SATEM-2019 Special Issue

J. Indian Chem. Soc.,
Vol. 97, April 2020, pp. 541-546

Removal of cadmium ions from water by using aluminum functionalized Graphene Oxide

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Manuscript received online 19 December 2019, accepted 09 March 2020

Cadmium is one of the four heavy metals in World Health Organization's list of ten chemicals of major public health concern. Removal of cadmium ions from contaminated water is a major challenge for engineers and researchers and new methodologies are being constantly investigated for achieving higher removal efficiencies. This article focuses on synthesis of aluminum functionalized Graphene Oxide (GO-Mn-Al) nanocomposite and its application in cadmium removal from contaminated water. Cadmium removal kinetics and relevant adsorption isotherm models were also analyzed. The effect of different parameters such as pH, time of contact and the dosage of adsorbent were investigated. The optimum pH for Cd removal was found to be 7. The capacity of adsorption of the synthesized nanocomposite for cadmium ions at pH of 7.0 was found to be 120.48 mg/g for an adsorbent dosage of 1 g/L and 120 min of contact time. This literature demonstrates that the synthesized GO-Mn-Al nanocomposite can be used for cadmium removal from contaminated water successfully.

Keywords: Cadmium, isotherm, adsorption, adsorbent, nanocomposite, GO-Mn-Al.

Introduction

Cadmium, being a toxic heavy metal has been gaining attention in the field of water and wastewater engineering as it exhibits bioaccumulation and is non-biodegradable even at very less concentrations[1]. The permissible concentration of cadmium as per Environmental Protection Agency and World Health Organization's recommendations in drinking water are 0.005 mg/L and 0.003 mg/L respectively. Accumulation of cadmium in humans affects various organs like placenta, liver, pancreas, intestines and lungs[2], higher exposure may cause itai-itai disease[3] and affect the levels of reproductive hormones[2,4]. Maximum reported concentration of cadmium in selected freshwater samples in India is about 1.46 mg/L approximately[5]. The prevalent technologies for removal of toxic heavy metals like cadmium from water include precipitation, coagulation and sedimentation, reverse osmosis, ion exchange, and adsorption on the surface of different adsorbents[6]. Amongst these physico-chemical processes, adsorption has established itself as one of the best alternatives for elimination of heavy metals from water due to its ease of operation, higher efficiency and lower cost[7]. Many adsorbents like Carbon Nanotubes (CNTs), Oxidized MWCNTs[8], Oxidized CNTs[9], Graphene Oxide[10], 3D Sulfonated Reduced Graphene Oxide[11] etc. have been used to achieve satisfactory removal of cadmium from compromised water. Graphene Oxide has been a hot topic of discussion amongst researchers and engineers due to its very high surface area to volume ratio and it has been functionalized with a number of metals and non-metals by introducing them in the Graphene Oxide structures.

This study focused on introduction of aluminum into the Graphene Oxide nano-structure to effect satisfactory adsorption of heavy metals like cadmium from synthetic aqueous solutions.

Materials and methods

(A) Material synthesis:

The synthesis of Graphene Oxide nanocomposite has been done according to the method suggested by Marcano *et al.*[12]. For this, H_2SO_4 and H_3PO_4 were mixed in 9:1 ratio and this was added to a mixture of Graphite Powder (3 g) and $KMnO_4$ (18 g) in a 2 L Borosil beaker and this resulted in a slight exotherm and raised the reaction temperature. The Graphite Powder was oxidized by potassium permanganate

