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Batch Studies for Removal of Cu from Simulated Wastewaters with Al_2O_3Nanoparticle

Koravangala Sree Harsha Ramaswamy[1], Dr. Lakshminarasimha Rao Udayasimha[2], Dr. Dinesh Rangappa[3], Mrs. Agale Venkataramaiah Suchetha[4]

[1]Research Scholar VTU and Environmrntal Consultant
[2] Professor Dept of Civil Engineering BMS College of Engg, Bangalore
[3] Professor, Centre for Nanoscience and Technology, VTU, Muddenhalli, Bangalore
[4] Environmental Engineer

Abstract: **In present paper experimental investigations are carried out to study the effect of Aluminium oxide (Al_2O_3) nanoparticles to remove Heavy metals Cu and Ni in simulated wastewaters with different experimental conditions. The experiments are performed by varying pH, time of contact and speed of mixing and also the initial concentration of heavy metals in synthetic solution. Experiments conducted using Aluminium oxide (Al_2O_3) nanoparticles by varying pH, time, Al_2O_3 dosage, concentration and speed of rotation. The result represents the reduction of Cu at 9 pH. The percentage removal after the addition of Al_2O_3 is observed to be as 95%.**

Keywords: **Aluminium Oxide, Synthetic Solution, Simulated Wastewater, Langmuir Isotherm.**

1. INTRODUCTION

Aluminium Oxide nanoparticles is known to be novel material used in different engineering applications. It has phase stability, high hardness, and very good dimensional stability. It is widely used in a variety of plastics, rubber, ceramics, refractory products for reinforcement toughening, in particular, significantly to improve the ceramic density, finish, thermal fatigue resistance, fracture toughness, creep resistance and wear resistance. α-phase ultrafine Al_2O_3 is a high performance material of far infrared emission, it is widely used in fibre fabric products and high pressure sodium lamp as far-infrared emission and thermal insulation materials. Alumina consist of either aluminum oxide (Al_2O_3) or aluminum hydroxide, such as aluminum oxide hydroxide (AlOOH), commonly referred to as boehmite, or aluminum trihyroxide [$Al(OH)_3$]. Aluminas are crystalline solids with high porosity and surface areas as well as acidic and basic properties, which make them suitable as adsorbents, catalyst, catalyst support and fabricated into filtration membranes as well as used as fillers or components in polymer/ inorganic composite materials with enhanced mechanical properties. Alumina nanofibers filters have the ability to remove contaminants.

Rompicherla J et al 2015, studied alumina nanoparticle adsorbent developed using solution combustion synthesis method and further utilized for the removal of zinc Zn(II)) and color black G (CBG) from wastewater by batch studies. The developed adsorbent is characterized using SEM–EDS technique. The effect of various parameters such as the initial concentration, the contact time, the mass of adsorbent and the solution pH are studied for the removal of Zn(II) and CBG. The equilibrium time for both, Zn(II) and CBG is obtained to be approximately 4.5 h. The maximum adsorption of Zn(II) is found at pH value of 7 while the maximum removal of CBG is obtained at pH value of 2. The Langmuir isotherm model is found to be best suitable for explaining the adsorption behavior of Zn(II) ($R2$ = 0.976) and CBG ($R2$ = 0.974) onto alumina nanoparticles, which supports the monolayer formation of Zn(II) and CBG during the adsorption process. The maximum adsorbent capacity of alumina nanoparticles for the removal of Zn(II) and CBG are obtained as 1,047.83 and 263.16 mg g−1, respectively[1].

Omnby et al 2012 investigated the removal of As (V) by adsorption from water solutions was studied different synthetic adsorbents. The adsorbents aluminium nanoparticles (Alu-NPs, <50 nm) incorporated in amine rich cryogels (Alu-cryo),were evaluated regarding material characteristics and arsenic removal in both batch tests and continuous mode. Results revealed that a composite design with particles incorporated in cryogels was a successful means for applying small particles (nano- and micro- scale) in water solutions with maintained adsorption capacity and kinetics. The adsorption capacities for the composites were 20.3 ± 0.8 mg/g adsorbent (Alu-cryo). Adsorption tested in real wastewater spiked with arsenic showed that co-ions (nitrate, sulphate and phosphate) affected arsenic removal for Alu-cryo[2].

