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HIGHLY EFFICIENT ADSORPTION OF CD(II) FROM AQUEOUS SOLUTIONS BY ALUMINUM OXIDE NANOPARTICLES

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ABSTRACT

In this study, Aluminum oxide nanoparticles were evaluated for Cd(II) removal from aqueous solution by batch adsorption method. The batch experiments showed that Aluminum oxide nanoparticles can be effectively used to remove Cd (II) from aqueous solution. Maximum removal of Cd (II) was obtained at pH=6 and adsorption equilibrium was achieved in 30 min. The adsorption kinetics well fitted using pseudo second-order kinetic model. The heavy metals sorption has been well explained using Langmuir and Freundlich isotherm model. The results indicated that the high adsorption capacity of Aluminum oxide nanoparticles makes them promising material for heavy metal ions removal from water samples.

KEYWORDS: Cadmium, Aluminum oxide nanoparticles, Adsorption Isotherm, Kinetics.

INTRODUCTION

Heavy metal pollution of wastewater is a common environmental threats, the excessive and uncontrolled discharge of heavy metal ions becomes a major problem. By means of bio concentration, bioaccumulation, and bio magnification through biological chain and drinking water, human health will be threatened seriously by heavy metal ions.[1-2] Cadmium is a toxic heavy metal of significant environmental and occupational concern.[3] It has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating and the manufacturing of batteries, pigments and screens.[4]

The problems associated with heavy metal pollution could be reduced or minimized by precipitation, ultra filtration, electrode deposition, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation–reduction and biosorption.[5] Among the different treatments described above, Adsorption has been found to be an effective, conventional and economic method with high potential for the removal, recovery, and recycle of toxic metals from waste water. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash, activated carbon have been used for cadmium removal.[6-9] In recent years nanoparticles and modified nanoparticles are a new challenge in adsorption methods. Nanoparticles have unique large surface areas, well-defined pore sizes, high pore volume and high adsorption capacity, ease of modification and diversity in surface functionalization Therefore, they can also be functionalized to increase affinity to metal ions and improved selectivity in removal of metal ions.[10] The objectives of this research were to investigate adsorption capacity, reaction kinetics and the effects of pH, contact time, initial concentration of cadmium and amount of adsorbent dosage on cadmium removal by performing batch experiments. Results from this study can be used to assess the utility of Aluminum oxide nanoparticles for heavy metal removal, in particular cadmium adsorption, at the field scale.

MATERIALS AND METHODS

Batch Adsorption experiments

To estimate the sorption capacity, experiments were carried out by mixing Aluminum oxide nanoparticles by Cd(II) solutions. Laboratory batch experiments were carried out due to its simplicity. The 99.9% pure form of Aluminum oxide nanoparticles made available directly from the manufacturer MK nano Sales of MK Impex Corp. Canada of desired particle size (20-30 nm). This adsorbent been used throughout the experimental work. The Cd metal ion solution as a model pollutant from industries was prepared by mixing $CdSO_4$ solution with Alzarin red S solution. HCl and NaOH were used for adjusting pH of solutions. The prepared solutions were standardized as per literature.[16] A known amount of Aluminum oxide nanoparticles (AON) was added to 50 ppm of the corresponding Cd solution over a period of time on a shaker at 120 rpm. The supernatants were collected and then used for analyzing cations concentration spectrophotometrically (shimatzu-

1211) at their respective wavelengths i.e.420 λmax. The effects of the experimental parameters to the adsorption capacity of modified AON in the experiments were investigated.

The adsorption of cadmium by Aluminum oxide nanoparticles was investigated at pH range of 3-11. The initial pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH. The effects of contact time (0, 5, 10, 15, 20, 25,30,35,40 min), initial concentration of cadmium (20,50,100,150 mgL^{-1}) and amount of adsorbent dosage (0.1, 0.2, 0.3, 0.4 g) were also examined throughout the experiments at 30±5 ^{o}C and 120 rpm shaking speed. The amount of Cd removal was calculated from the difference between Cd take and that remained in the solution. Experimental data obtained from batch equilibrium tests have been analyzed using different sorption isotherm models, namely Langmuir and Freundlich. Also, kinetic investigations were carried out using two kinetic models, pseudo-first-order and pseudo-second-order models.

Theory

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores.

Adsorption isotherm models

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Cd^{2+} ions by AON was modeled using two adsorption isotherms.

The Langmuir isotherm (1918) assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved.[11-12]

The Freundlich isotherm (1906) is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent.[13]

RESULTS AND DISCUSSION

Adsorption studies

Nanoparticle selected for the present work was Aluminum oxide nanoparticles (AON) of desired particle size (20-30 nm).

