

Removal of Chromium and Cadmium Ions from Water Using Graphene Oxide and Sodium Graphene Oxide Nanocomposites

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Abstract: -

Contamination of underground and surface water by industrial and agricultural activities is a great threat to environmental health. Easy and economically cost effectively available technology for removal of these toxic heavy metals from wastewater is therefore required. Traditional methods of heavy metal removal include reverse osmosis, ion exchange mechanism, chemical precipitation, electrochemical treatment techniques, membrane filtration, coagulation, extraction, irradiation and adsorption. Adsorption is the most preferred technique due to its high efficiency and cost. Activated carbon, clay minerals and natural zeolite, chelating materials, metal oxide nanoparticles and carbon nanosheets have been used for adsorption. In this study, graphene oxide nanocomposites were synthesized using modified Hummer's method. Sodium graphene oxide was prepared by neutralizing graphene oxide using sodium hydroxide and rinsing with HCl. Surface morphology of the nanocomposites were studied using Fourier transform infrared spectrophotometer. Graphene oxide and sodium graphene oxide were used for removal of Cadmium and Chromium ions. Parameters pH, metal ion concentration, mass of the adsorbent required for adsorption and time of adsorption were optimized. Metal ion concentrations were analyzed using Atomic absorption spectrophotometer. Optimum pH for adsorption was found to be pH 6. A concentration of 200 ppm was experimentally chosen as the optimum for the batch experiments. The optimum mass of the nanocomposites was found to be 0.1g. Equilibrium for adsorption was achieved after 60 minutes for the sodium graphene oxide and 90 minutes for the graphene oxide nanocomposites. The experimental data was fit in both Langmuir and Freundlich isotherms.

Keywords: Adsorption, industrialization, nanocomposites, optimization, synthesis.

Introduction

Since beginning of industrialization, surface and groundwater contamination by heavy metals has been a major threat because their toxicity towards aquatic life, plants, animals, human beings and the environment (Shen *et al.*, 2009). Heavy metal pollution is known to result from various sources such as lead in petrol, industrial effluents, leaching of mineral ions into lakes and rivers by acid rain, preparation of nuclear fuels and electroplating. They enter into soil, underground water and surface water. Unlike organic contamination, heavy metals do not normally undergo biodegradation and are thus considered a challenge for remediation. Though many governments have enacted laws barring discharging of heavy metals to water bodies using toxic substances such as lead, heavy metals still find their way to water sources (Amarasinghe, 2007). Heavy metal ions could be removed by several traditional techniques (Fu and Wang, 2011) including chemical precipitation (Wang *et al.*, 2005), reverse osmosis (Bodalo *et al.*, 2003), electrochemical techniques (Walsh *et al.*, 1994), ion exchange (Xing *et al.*, 2007), membrane filtration (Ersahim *et al.*, 2012), coagulation (Zhang *et al.*, 2003)

irradiation (Batley *et al.*, 1978) and adsorption (Srivastava *et al.*, 2011). Due to its low cost effective, high efficiency, and simple to operate for removing trace levels of heavy metal ions, adsorption technology is regarded as the most promising technique (Zambous *et al.*, 2011). Several materials including activated carbons (Koby *et al.*, 2005), clay minerals (Oubagaranadn *et al.*, 2009), chelating materials (Sun *et al.*, 2006), and chitosan/natural zeolites (Wang *et al.*, 2009) have been researched to adsorb metal ions from aqueous solutions.

Even though activated carbon is the most familiar adsorbent, its wide spread use is limited because of factors associated with cost and low capacity for adsorption of metal ions (Li *et al.*, 2009). Adsorption technique though robust in nature, massive mass transfer resistance due to size of convectional adsorbents is a big issue (Setshedi *et al.*, 2013). Most of traditional micro-scale adsorbents have low adsorption capacities and are time consuming owing to large diffusion paths (Bhaumik *et al.*, 2011). These drawbacks can be overcome by application of nano-sized materials or nanostructured adsorbent materials. Factors such as high surface area, short diffusion paths and high attraction

efficiencies make nanostructured materials attractive as adsorbents for removal of contaminants from wastewater (Ghanemi *et al.*, 2011). Graphene oxide initially synthesized is acidic and this limits its efficiency in adsorbing metal ions. This study investigates the effectiveness of sodium graphene oxide which is neutralized graphene oxide in the adsorption of target heavy metals ions chromium and cadmium at optimized parameters.

Materials and Methodology

Experimental procedure for Preparation of graphene oxide nanocomposites

Graphene oxide was synthesized using the modified hummer's method (Krishna *et al.*, 2012)

In a typical reaction, 2 g of graphite, 2 g of NaNO₃, and 90 mL H₂SO₄ (98%) were stirred together in an ice bath (0-5°C) for 4 hours. 12 g of KMnO₄ was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 15 °C. Subsequently, 184 mL of de-ionized water was added. The resulting mixture was removed from the ice bath and stirred for two hours. The temperature was raised to 98 °C resulting to a brown color being observed. The solution was diluted further with 100 mL of de-ionized water and stirred continuously for another two hours. The mixture was then treated with 40 mL of 30% H₂O₂ solution to terminate the reaction. The mixture was rinsed severally with 10% HCl to remove metal ions and then with deionized water, filtered and freeze dried. Sodium graphene oxide was prepared by neutralizing graphene oxide already synthesized with 1M sodium hydroxide in aqueous solution until a pH 7 was obtained. Surface morphology of the prepared graphene oxide and sodium graphene oxide was analyzed by FTIR spectrophotometer; model-IR Affinity-1S.