in a very strong acidic environment ensured by H_2SO_4 and H_3PO_4. The nascent oxygen released during conversion of sulphuric acid to sulphurous acid, also helped in oxidation of graphite. This lead to exfoliation of the Graphite sheets in order to form Graphene Oxide (GO). The resulting solution was then stirred at 1200 rpm for 12 h. 400 ml of ice cold water was added to it along with 3 ml 30% H_2O_2. The solution was then stirred and allowed to rest. The hydrogen peroxide was added to help in reaction quenching and to remove excess potassium permanganate[13]. The supernatant was decanted and remaining graphene oxide solution was then washed repeatedly and filtered. Aluminium chloride solution was then added to this GO suspension. The (C + Mn):Al ratio was kept as 1:3 and the reaction was performed in an icebath so as to avoid any explosive conditions. The pH was then raised to 7 to form hydroxide precipitate with C-Mn nanocomposite. The solution was then filtered, subjected to several distilled water washes, dried and kept in vacuum desiccator. After complete drying, the material was crushed to obtain fine powdered GO-Mn-Al nanocomposite. Henceforth this material referred to as Aluminum Functionalized Graphene Oxide or GO-Mn-Al.

The material thus obtained was characterized with Scanning Electron Microscope (SEM) for visualisation of the surface topography of the nanocomposite as shown in Fig. 1. The Energy Dispersive Spectroscopy (EDS) was used to show the elemental composition of the functionalized material. The presence of carbon (C), oxygen (O), manganese (Mn) and aluminum (Al) in GO-Mn-Al nanocomposite was observed in the EDS image as shown in Fig. 2.

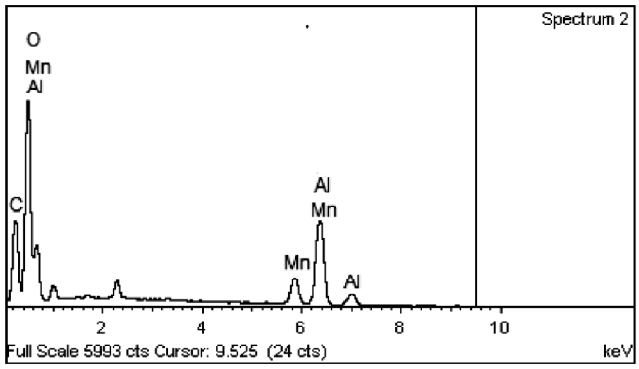

Fig. 2. EDS image of GO-Mn-Al.

(B) Batch adsorption experiments:

The study has been conducted under batch mode to find the ideal operating conditions. To determine the adsorption capacities of GO-Mn-Al for Cd ions, as well as to study the impact of the initial Cd concentration, pH of the solution, time of contact between adsorbate and adsorbent and temperature dependence, adsorption experiments were performed by batch equilibrium technique. The synthetic cadmium solution was prepared from cadmium standard solution of 1000 mg/L by preparing a working standard of 10 mg/L by dilution with distilled water. The batch studies (other than pH study) were conducted at pH 7. The pH adjustment was done by using 0.01 *M* H_2SO_4 and/or 0.01 *M* NaOH as per requirement. The initial and final Cd concentrations were determined by using Atomic Absorption Spectrometer (Thermo Scientific, USA, iCE 3000 AA05182611 v1.30) in flame mode with air/acetylene flame type at primary wavelength of 228.8 nm (Fig. 3). The experiments were carried out in a 250 ml Erlenmeyer's flask. The samples with required concentra-

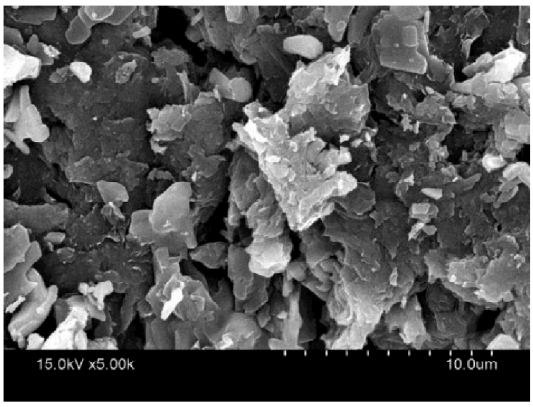

Fig. 1. Scanning Electron Microscope image of GO-Mn-Al.

