This is compatible with the removal percentage data, where the removal percentage was observed as follows $Ni^{2+} > Cd^{2+} > Zn^{2+}$, similarly and following the same trend, the order of $\Delta \bar{\nu}$ was as follows: $\Delta \bar{\nu} (Ni^{2+}) > \Delta \bar{\nu} (Cd^{2+}) > \Delta \bar{\nu} (Zn^{2+})$.

3.2. Batch Adsorption Isotherms of heavy metals by Graphite Oxide

The presence of heavy metal ions from the transition series, viz, Chromium, Zinc, Nickel, Lead, Cadmium, etc. in the environment is of major concern due to their toxicity to many life forms [20]. The batch adsorption isotherm experiments indicated that the adsorption behavior of heavy metal ions on the graphite oxide dispersion can be represented by Langmuir and Freundlich type adsorption models. In order to represent the equilibrium adsorptive behavior successfully, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Two kinds of several isotherms equations were tested to fit the experimental data [5, 21].

Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{b\theta} + \frac{C_e}{\theta} \tag{2}$$

Freundlich equation

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \tag{3}$$

Where,

$$\tag{4}$$

$$q_e = \frac{C_i - C_e}{m} V$$

Where q_e is the amount of metal ions adsorbed at equilibrium (mg.g^{-1}), C_i and C_e are the initial and equilibrium concentrations of metal ions in solution (mg.L^{-1}), m is the mass of adsorbent (mg), and V is the volume of the heavy metal solution (L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, θ (mg.g^{-1}) is the measure of monolayer adsorption capacity under the experimental conditions and b is Langmuir adsorption constant related to the energy of adsorption. These values can be obtained from the plot of C_e/q_e against (C_e) [22]. Freundlich treatment gives the parameters, n , is the adsorption intensity and indicative of bond energies between metal ion and the adsorbent and K , is Freundlich constant with multilayer adsorption which related to bond strength and these values can be obtained from the plot of $\ln q_e$ against $\ln C_e$. Moreover, the correlation coefficient R^2 values were used to obtain the best-fit linear equation.

Langmuir isotherm is an empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [23]. Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer [24]. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface [23,25].

The estimated model parameters with correlation coefficient (R^2) for the different models are shown in Table 3. The values of R^2 are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's models. The Langmuir constants θ and b , were calculated using the slope and intercept of the line, obtained from the plot of C_e/q_e vs C_e . The value of θ (i.e. maximum uptake) appeared to be higher for Pb^{2+} with GO in comparison with the uptake of other heavy metals by the GO (Table 3). A large value of b for Cadmium implied strong bonding of Cd^{2+} to the GO. Langmuir parameters of GO indicated a maximum adsorption capacity of 555.55, 322.58, 250, 204.08 and 60.24 mg/g , with energy parameter of 0.01, 0.01, 0.03, 0.04 & 0.03 for Pb^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} and Cr^{2+} respectively (Table 3). Moreover, The results showed that the uptake of Cd^{2+} , Pb^{2+} , Cr^{2+} & Ni^{2+} ions by graphite oxide fit the Langmuir adsorption isotherm, since the correlation coefficient was nearly 0.90 (Table 3), which attributed to the homogenous distribution of active sites on the adsorbent surface and indicating the formations of monolayer coverage of the adsorbate at the outer surface of the adsorbent. [26]. On the other hand, the obtained correlation coefficient (R^2) for Zinc suggested poor fitting of the experimental data to Langmuir isotherm. The correlation coefficient (R^2) for adsorbents indicated that the Freundlich model fit the experimental data well. It was reported by Itodo. (2011) that a value of $1/n$ below one indicates a Langmuir-type isotherm because it becomes more and more difficult to adsorb additional adsorbate molecules at higher adsorbate concentrations [27]. Therefore, the values of $1/n < 1$ obtained for Cd^{2+} , Pb^{2+} , Cr^{2+} , Ni^{2+} & Zn^{2+} ions suggest monolayer type of adsorption and the adsorption is favourable. According to Freundlich treatment the variation of the parameter K , is in the following order:

$$\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cr}^{2+} > \text{Pb}^{2+}$$

This indicated that Nickel ion had the highest bond strength to graphite oxide and Lead ion has the lowest one. Overall, the adsorption model results indicated that the adsorption process of different heavy metals on graphite oxide would result either in monolayer formation on a homogeneous surface, or in simple multilayer formation. It is possible that each heavy metal possesses different mechanism of adsorption. Moreover, Adsorption isotherms suggest that the adsorption of metal ions on GO nanosheets is controlled by chemical adsorption involving strong surface complexation of metal ions with oxygen-containing groups on the surface of GO [15].