Preparation of the stock solution

Stock solution was prepared from chromium nitrate and Cadmium nitrate respectively. Serial dilutions were made from the stock solutions.

Batch Experiments

Determination of optimum pH for adsorption

Optimization of the pH was done by varying the pH of the samples of concentration 100 ppm to pH of 2, 4, 6 and 8. The pH of each sample was adjusted using 1M hydrochloric acid and 1M sodium hydroxide. 50 mL of 100 ppm sample was exposed to 0.1g of NC and adsorption mechanisms conducted for a period of 3 hours in all the 4 runs. The mixture was filtered and the concentration of the metal ions

in the filtrate analyzed using Atomic Absorption Spectrophotometer (AAS PG -990).

Determination of the effect of metal ion concentration on adsorption

Effect of metal ion concentration was studied at optimum pH, constant dosage of sorbent and same time interval. Concentrations of 50 ppm, 100 ppm, 150 ppm, 200 ppm in 50 mL volume were exposed to 0.1g NC1 and the adsorption allowed to take place for 3 hours. The mixture was filtered and the metal concentration in the filtrate analyzed using Atomic Absorption Spectrophotometer (AAS- PG -990).

Determination of effect of dosage of adsorbent on adsorption

The effect of the dosage of the adsorbent was studied at optimum pH, optimum concentration and same time interval. A mass of 0.1g, 0.2g, 0.3g and 0.4g NC was exposed to 50 mL of 200 ppm samples. The mixture was filtered and the metal concentration in the filtrate analyzed using Atomic Absorption Spectrophotometer (AAS- PG -990).

Determination of the optimum time for adsorption

Effect of time of exposure was studied at constant concentration of metal ion solutions, Optimum pH, and a constant dose of adsorbent. At optimum pH, 0.1g of NC was exposed to 50 mL of 100 ppm samples and adsorption of metal ions analyzed after 0.5 hrs, 1 hour, 1.5 hours, 2 hours and 2.5 hours.

Results and Discussion

Surface morphology of graphite powder as a starting material

The FTIR-spectra of graphite (Figure 1) had a characteristic absorption band at 1635cm⁻¹ that were used to identify the structure of graphite. The peak observed at 1635cm⁻¹ is associated to the C=C skeleton of the graphite. This confirms that the original structure of the graphite has not been altered in any way. Other bands used to describe the structure of graphite, that is intensive bands includes 1705cm⁻¹, 1658cm⁻¹, 1566cm⁻¹, 1527cm⁻¹, 1026cm⁻¹, 455cm⁻¹ and 416cm⁻¹. The band between 1026cm⁻¹ to 1416cm⁻¹ is observed in case graphite is splitted. The absorption band observed at 2368.59cm⁻¹ as a duplet is attributed to the conjugate C=C of the graphite. However, in the IR- spectra, intensive bands were observed at region stretching vibration of hydroxyl group and carboxyl group. This testifies the existence of carboxyl and hydroxyl groups on the surface of graphite.