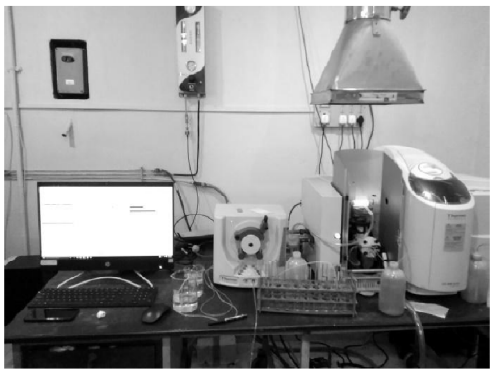

Fig. 3. AAS analysis setup.

tion of cadmium ions were diluted to 100 ml and were shaken vigorously after addition of required amount of GO-Mn-Al. For development of kinetic expression the sampling was done at pre-determined time intervals and the supernatant liquid was filtered through 0.45 μ filter paper (Whatman) and the treated samples were kept for final cadmium ion concentration determination.

Results and discussion

Batch studies were conducted for determination of the optimum value of the parameters required for successful adsorption of cadmium from water. To calculate the adsorption percentage and adsorption capacity following equations were used:

$$\text{Adsorption (\%)} = \{(C_o - C_e)/C_o)\times 100\}\% \quad (1)$$

$$q_e = (C_o - C_e)\times(v/m) \quad (2)$$

where, C_o = initial Cd concentration in mg/L, C_e = equilibrium Cd concentration in mg/L, m = mass of the adsorbent in grams, v = volume of the suspension in L, and q_e = equilibrium adsorption capacity in mg/g.

All the experiments were performed thrice and average value was taken to get more precise and accurate results.

Effect of contact time:

To study the impact of time of contact between adsorbate and adsorbent, samples were collected after 5, 10, 15, 30, 60, 90, 105, and 120 min keeping temperature 27°C, pH 7, initial Cd concentration of 5 mg/L and adsorbent dosage of 1 g/L. It is clear from Fig. 4 that more than 90% removal took place within initial 60 min and the equilibrium was achieved after 120 min of contact. The adsorption increased with time of contact till 90 min after which the adsorption reached a saturation point and with further increase in time of contact a constant percentage of removal was noted. The optimum time of contact was taken as 90 min.

Adsorption kinetics:

The kinetics of cadmium adsorption were studied by varying the time of contact from 10 min to 120 min. From Fig. 4 it is seen that the removal of cadmium seemed to take place in two different phases. 1st phase involved rapid cadmium adsorption within 10 min followed by slower adsorption of cadmium. About 60% of cadmium was absorbed in first 10 min, and about 90% cadmium ions were adsorbed within the first hour. Equilibrium is achieved after 120 min of contact time. At equilibrium the removal efficiency of cadmium is more than 95%.The cadmium removal data was plotted in two different kinetic models: pseudo-first order, and pseudo-second order model. The two types of models are described below.

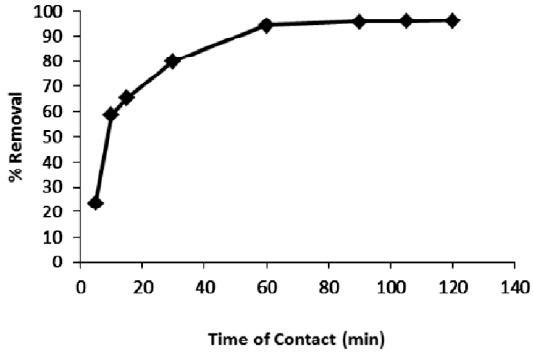

Fig. 4. Effect of contact time between adsorbate and adsorbent on removal.

Pseudo-first order model:

$$\ln (q_e - q_t) = \ln q_e - k_t \quad (3)$$

Pseudo-second order model:

$$t/q_t = 1/(q_e^2 k) + t/q_e \quad (4)$$

where, q_e = Cd adsorbed on GO-Mn-Al at equilibrium in mg/g, q_t = Cd adsorbed on GO-Mn-Al at time t (min) in mg/g and k = reaction rate constant.