3.3. Removal of Nickel by GO, Silica and Silica/GO composite

3.3.1. Characterization of the adsorbents under test

Figure (1) illustrated the scanning electron microscope images of graphite oxide sheets, silica and silica/ graphite oxide composite (2:3) at different magnifications. Figure (1b) revealed that graphite oxide sheets with particle size of $21\mu\text{m}$ and can be clearly identified as coarse powders. Moreover, at higher magnifications ($1\mu\text{m}$), it appeared as sheets with distinct edges, wrinkled surfaces, and porous membrane. However, the average particle size of silica was 12 nm, so it is considered as nanoparticle. Moreover, Figure (1) showed that the surface of silica/ GO composite were clearly decorated with silica nanoparticles and appeared as aggregates of white silica particles on the surface and

within the pores of brown graphite oxide, as indicated by arrows (Figure 1 d & e).

Table 1. Removal percentage of heavy metal ions using Nanostructured Graphite Oxide

| Heavy metal ions | Initial Concentration (C _i) (ppm) | Residual Concentration (C _e) (ppm) | Removal Percentage (%) |
|--|--|---|------------------------|
| Cadmium (Cd ²⁺) | 30.0 | 3.5 | 88.33 |
| | 50.0 | 6.85 | 86.30 |
| | 100.0 | 16.5 | 83.50 |
| | 200.0 | 56.85 | 71.60 |
| Lead (Pb ²⁺) | 30.0 | 4.5 | 85.00 |
| | 50.0 | 7.95 | 84.00 |
| | 100.0 | 17.41 | 82.59 |
| | 200.0 | 38.59 | 80.71 |
| Zinc (Zn ²⁺) | 30.0 | 4.3 | 85.60 |
| | 50.0 | 9.6 | 80.70 |
| | 100.0 | 22.3 | 77.70 |
| | 200.0 | 49.7 | 75.10 |
| Chromium (Cr ²⁺) | 30.0 | 11.1 | 63.00 |
| | 50.0 | 22.2 | 55.60 |
| | 100.0 | 66.7 | 33.30 |
| | 200.0 | 148.1 | 25.90 |
| Nickel (Ni ²⁺) | 30.0 | 3.0 | 89.90 |
| | 50.0 | 6.1 | 87.90 |
| | 100.0 | 15.2 | 84.90 |
| | 200.0 | 43.9 | 78.00 |

Table 2. FTIR results for pure metal ions and adsorbed metals with Nanostructured graphite oxide

| Metal ion | Wave number $\bar{\nu}$ (cm ⁻¹) | | |
|------------------|---|------------------------------|--------------------|
| | $\bar{\nu}$ (Pure metal) | $\bar{\nu}$ (adsorbed metal) | $\Delta \bar{\nu}$ |
| Ni ²⁺ | 796.6 | 877.61 | 81.01 |
| Cd ²⁺ | 825.53 | 863.7 | 38.17 |
| Zn ²⁺ | 1066.64 | 1097.50 | 30.86 |

Table 3. Estimated isotherm models and their constants values for the adsorption of graphite oxide with different metals.

| Heavy metal | Langmuir isotherm model | | | Freundlich isotherm model | | | |
|-----------------|-------------------------|-----------------|---------|---------------------------|-------|------|------|
| | R ² | θ (mg/g) | b(L/mg) | R ² | K | 1/n | n |
| Lead | 0.96 | 555.55 | 0.01 | 0.99 | 7.05 | 0.86 | 1.16 |
| Cadmium | 0.99 | 204.08 | 0.04 | 0.98 | 13.23 | 0.60 | 1.64 |
| Chromium | 0.94 | 60.24 | 0.03 | 0.95 | 8.35 | 0.35 | 2.81 |

| | | | | | | | |
|---------------|------|--------|------|------|-------|------|------|
| Zinc | 0.82 | 322.58 | 0.01 | 0.99 | 8.38 | 0.72 | 1.37 |
| Nickel | 0.98 | 250.00 | 0.03 | 0.99 | 13.36 | 0.66 | 1.51 |