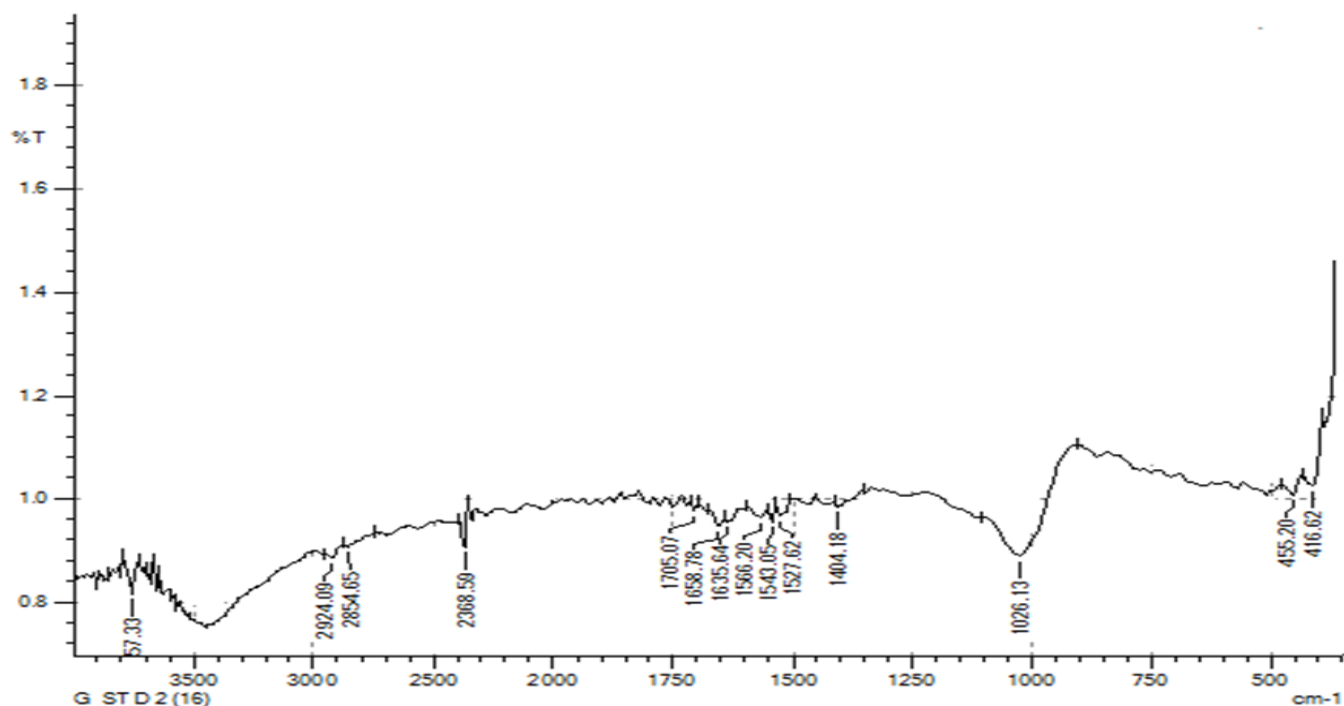


Figure 1. FTIR spectra for graphite powder

From the Fourier transform infrared spectrum of graphene oxide is depicted in figure 2. The peaks observed at 3400cm⁻¹ corresponds to an absorption band of hydroxyl group (-OH). The peak at 1720.5cm⁻¹ corresponds to an absorption band for a carboxyl group (C=O) while that at 1056.99cm⁻¹ corresponds to an absorption band for an epoxy group (C-O). The peak observed at 1620.1cm⁻¹ is associated to the C=C skeleton of the graphite. This confirms that the original

structure of the graphite has not been altered in any way. However, several functional groups -OH, C=O, C-O have been introduced into the graphite skeleton. The above functional groups are the active sites responsible for the adsorption mechanism of metal ions. There is no difference between the FTIR spectrum of graphene oxide and sodium graphene oxide (Figure 3).

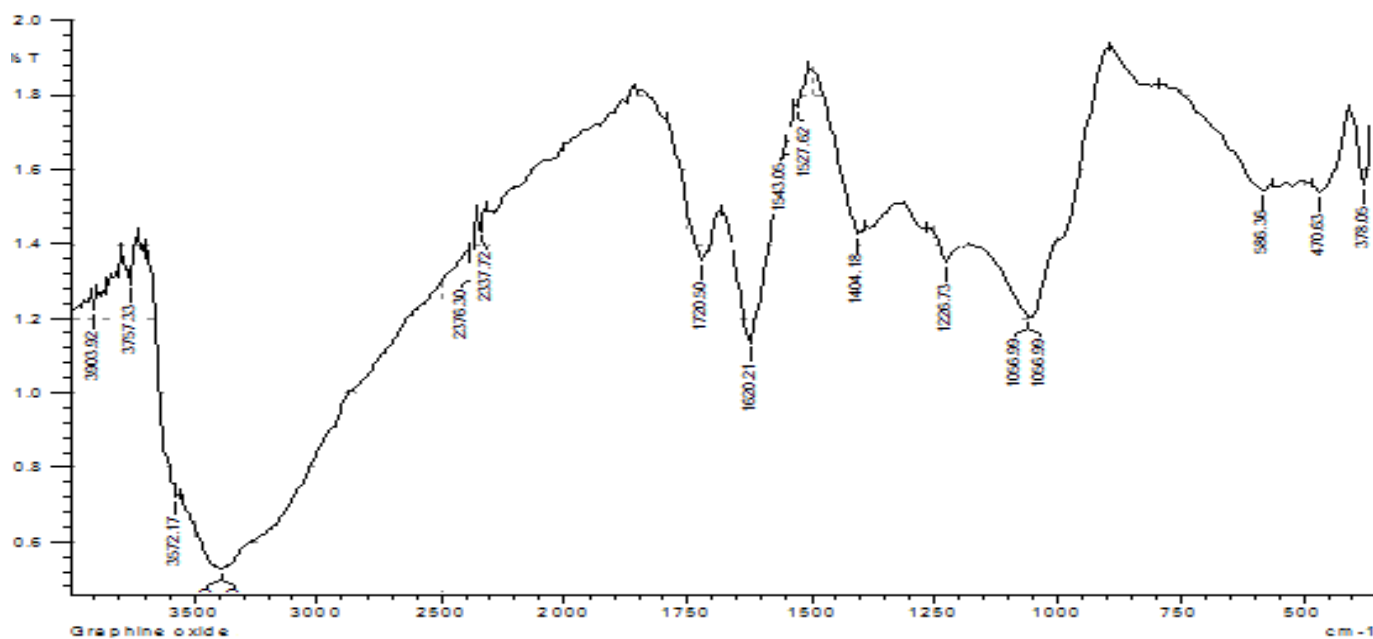


Figure 2: FTIR spectra of graphene oxide

These functional groups on the surface of graphene oxide and sodium graphene oxide can provide abundant sorption

sites and thereby effectively increase the sorption capacity of for heavy metal ions (Kuo 2009).