As it is quite evident from Table 1, the adsorption fits better in pseudo-second order model (R^2 = 0.9995) then the pseudo-first order kinetic model (R^2 = 0.6008). Since the pseudo-second order kinetic model fits better than pseudo-first order, it can be postulated that chemisorption is pre-

Table 1. Adsorption kinetics study

Model	Equation of linear fit line	q_e (mg/g)	k	R^2
Pseudo-first order kinetic model	$\ln (q_e - q_t) = 1.4686 - 1.7514\ t$	4.343	1.7514	0.6008
Pseudo-second order kinetic model	$t/q_t = 0.0501 + 0.0078\ t$	128.20	1.21×10^{-3}	0.9995

dominant mechanism of removal. However, from the kinetic study (Fig. 5) we can ascertain that some role of physisorption also exists in the later stages of the adsorption process.

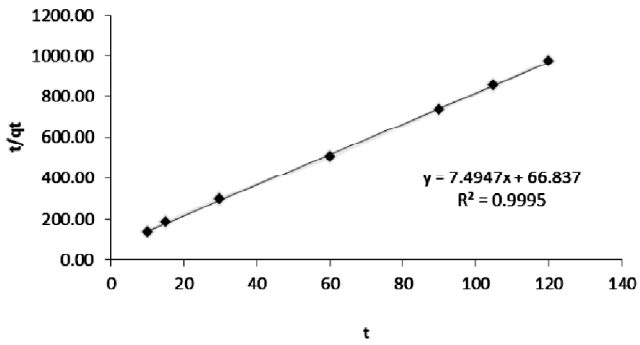

Fig. 5. Pseudo-second order model.

Effect of pH:

For testing the effect of pH, the samples were subjected to normal room temperature (27°C) and 1 g/L of GO-Mn-Al was used. The initial cadmium ion concentration was 5 mg/L and the contact time between GO-Mn-Al and Cd ions was 90 min. The maximum removal efficiency was noted at a pH of 11.2, which can be attributed to the formation of cadmium hydroxide at that pH as is evident from the solubility diagram of cadmium (Fig. 6). However, drinking water pH should be maintained within a pH range of 6.5 to 8.5. Satisfactory removal (around 95.8%) has been observed (Fig. 7) at pH 7 and henceforth the other studies were conducted at this neutral pH range.

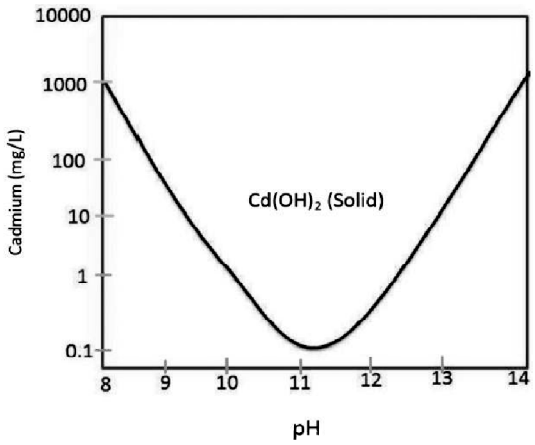

Fig. 6. Solubility of cadmium in aqueous medium (modified from climate policy watcher's representation).

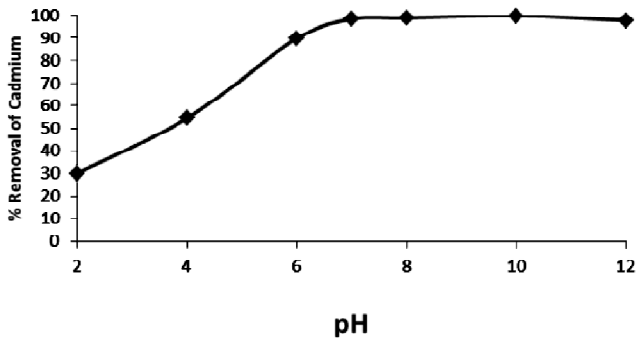

Fig. 7. Effect of pH on removal.