Effect of pH

To study the effects of change in pH on metal ions sorption with Aluminum oxide nanoparticles, batch type adsorption experiments with AON and 50 ppm aqueous solutions of Cd(II) in single mode were performed. Different solutions with pH values between 3 to 11 were prepared to determine the influence of this parameter on the sorption process. (figure 1.1) The pH is one of the important factors in heavy metal removal using nanoparticles, removal efficiency decreases rapidly with further increase in pH. Decrease of cadmium adsorption at pH>6 was due to formation of dissolved hydroxyl groups.[14]

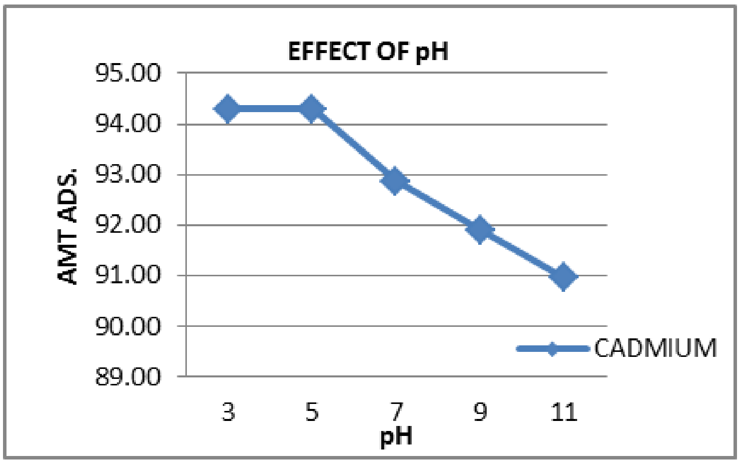

Fig. 1.1

Effect of contact time

The variation in the amount adsorbed as a function of time for Cd is shown in figure 1.2. The removal efficiency increases rapidly in initial stage and it decreases slowly after some time because large number of available sites are occupied by the metal ions with time in the first 30 min. Then the adsorption curve reached equilibrium after this time.[15]

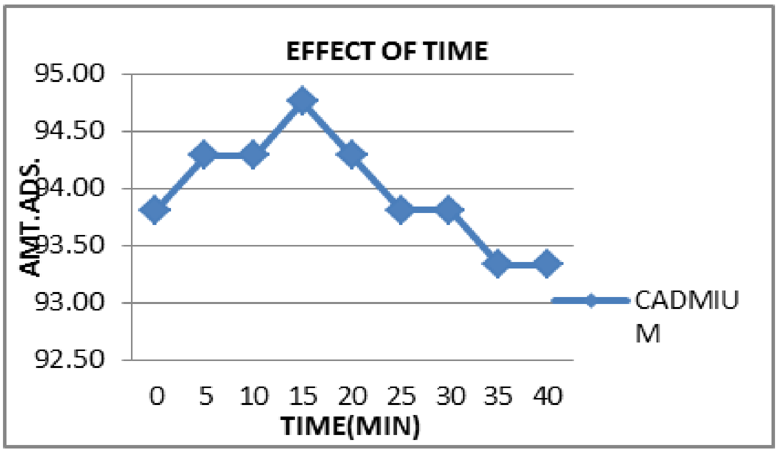

Fig. 1.2

Effect of initial Cd (II) concentration

Solutions of different initial concentrations (20, 50,100,150 ppm) were used to investigate the effect of initial metal concentration on removal of Cd(II) from aqueous solution. Sorbent used was 0.2 gm. at pH=6.(figure 1.3).

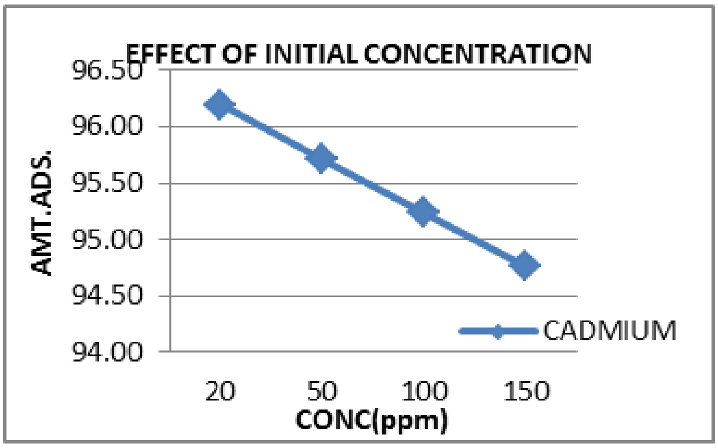

Fig. 1.3

At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high and the Cd(II) ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of Cd(II) ions with increase in initial metal concentration.

Effect of adsorbent dosage

The amount of adsorbent, which was varied from 0.1 to 0.4 g while keeping the Cd(II) concentration as 50 mgL^{-1} (Fig. 1.4). The increase in adsorbent dosage from 0.1 to 0.4 g resulted in an increase from 94 to 97% in adsorption of Cd(II). This was because of the availability of more binding sites for complexation of Cd(II) ions.