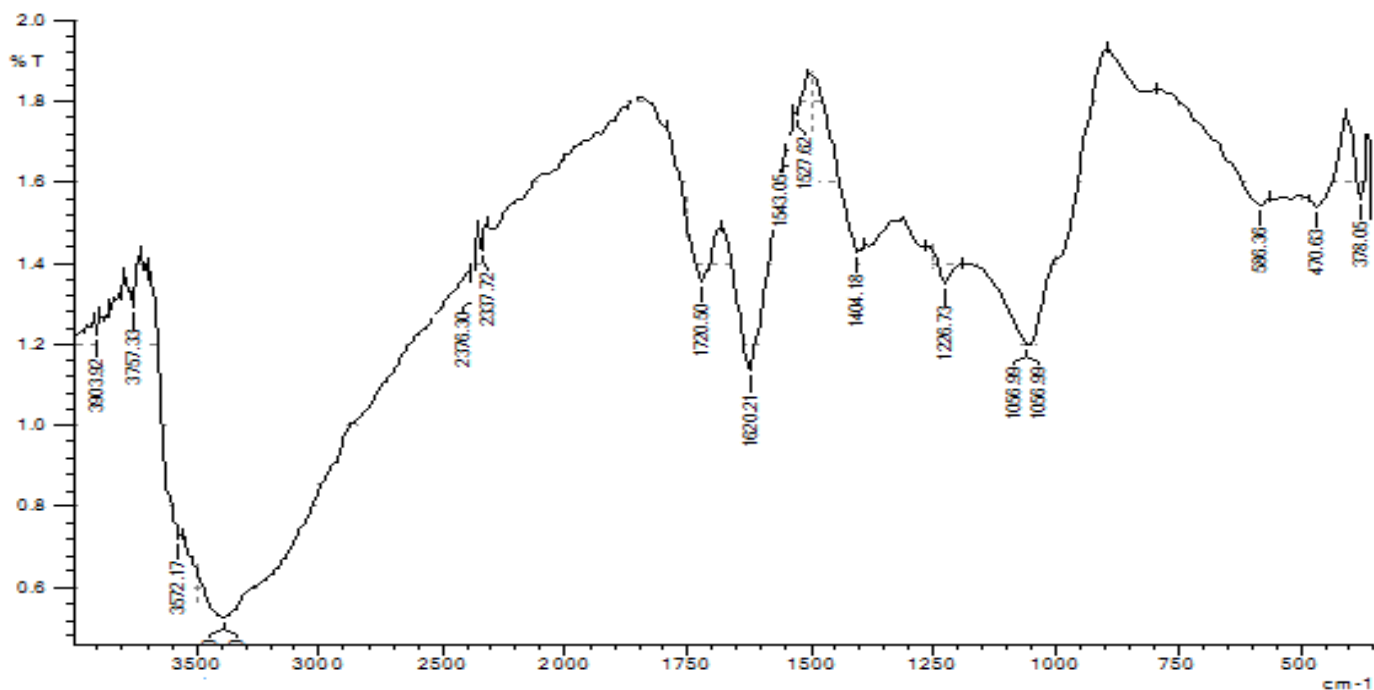


Fig 3. FTIR-spectra for sodium graphene oxide.

Batch experiments

Effect of pH on adsorption of chromium and cadmium ions

The effect of pH on adsorption of both Cr and Cd ions were studied by varying the pH of the samples from pH 2 to pH 8 (Figure 4) having a constant concentration and mass of the nanocomposites. Adsorption was carried out by stirring by a magnetic stirrer for a period of three hours to ensure that maximum adsorption had taken place. Percent removal of both Cr and Cd ions were observed to increase from pH 2 to

pH 6 from which it decreased slightly at pH 8 for both graphene oxide and sodium graphene oxide nanocomposites. The percentage removal at pH 2 for both Cr and Cd ions was 20.75% and 20.59% for graphene oxide (NC1) and 76.18% and 59.93% for sodium graphene oxide (NC2) respectively. At pH 4, it was 30.92% and 21.98% for NC1 and 87.83% and 74.35% for NC2 respectively. High percent removal was observed at pH 6 with 95.28% and 86.66% for NC1 and 99.665% and 98.57% for NC2 respectively. A slight decrease was observed at pH 8 with percent removal of 93.61% and 60.85% for NC1 and 95.71% and 97.66% for NC2 respectively.