Effect of temperature:

The batch equilibrium experiments were carried out at 20°C, 24°C, 27°C, 30°C and 35°C and at pH7 (±0.25), GO-Mn-Al dosage 1 g/L, contact time of 90 min, and initial Cd ion concentration of 5 mg/L. A significant change in removal percentage could be seen with variance in temperature. The maximum removal efficiency was noted at 27°C as is evident from Fig. 8. Higher temperatures discouraged the adsorption of Cd ions. The slight reduction in adsorption of Cd ions may be attributed to increase in tendency to desorb Cd^{2+} from the GO-Mn-Al surface to the solution. From the desorption of Cd^{2+} into the solution it can be postulated that the major force (electrostatic interaction) between the binding sites of GO-Mn-Al and Cd^{2+} ions may be weakened by rise in temperature. Similar results are also reported by other researchers[15].

Effect of adsorbent dose:

For determination of the ideal adsorbent dosage for effi-

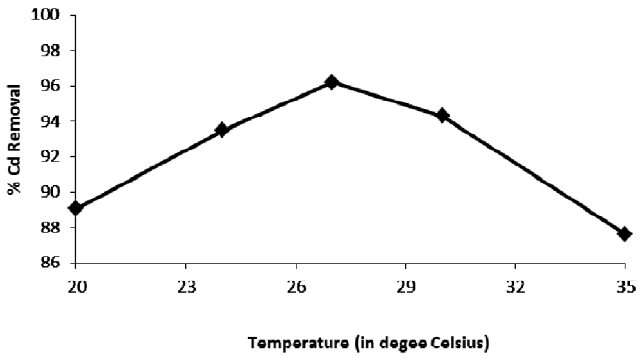

Fig. 8. Effect of temperature on cadmium removal.

ciency and economic feasibility, the dose of adsorbent was varied from 0.5 g/L to 2 g/L. The test condition maintained was: volume of the sample 100 ml, pH 7, initial concentration of cadmium ion 5 mg/L, contact time 90 min and temperature 27°C. The maximum removal was noted at 1.0 g/L of adsorbent dose (Fig. 9). It is clear from the figure that further increase of adsorbent dosage did not significantly improve removal which is due to the fact that after the equilibrium has been attained, the removal did not improve significantly.

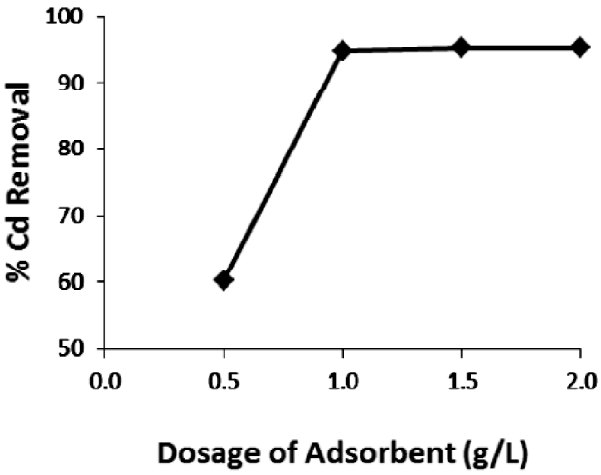

Fig. 9. Effect of dosage of adsorbent on removal.

Effect of initial concentration:

The initial concentration of cadmium ions were varied from 1 mg/L to 10 mg/L. The tests were conducted at 27°C temperature, pH 7, time of contact 90 min and adsorbent dosage of 1 g/L. It is evident from Fig. 10 that removal varied from 98% to 91% with increase in dose.

Adsorption isotherm:

The isotherms are used to draw a relation between the adsorption of Cd ions per unit weight of GO-Mn-Al to the equilibrium adsorbate concentration in the bulk fluid phase.