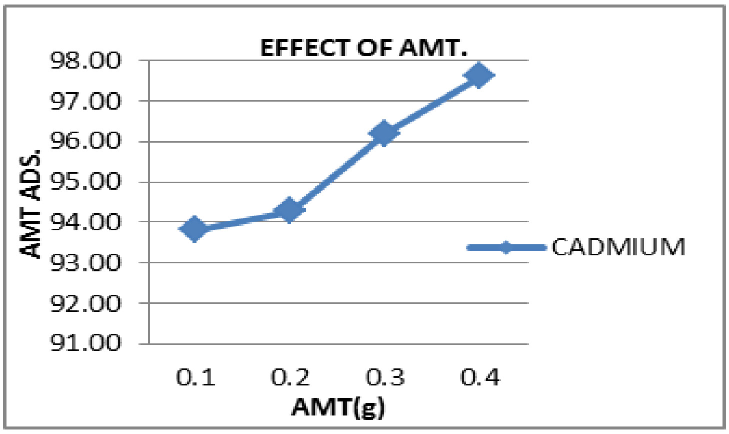

Fig. 1.4

Kinetic Study

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent as a function of equilibrium concentration in bulk solution at constant temperature, were also studied. Freundlich and Langmuir equations were used to find the patterns of adsorption by adsorbent AON for Cadmium removal. The Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface. The Freundlich equation deals with physico-chemical adsorption on heterogeneous surfaces (indicates the adsorptive capacity or loading factor). The linearized form of the Freundlich equation is given as:

$$\text{Log}(x/m) = \log K + 1/n \log Ce$$

Where x is the amount of the solute adsorbed, m is the mass of adsorbent used, Ce (mg/L) the equilibrium solute concentration in solution and K, a constant, which is a measure of the adsorption capacity, and n is a measure of the adsorption intensity.

The Langmuir isotherm is valid for single-layer adsorption. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir equation is $Ce/ (x/m) = 1/a + (1/b)\, Ce$

where x is the amount of the solute adsorbed, m is the mass of the adsorbent, Ce (mg/L) is the concentration of Cadmium at equilibrium, a is the amount of solute adsorbed per unit mass of adsorbent required for monolayer coverage of the surface, also called monolayer capacity, and b (Lmg^{-1}) is the Langmuir constant related to the affinity between the sorbent and the sorbate. According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent and once an adsorbate occupies a site, no further adsorption can takes place from this site.

The system was equilibrated with adsorbent concentration of 0.5g for 30 min with different metal concentrations at room temperature. The equilibrium data obtained were fitted to the Freundlich and Langmuir isotherms. The linearity of the plot log Ce versus log (x/m) for shows the applicability of Freundlich adsorption isotherm for the adsorption in the case of Cadmium.

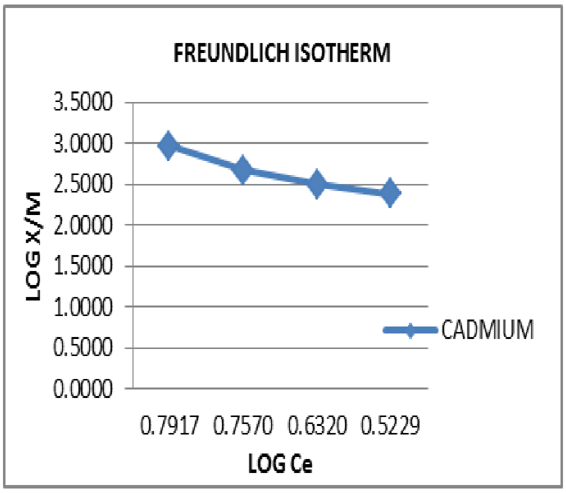

Fig. 1.5

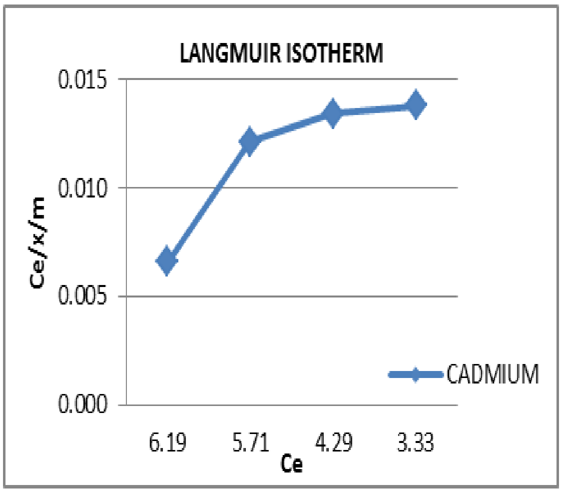

Fig. 1.6

The values of K and n were obtained from the slope and intercept of the plot between log (x/m) and log Ce for Cadmium removal. (Fig. 1.5) and also the values a and b from siope and intercept of plot between Ce and Ce/ (x/m) from Langmuir isotherm. (Fig. 1.6) The estimated goodness of fit is R^2=0.981 and enables applicability of the Langmuir model to Cd(II) adsorption on the surface functionalized nanoparticles.

CONCLUSION

Application of Aluminum oxide nanoparticles for removal of heavy metal like Cadmium from the aqueous systems developed as highly efficient nanoadsorbents. Characteristic surface properties enhanced their adsorption efficiency. The effect of parameters, such as pH, contact time, adsorbent doses and initial metal concentration was investigated. The results suggested that the adsorption processes were moderately pH dependent. The kinetic studies revealed that the adsorption data were fitted with different isotherm models. Nanoadsorbent technology for water remediation is more convenient and appropriate for removing and separating heavy metals.

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