Ozge Can et al. 2010 studied ion exchange method which is considered to be one of the most cost effective methods if low cost ion exchangers such as natural zeolites are used in waste water treatment. In this study, a zeolitic tuff rich in clinoptilolite from Gördes Manisa Turkey was examined to evaluate its ion exchange performance for the removal of copper, nickel and cobalt ions from metal (II) nitrate solutions at various concentrations by performing both batch and packed column experiments. A clinoptilolite tuff with purity around 60% was used in ion exchange experiments. Copper, nickel and cobalt exchange capacities of the tuff were determined as 8.3 mg (0.26 meq) Cu2+/g, 6.6 mg (0.23 meq) Ni2+/g and 4.5 mg (0.15 meq) Co2+/g, respectively. The equilibrium behavior of the system was best described by classical Langmuir model. The experimental breakthrough curves from the column experiments were fitted to solid diffusion control model. The study showed that efficient metal ion removal can be done by using the local clinoptilolite rich tuff.[3]

Abbas Afkhami 2010 et al. studied 2,4-Dinitrophenylhydrazine (DNPH) immobilized on sodium dodecyl sulfate coated nano-alumina developed for the removal of metal cations Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Mn(II) from water samples. The research results displayed that adsorbent has the highest adsorption capacity for Pb(II), Cr(III) and Cd(II) in ions mixture system. Optimal experimental conditions including pH, adsorbent dosage and contact time have been established. Langmuir and Freundlich isotherm models were applied to analyze the experimental data. The best interpretation for the experimental data was given by the Freundlich adsorption isotherm equation for Mn(II), Pb(II), Cr(III) and Cd(II) ions and by Langmuir isotherm equation for Ni(II) and Co(II) ions. Desorption experiments by elution of the adsorbent with a mixture of nitric acid and methanol show that the modified alumina nanoparticles could be reused without significant losses of its initial properties even after three adsorption-desorption cycles. Thus, modified nano-alumina with DNPH is favorable and useful for the removal of these metal ions, and the high adsorption capacity makes it a good promising candidate material for Pb(II),Cr(III) and Cd(II) removal.[4].

Shahriar Mahadavi et al 2015 prepared novel Al2O3 nanoparticles (NPs) modified with humic acid (Al-H), extractant of walnut shell (Al-W), and 1,5-diphenyl Carbazon (Al-C). The present study was conducted to evaluate the feasibility of modified nano-alumina (Al-H, Al-W, and Al-C) for Cd2+, Cu2+, and Ni2+ removal from single and competitive aqueous solutions. The nature and morphology of sorbents were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, and Scanning electron microscopy (SEM) analysis. The SEM results revealed that the three modified nanoparticles had larger size in comparison with bare nanoparticles and with an average diameter of around 61 nm. Batch adsorption studies were performed as a function of contact time, initial heavy metals concentration (isotherm), and pH. Heavy metals sorption kinetics was well fitted by pseudo-second-order kinetic model. The maximum uptake values (sum of 3 metals) in competitive component solutions were 92.0, 97.0, and 63.8 mg g−1, for Al-H, Al-W, and Al-C, respectively. The heavy metals sorption has been well explained using Langmuir isotherm model. SEM–EDX before and after metal sorption, and soil solution saturation indices showed that the main mechanism of sorption for Cd2+ and Ni2+ was adsorption, whereas for Cu2+ sorption was due to adsorption and precipitation. Thus, the new nanoparticles are favorable and useful for the removal of Cd2+, Cu2+ metal ions particularly, in single solutions and with Al-C NPs. The high adsorption capacity makes them good promising candidate materials for heavy metal ions removal from water samples [5].

Shahriar et al 2013 investigated the removal of Cd2+, Cu2+, Ni2+, and Pb2+ from aqueous solutions using nanoparticle sorbents (TiO2, MgO, and Al_2O_3,) with a range of experimental approaches. The maximum uptake values (sum of four metals) with multiple component solutions were 594.9, 114.6, and 49.4 mg g−1, for MgO, Al_2O_3, and TiO_2, respectively. The sorption equilibrium isotherms were described using the Freundlich and Langmuir models. The best interpretation for experiment data was given by the Freundlich model for Cd2+, Cu2+, and Ni2+ in single- and multiple-component solutions. A first-order kinetic model adequately described the experimental data using MgO, Al_2O_3,, and TiO_2. SEM-