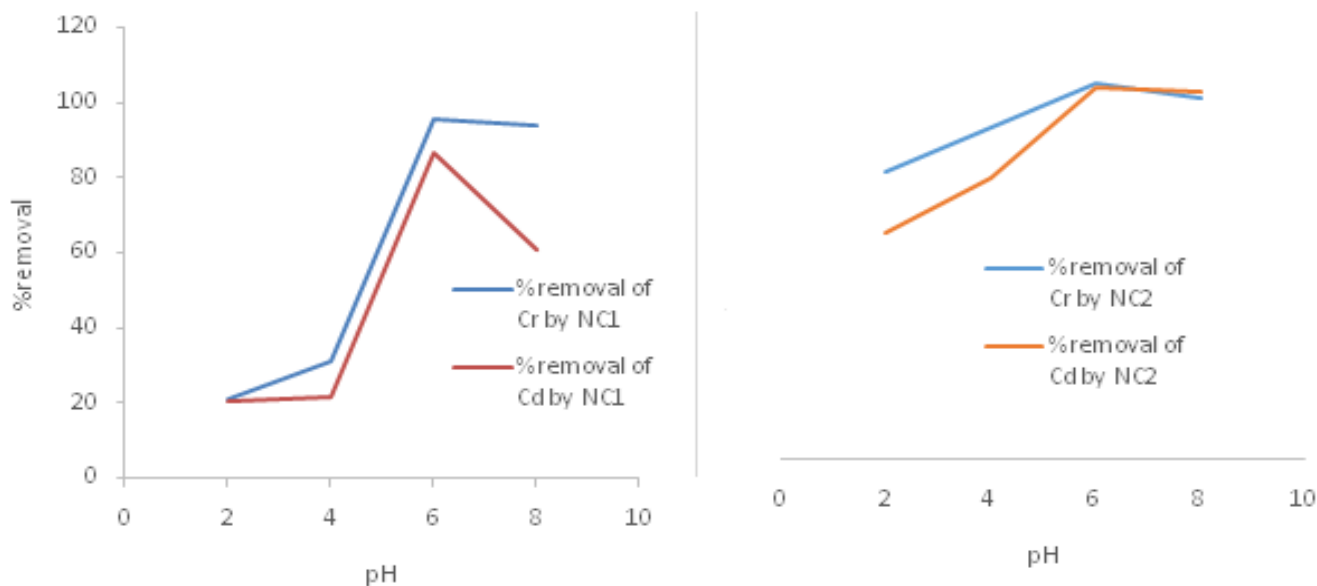


Figure 4. Percent adsorption of Cr and Cd ions at different pH values

The trend above can be explained by the fact that changes in pH affects the surface charge characteristics of the graphene oxide and the sodium graphene oxide. Increasing the pH increases the negative charge of the adsorbent and as a result, reactions between Cr and Cd ions and the functional groups ($-\text{COO}^-$ or $-\text{O}^-$) are favored forming metal complexes. According to Madad *et al* 2012, H^+ , COOH , $-\text{OH}$ is released into the solution at the same time. This is further confirmed by the fact that equilibrium pH was measured to be lower than the initial pH value. Increasing the pH above six leads to precipitation of the metal ions as hydroxo complexes. Basic pH changes the surface charge of the nanocomposites and as a result, electrostatic repulsion occurs. Precipitation is responsible for the percent removal of the Cr and Cd ions at pH 8. High adsorption capacities are observed for the sodium graphene oxide. This can be attributed to the fact that it being neutralized, it does not alter the pH of the sample thus adsorption at exact sample pH is measured. Graphene oxide prepared in this method is acidic and this acidity together with the H^+ released from its skeleton lowers the pH of the samples from the exact

measured values and as a result lower adsorption capacities are observed. The optimum pH was thus chosen to be pH 6 for the next batch experiments.

Effect of change in concentration on the removal of Cr and Cd ions

The effect of change in the concentration was studied by varying the concentration of the samples from 50 ppm to 200 ppm at optimum pH (Figure 5) and constant mass of the nanocomposites. Adsorption was carried for three hours to ensure maximum adsorption takes place. Percentage removal of Cr and Cd ions increased with increase in initial concentration of Cr and Cd ions solutions. Observed percent removal for Cr and Cd at 50 ppm was 80.15% and 35.72% for graphene oxide (NC1) and 91.6% and 43.3047% for sodium graphene oxide (NC2). At 100 ppm were 94.89% and 58.71% for NC1 and 96.86% and 56.67% for NC2. At 150 ppm were 94.56% and 60.26% for NC1 and 98.95% and 55.56% for NC2 while at 200 ppm were 99.02% and 65.87% for NC1 and 97.9% and 64% for NC2 respectively.