3.3.1. Batch adsorption test

Batch adsorption experiment was conducted in order to evaluate the effectiveness of the different adsorbents under test (graphite oxide, silica and silica/ graphite oxide composite) in the removal of nickel ion concentrations (200 and 30 ppm). Data in Table (4) showed that Silica/ GO (2:3) composite revealed the greatest removal percentage at 30 & 200 ppm (91.8 & 84.7% respectively), followed by GO then silica. It's worth noting that as the concentration of Nickel ions increased, the removal percentages by GO, silica and silica/ GO composite decreased. The results of the present work were in agreement with that reported by Tanguank et al. & El-Ashtouky et al. who reported that at low concentration, metals are adsorbed at specific sites, while with increasing metal concentration, the specific sites are saturated and the exchange sites are filled [2,28]. Therefore, it is clearly inferred that silica/ graphite oxide composite is more effective in the removal of nickel ions than pure graphite oxide or silica nanoparticles.

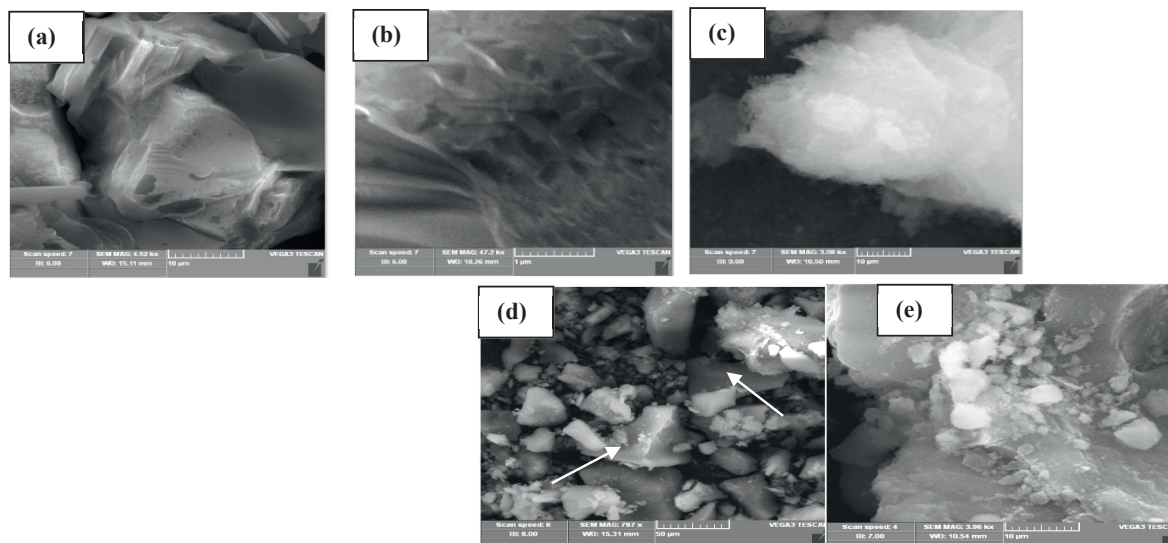


Figure 1. Scanning electron microscopy (SEM) of: (a) graphite oxide sheets (bar= 10 μ m); (b) GO at high magnification (1 μ m); (c) aggregate of silica (10 μ m); (d) silica/ GO composite (50 μ m) and (e) silica/ GO composite at high magnification (bar= 10 μ m).

Table 4. The removal percentage of nickel ions using GO, GO/Silica composite and Silica nanoparticles

| Adsorbent | Removal percentage of Nickel (%) | |
|---------------------------|----------------------------------|---------|
| | 30 ppm | 200 ppm |
| GO | 89.9 | 78.0 |
| Silica | 70.3 | 60.1 |
| Silica/GO (2:3) composite | 91.8 | 84.7 |

4. Conclusions

The present study clearly investigated that graphite oxide successfully removed nearly 90% of heavy metal ions from aqueous solutions under optimum experimental conditions. However, silica/ graphite oxide (2:3) composite was the most effective adsorbent for the heavy metal removal and it is highly recommended to be used in water treatment for its high adsorption capacity followed by Graphite Oxide and Silica nanoparticles.

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