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EDX both before and after metal sorption and soil solution saturation indices (SI) in MgO nanoparticles indicated that the main sorption mechanism for heavy metals was attributable to adsorption and precipitation, whereas heavy metal sorption by TiO_2 and Al_2O_3, adsorbents was due to adsorption. These nanoparticles may potentially be used as efficient sorbents for heavy metal removal from aqueous solutions. MgO nanoparticles were the most promising sorbents because of their high metal uptake [6]

2. MATERIALS AND METHODOLOGY

The present analysis includes synthesis of Al_2O_3 nanoparticles, preparation of stock solutions of Copper and Nickel. Further, the synthesis of Alumina Nanoparticle has been carried out using combustion method using aluminium nitrate (Al $(NO_3)_3$), lanthanum nitrate La $(NO_3)_3$ and urea (CO $(NH_2)_2$) as reactants. The Alumina Nanoparticle produced as white precipitate is filtered and oven dried.

Fig 1 is the SEM of Al_2O_3 nanoparticles, which clearly indicates the combustion process.

The X RAY Diffraction of Al_2O_3 is represented in figure1 which shows that it follows alpha phase. And by fitting Debye–Scherrer equation the crystalline size of the highest peak is calculated which is found to be 36nm.

Debye–Scherrer equation:

$D=0.9\lambda/\beta cos\theta$

Where, λ= Wavelength of X-ray used;

β= Full width at half maximum;

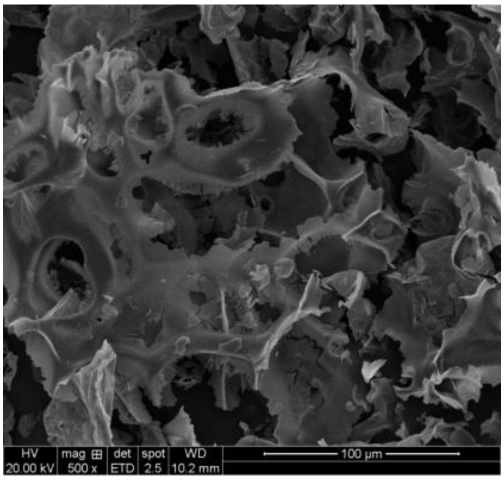

Fig 1: SEM of Al2O3 nanoparticles with particle size >100 nm

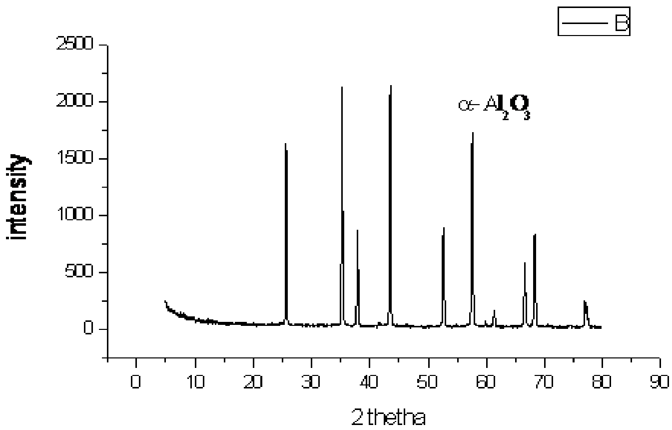

Fig 2: XRD of Al_2O_3 nanoparticles

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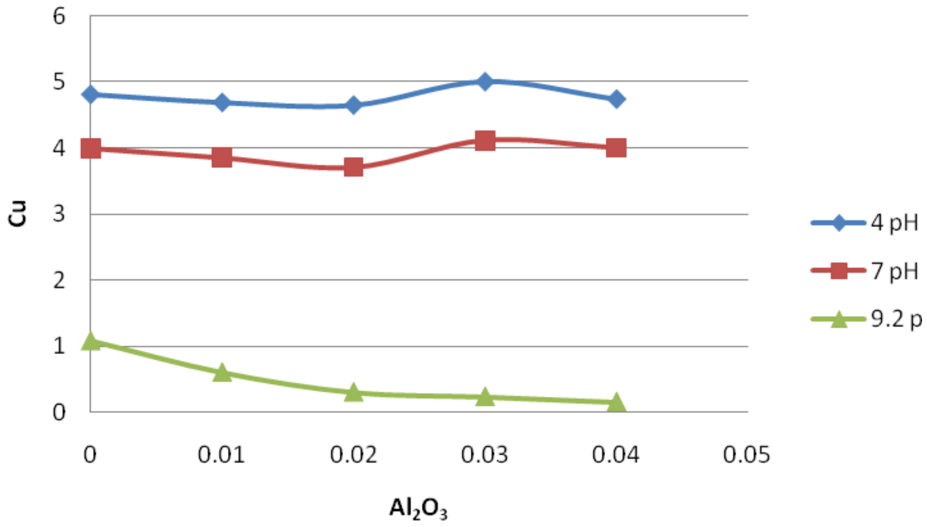
2.1 Batch Experimental studies:

Basically four variables are considered which would affect the removal efficiency of Cu and Ni from simulated wastewaters to arrive at the optimum/operating parameters. Experimental schedule is prepared by varying all the four variables i.e Initial Concentration, pH, speed of rotation and contact time.

3. RESULTS & DISCUSSIONS

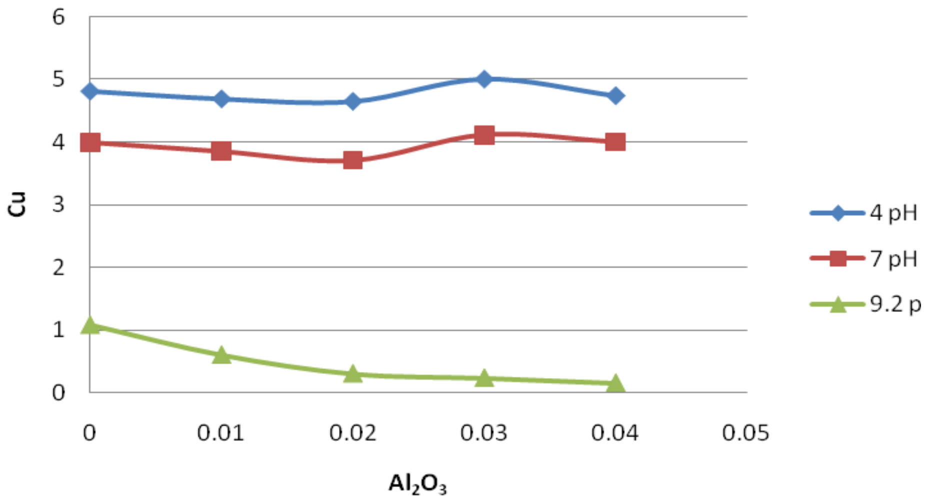
(i) Optimum Ph.:

Set of experiments are carried out to fix the optimum pH by keeping all other parameters, viz., time of contact 15 min, rotation speed 200 rpm, concentration of synthetic samples as constants.. There is a reduction in concentration of Cu after addition of pH (4, 7, 9.2) from 5ppm.



Graph1: Cu adsorption on Al_2O_3 nanoparticles at different concentration

It can be seen from the above variation that the pH has effect on the removal efficiency. It can be observed in this variation that there is a small reduction in pH 7 level. However in the present case the removal is found to occur at pH 9.2. Hence for the further investigation pH 9.2 is considered as optimum. Further set of experiments are carried out to fix the optimum pH by keeping all other parameters, viz., time of contact 15 min, rotation speed 200 rpm, concentration of synthetic samples as constants.. There is a reduction in concentration of Cu at pH (4, 7, and 9.2).