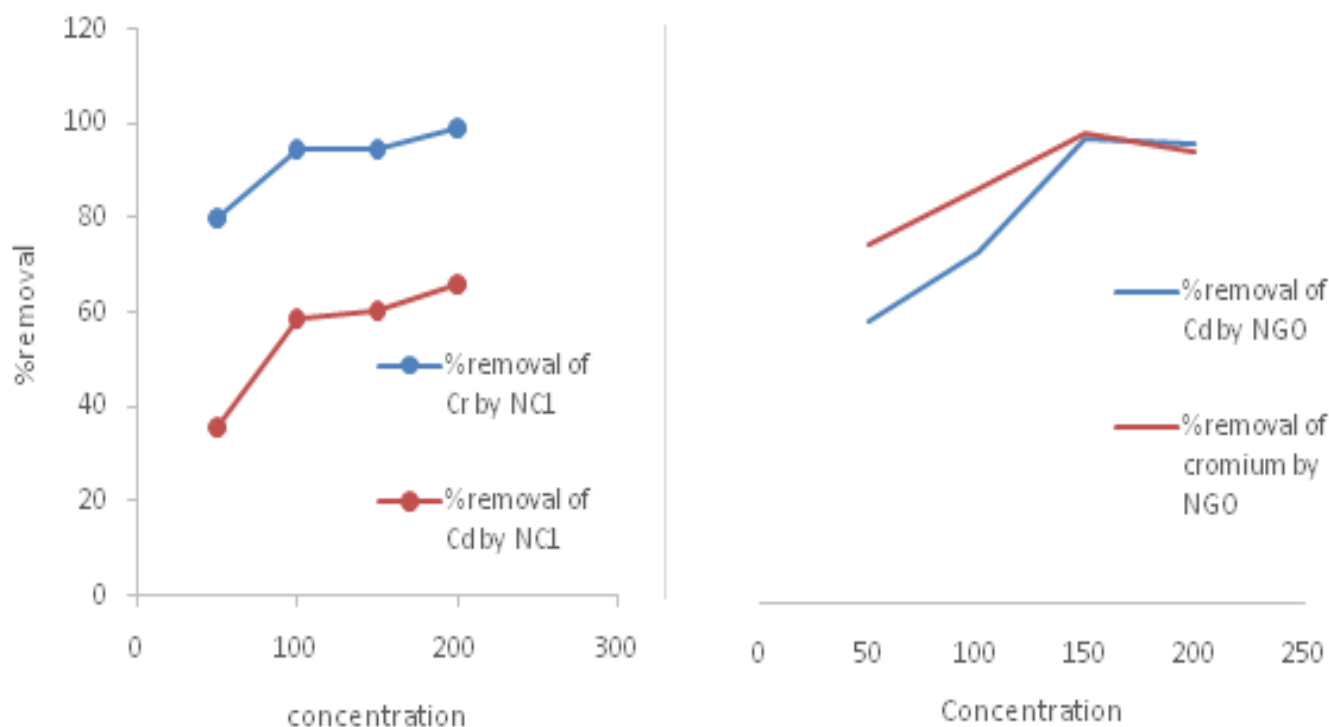


Fig 5. Percent removal of Cr and Cd ions at different concentrations

Low initial concentrations indicate that the active sites of both NC1 and NC2 are not fully utilized and as a result, electrostatic attractions are low. Increasing the concentration favors utilization of the active sites and as a result a high percentage removal is observed. However, this is guided by metal ion to the active site ratio. It can therefore be concluded that adsorption of both Cr and Cd ions is concentration dependent.

Effect of nanocomposites dosage

The effect of mass of the nanocomposites was studied at optimum pH, concentration of 200 ppm and varying the mass of NC1 and NC2 from 0.1g to 0.4 g in a 50 mL (Figure 6) sample solution respectively. The adsorption was carried out for a period of three hours to ensure that maximum adsorption takes place. Maximum percentage removal per gram of the nanocomposites was observed for 0.1g of both NC1 and NC2.

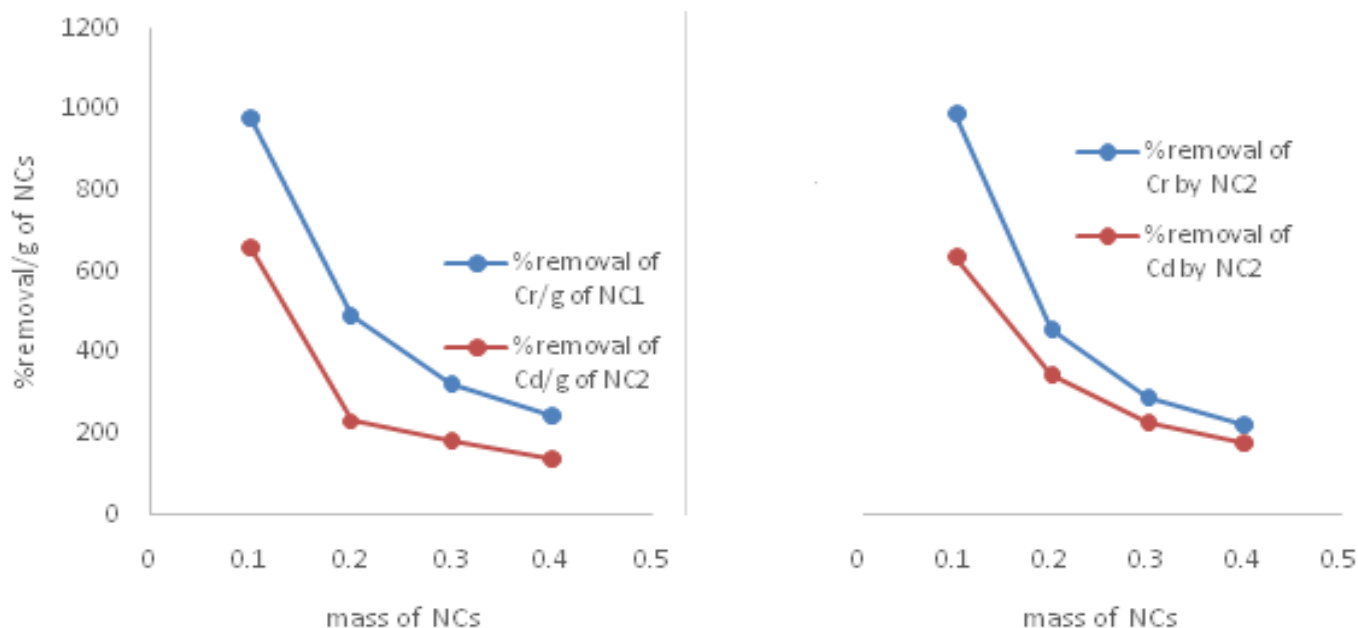


Figure 6; Effect of mass of nanocomposites on the percent removal of Cd and Cr ions

The trend above can be attributed to the fact that active sites can be favorably accommodated at low nanocomposite dosage. Changing the dosage of the NC1 or NC2 alters the metal ion ratio to the active sites ratio. This therefore alters the adsorption mechanism.