Two basic adsorption isotherm namely Freundlich and Langmuir isotherm were investigated for cadmium removal by GO-Mn-Al. The Langmuir isotherm deals with a monolayer adsorption morphology whereas Freundlich isotherm is used to characterize a heterogenous surface with low and intermediatary concentrations[14]. The findings from the batch

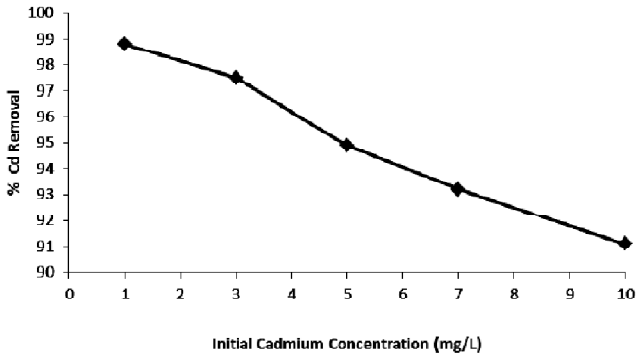

Fig. 10. Comparison of removal with initial cadmium ion concentration variation.

experiments have been processed and presented in Table 2 and Fig. 11.

Table 2. Isotherm model determination

Model	Parameters	Values
Langmuir isotherm model	Equation	$1/q_e = 0.1145/C_e + 0.0083$
	Maximum adsorption capacity, q_{max} (mg/g)	120.48
	Constant related to energy of sorption system, b	0.072
	R^2	0.9979
Freundlich isotherm model	Equation	$\ln q_e = 0.6195 \ln C_e + 2.9608$
	Freundlich constant related to adsorption capacity k_f (mg/g)	19.31
	Adsorption intensity ($1/n$)	0.6195
	R^2	0.9849

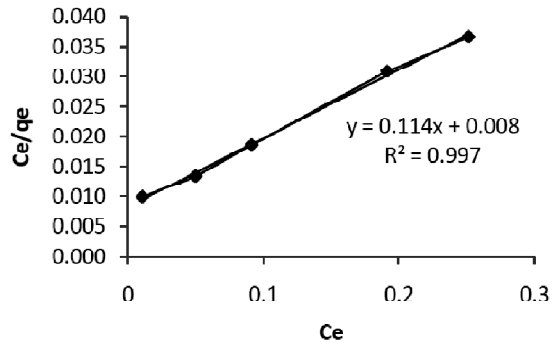

Fig. 11. Lagmuir isotherm model for the GO-Mn-Al nanocomposite.

The Langmuir isotherm was exhibited in the following linearised form[16]:

$$C_e/q_e = (1/q_m)\ C_e + 1/K_a q_m \quad (5)$$

where C_e = equilibrium concentration of solute in mg/L, q_e = equilibrium capacity of sorption in mg/g, q_m = maximum sorption capacity in mg/g, K_a = Langmuir constant related to the intensity of adsorption in L/mg.

The Freundlich isotherm model was exhibited in the following linearised form:

$$\log (q_e) = \log (K_F) + (1/n) \log (C_e) \quad (6)$$

where, C_e = equilibrium concentration in mg/L, q_e = equilibrium capacity of sorption in mg/g, K_F = adsorption capacity in mg/g, n = adsorption intensity in L/g.

The synthesised nanocomposite has given a better response to Langmuir isotherm model with a R^2 value of 0.9979 and hence it can be assumed that adsorption behaviour of the synthesised nanocomposite follows monolayer adsorption morphology.

Conclusion

The present study has focused on successful functionalization of Graphene Oxide with aluminum and its use in adsorption of Cd ions from contaminated synthetic water samples. Some noteworthy observations about the synthesized nanocomposite towards adsorption of Cd ions include optimal removal at pH 7, ambient temperature of 27°C and adsorbent dosage of 1 g/L. The optimum contact time between adsorbate and adsorbent for satisfactory removal of Cd ions was found to be 90 min. The rate of reaction was very fast in the first hour which can be attributed to the process of chemisorption. The material showed a better response to Langmuir isotherm model which indicated the predominance of the monolayer adsorption morphology. The adsorption behaviour resembled the pseudo-second order kinetic model which implied the dependence of rate of reaction on the remaining adsorption capacity of the nanocomposite. The equilibrium adsorption capacity was found to be 120.48 mg/g. Hence it can be said that the synthesized GO-Mn-Al nano-material can be used for removal of cadmium ions from contaminated water.

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