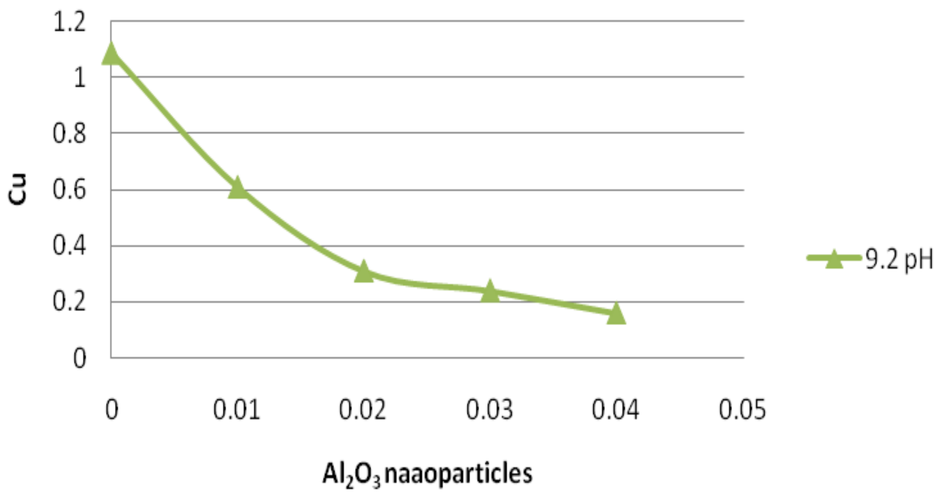


Graph 2 : Cu adsorption on Al_2O_3 nanoparticles at different Al_2O_3 concentration and pH at 15 minutes and 200rpm

It can be seen from the above variation that the pH has effect on the removal efficiency. It can be observed in this variation that there is a small reduction in pH 7 level also but not as much as effective as nano TiO_2. However as in the earlier case, in the present case also the more removal is found to occur under pH 9.2. Hence for the further investigation pH 9.2 is considered as optimum.

(ii) Optimum Dosage:

To arrive at the optimum dosage of the nano size Al_2O_3, experiments are carried out by keeping pH at 9.2, contact time at 15min and speed at 200 rpm. The results of this set are given in Fig 3.32.

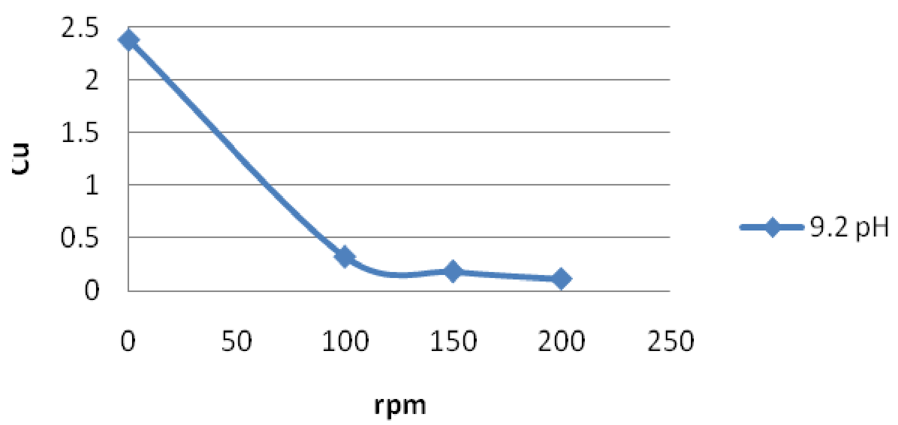


Graph 3 : Ni adsorption on Al_2O_3 nanoparticles at different Al_2O_3 concentration

From the figure 4 it can be noticed that the concentration of Cu reduces with the dosage of Al_2O_3 nanoparticles. The more reduction is found to occur in the range of 0.03-0.04 g of dosage with reduction efficiency between 78-85%. The dosage of 0.03g is opted as not much of variation observed between 0.03 -0.04 g of dosage. The same is fixed as the operating parameter for the further experimentation.

(iii) Operating Speed of Rotation:

This set of experiments are carried out to fix the optimum speed by taking all other parameters viz., 0.03g Al_2O_3 nanoparticles, rotational speed 200 rpm , pH 9.2,contact time 15 minutes and the initial concentration of copper in solution as constants. The results are shown in Table 3.19 and Fig 3.33.



Graph 4: Cu adsorption on Al2O3 nanoparticles at different rpm

As per the above figure, the variation showed the trend of reducing the Cu concentration drastically from 0 to 120 rpm and then onwards the removal efficiency is almost independent with the speed. However to have sufficient contact time