Effect of time of adsorption

Effect of time of exposure was studied at constant concentration of metal ion solutions, Optimum pH, and 0.1g of adsorbent (Figure 7). At optimum pH, 0.1g of NC1 and NC2 was exposed to 50 mL of 200 ppm samples and adsorption of metal ions analyzed after 0.5 hrs, 1 hour, 1.5 hours, 2 hours and 2.5 hours.

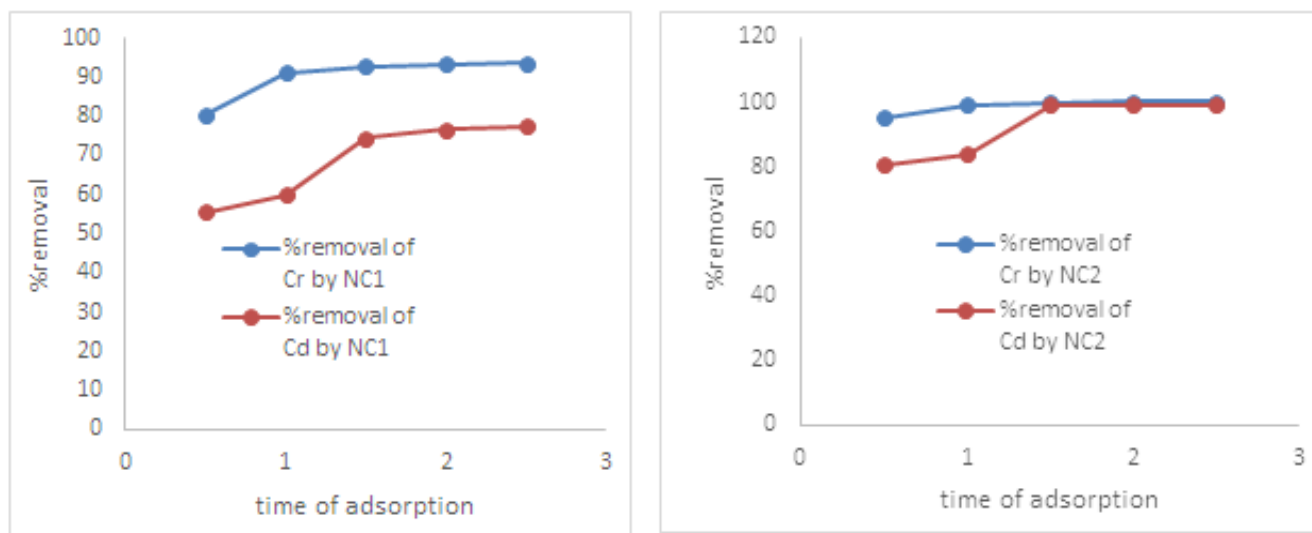


Figure 7; Percent removal of Cr and Cd ions at varying time for both NC1 and NC2.

Percent removal of Cr and Cd ions was observed to increase sharply from 0.5 hours of adsorption to 1.5 hours from which equilibrium adsorption was achieved for the Graphene oxide while for the sodium graphene oxide, equilibrium adsorption was attained after 1 hour adsorption. It can be seen that adsorption equilibrium was not achieved earlier for the graphene oxide. This can be explained by the fact that graphene oxide being acidic, the hydrogen ions released from $-COOH$, $-OH$ on the surface of NC1 to the solution

during the process of Cr III and Cd II ions adsorption and the acidity of the adsorbent resulted to decreased sample pH. The resulting effect was change of the sample pH which in effect reduced the adsorption rate. Sodium graphene oxide being neutral has no great influence on the alteration of sample pH hence equilibrium is achieved faster. The optimum time of adsorption is thus 150 minutes for the graphene oxide and 120 minutes for the sodium graphene oxide.

Adsorption isotherms

The relationship between metal ions and adsorbents is essential to reach an effective adsorption. In order to demonstrate the effect of the Cr and Cd ion concentration on adsorption, experiments were carried out at different initial concentration. It is observed that the adsorption capacity increases with an increase in initial concentration. The relationship between adsorbed metal ions and its concentration in solution under equilibrium is described Langmuir (Figure 8) and Freundlich (Figure 9) models. The experimental data could be fit in Langmuir and Freundlich isotherm models as described below:

The linear Langmuir model is:

$$\frac{1}{qe} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}} \cdot \frac{1}{Ce}$$

Where Q_{max} (in mg/g) represents the maximum amount of metal ions adsorbed per unit weight of adsorbent to form a complete monolayer on the surface, b is the equilibrium adsorption constant, q_e is the amount of metal ions adsorbed by adsorbent at equilibrium, and C_e is the equilibrium concentration of metal ions.

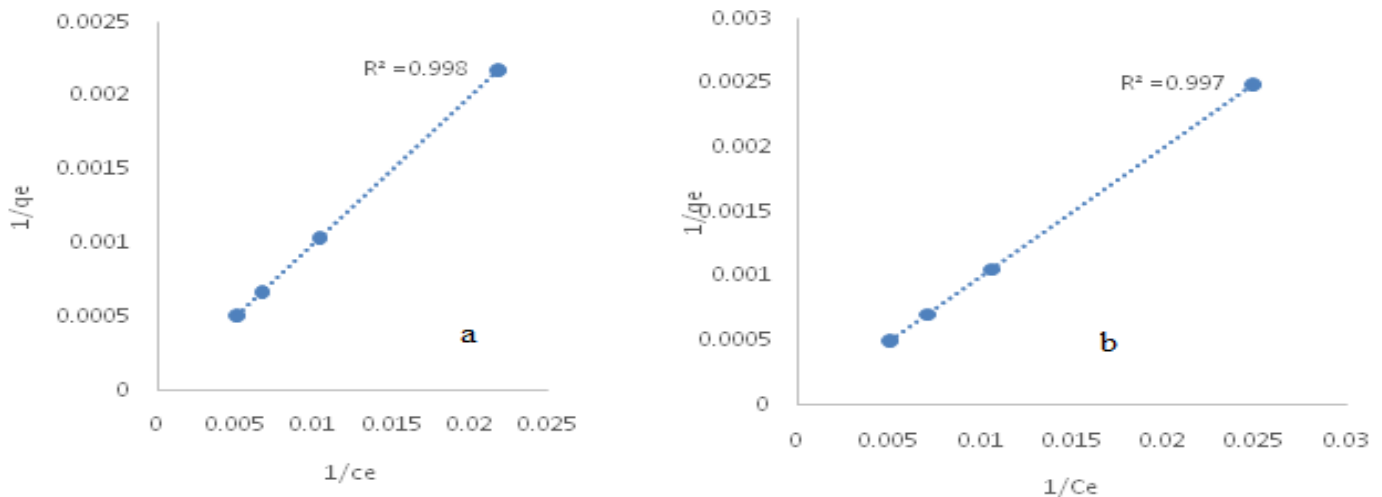


Figure 8; Langmuir isotherm for Cr removal using NC1 (a) and NC2 (b)

The Freundlich model is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e$$

Where $1/n$ represents Freundlich intensity parameter and k indicates the adsorption capacity of adsorbent.

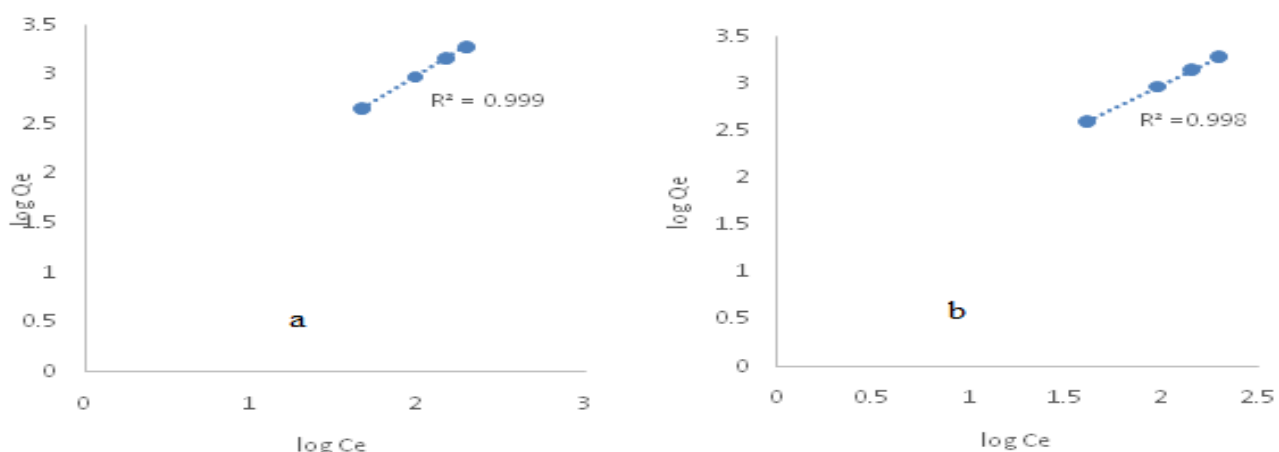


Figure 9; Freundlich isotherm for Cr removal using NC1 (a) and NC2 (b)

CONCLUSION

From the experimental data, it has been observed that both graphene oxide and sodium graphene oxide are good adsorbents for toxic heavy metal ions. It can also be concluded that the adsorption is depended on pH, concentration, mass of the adsorbent and the time of

adsorption. The data collected observed the Langmuir and Freundlich linear equations. Chromium ions were adsorbed more than Cadmium ions due to its trivalent chemistry. The effect of the sodium hydroxide on the surface of the graphene oxide was only changing the surface charge rather did not affect the surface morphology in any way. The chemistry of adsorption was governed by the ion exchange

mechanism between the functional groups on the graphite skeleton and the ions in the solutions. This resulted to the increase of the potential of hydrogen ions in the solution.

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