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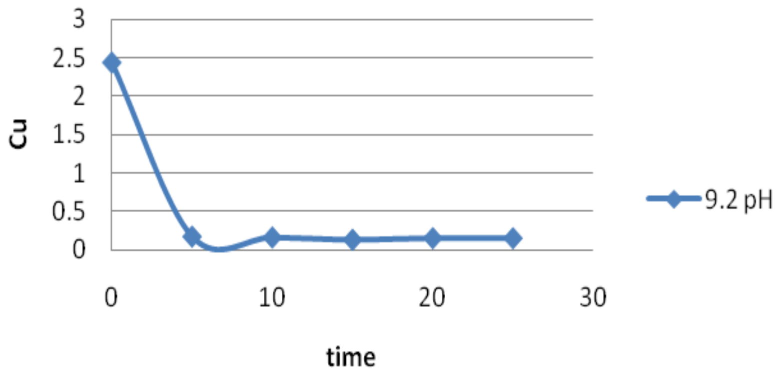
for the reactions, speed of 200 rpm is considered as operating speed and same will be used in the further experimentation.

(iv) Optimum Contact time:

This experiments are carried out to fix the optimum time by taking all other parameters, viz., dosage of 0.03g Al_2O_3 nanoparticles, speed of rotation 200 rpm , pH 9.2 and initial concentration of Cu as constants. The results are tabulated in Table 3.20 and graphical representation in Fig 3.34.



Graph 5: Cu adsorption on Al2O3 nanoparticles at different time

From the figure it can be observed that 94 % removal has occurred within contact time of 10 minutes. After this it showed trend that the time of contact has no effect on removal efficiency. To allow for a sufficient contact time, duration of 15 minutes is chosen as operating contact time.

Adsorption Behaviour:

The adsorption behaviour of Al_2O_3 nanoparticles is determined by considering the various isotherm analysis and finding which isotherm process it is following. In the present case it is found that the experimental data follow the Langmuir isotherm

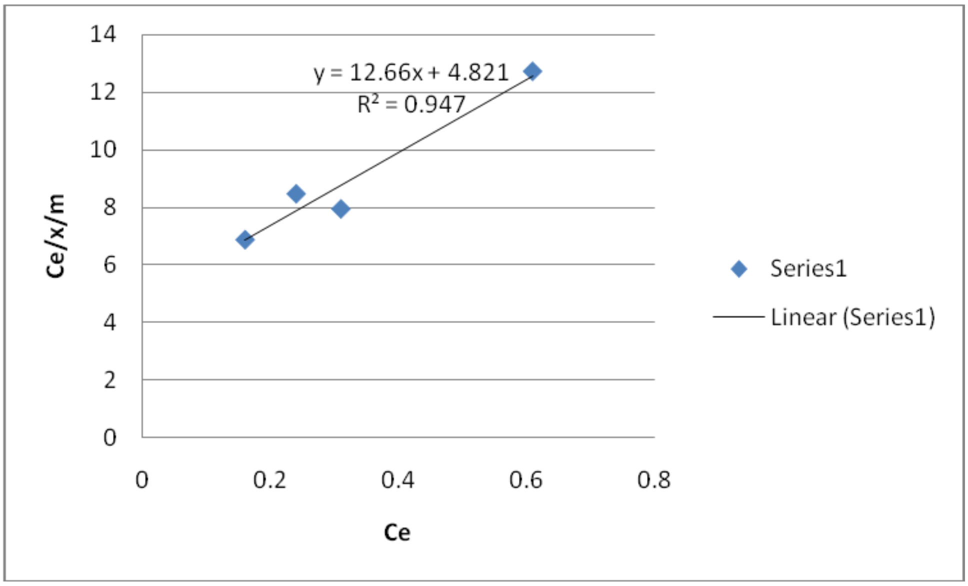


Figure 6 : Langmuir adsorption isotherm for nano Al_2O_3 (Cu analysis).

The adsorption behaviour of Al_2O_3 nanoparticles is determined by evaluating the various isotherm analysis and apprehending which isotherm process it is following. In the present case it is found that the experimental data follow the Langmuir isotherm (Figure 5) represented by the below equation :

$$\frac{x}{m} = \frac{abC_e}{1+bC_e}$$

where, x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon.

a,b= empirical constants,

C_e= equilibrium concentration of adsorbate in solution after adsorption, mg/l.

4. CONCLUSION

The operation experimental conditions in removal of copper by nano Al_2O_3 are found to be as 9.2 pH, 0.03g of Al_2O_3, 15 minutes contact time and 200rpm speed. The percentage removal after the addition of 9.2 pH is for Cu is 56%. The percentage removal after the addition of Al_2O_3 is observed to be as 95%.

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