

Eco-Friendly Method for Synthesis of Copper Nanoparticles and Application for Removal of Aqueous Sulphur Dioxide (SO₂) and Nitrogen Dioxide (NO₂)

D. Sirisha¹, N. Gandhi¹, M. Hasheena¹ and Smita Asthana²

1. Center for Environment and Climate Change,

Jawaharlal Nehru Institute of Advanced Studies (JNIAS) Hyderabad, Telangana.

2. Department of Chemistry, St. Ann's College for Women, Mehdipatnam, Hyderabad.

Abstract:- Sulphur dioxide (SO₂) gas is a colour less with a pungent smell and is efficiently adsorbed in upper respiratory tract. Lacrimation, rhinorrhoea, cough, bronchial secretion and bronchospasm occur at high concentrations of SO₂. High concentrations of sulfur dioxide can produce acute injury in the form of foliar necrosis, even after relatively short duration exposure. Sulfur dioxide tends to have more toxic effects when acidic pollutants, liquid or solid aerosols, and particulates are also present. Nitrogen dioxide is an irritating gas with an acrid, pungent odour. In the presence of sunlight, nitrogen dioxide can lead to the formation of ozone, nitric acid and nitrate-containing respirable particles. Anthropogenic emissions of nitrogen dioxide are mainly due to combustion processes, including vehicle exhaust, coal, oil, and natural gas, with some emissions occurring as a result of use in industrial processes. Both SO₂ and NO₂ have major contribution towards Global warming and hence they are known as major greenhouse gases. The present study deals with the adsorption studies that have been carried out by traditional batch processes. The experiments were conducted with respect to contact time, with respect to different dosages of Copper nanoparticles and Copper immobilized beads, with respect to different concentrations of aqueous solutions of SO₂ and NO₂. It was found that by using Copper nanoparticles adsorbent, percentage removal of SO₂ was 90% and in case of NO₂ it was 85%.

1. INTRODUCTION

As a necessary component of biological systems, sulfur is ubiquitous in the biosphere. As a result, sulfur often occurs in relatively high concentrations in fossil fuels, with coal and crude oil deposits commonly containing 1–2% sulfur by weight [1-4]. The widespread combustion of fossil fuels has, therefore, greatly increased sulfur dioxide emissions into the atmosphere, with the anthropogenic component now substantially greater than natural emissions on a global basis. Anthropogenic emissions have resulted in increased sulfur dioxide and atmospheric sulfate loadings in many areas. Early attention to these emissions has focused on their impacts on ecosystems and human health, which occur on both a local level and on regional scales [5-8]. Sulphur dioxide can be detrimental to ecosystems, harming aquatic animals and plants, and can be damaging to a wide range of terrestrial plant life. In addition, aerosol particles have adverse effects on human health, especially in the form of respiratory ailments. However, that any

lower threshold and the attribution by species for these effects is still uncertain. These impacts have prompted regulations in the most affluent countries to limit emissions of sulfur dioxide. In addition to the aforementioned effects, sulfur dioxide forms sulfate aerosols that are thought to have a significant effect on global and regional climate. Sulfate aerosols reflect sunlight into space and also act as cloud condensation nuclei, which tend to make clouds more reflective and change their lifetimes [9-13]. The radiative forcing change wrought by sulfate aerosols may be second only to that caused by carbon dioxide, albeit in the opposite direction. The radiative effects of aerosols are, however, still very uncertain. Modeling aerosols is significantly more difficult than modeling greenhouse gases such as carbon dioxide [14-17].

On the other hand the evidence on NO₂ and health comes from different sources of information, including observational epidemiology, controlled human exposures to pollutants and animal toxicology. The observational data are derived from studies outdoors where NO₂ is one component of the complex mixture of different pollutants found in ambient air and from studies of NO₂ exposure indoors where its sources include unvented combustion appliances. Interpretation of evidence on NO₂ exposures outdoors is complicated by the fact that in most urban locations, the nitrogen oxides that yield NO₂ are emitted primarily by motor vehicles, making it a strong indicator of vehicle emissions (including other unmeasured pollutants emitted by these sources). NO₂ (and other nitrogen oxides) is also a precursor for a number of harmful secondary air pollutants, including nitric acid, the nitrate part of secondary inorganic aerosols and photo oxidants (including ozone). The situation is also complicated by the fact that photochemical reactions take some time (depending on the composition of the atmosphere and meteorological parameters) and air can travel some distance before secondary pollutants are generated [18-21]. Health risks from nitrogen oxides may potentially result from NO₂ itself or its reaction products including O₃ and secondary particles. Epidemiological studies of NO₂ exposures from outdoor air are limited in being able to separate these effects. Additionally, NO₂ concentrations closely follow vehicle emissions in many situations so that NO₂ levels are

generally a reasonable marker of exposure to traffic related emissions [22-23].

The multifaceted impacts of sulfur dioxide and nitrogen dioxide emissions motivates a close examination of possible future paths for regional and global sulfur dioxide and nitrogen dioxide emissions, which is the goal of the present paper.

2. MATERIALS AND METHODS

A. Selection of adsorbent

There are many commercially available materials for controlling SO₂ and NO₂, but an attempt was made to find efficient and that which is effective even when used at minute concentrations. Copper Nanoparticles were screened by adding 0.04gm of Copper nanoparticle to 100ml of aqueous solution of SO₂ and NO₂.

B. Preparation of Copper Nanoparticle:

Source of Copper

Chemicals used in the present study all are including Copper Sulphate (CuSO₄ · 5H₂O) are analytical grade and used as it is. There is no further purification procedures are followed.

Preparation of Seed Extract:

The *Sesamum indicum* seeds were purchased from local super market of Hyderabad city. 5 gm of *Sesamum indicum* seeds were weighed and grounded into powder using mortar and pestle. Powder was soaked into 100 ml of distilled water and allowed it for continuous stirring with help of magnetic stirrer for 8 hours. After completion of stirring the solution was filtered by using whatmann No. 41 paper twice. The solution was kept in refrigerator for further use.

Preparation of Copper Nanoparticles:

Many techniques, including chemical and physical means, have been used to prepare metal nanoparticles, such as chemical reduction using a reducing agent, electrochemical reduction, photo chemical reduction and heat evaporation method. Not only physicists and chemists, but also the biologists are highly interested in synthesizing nanoparticles of different shapes and sized by employing bio-based synthesis of nanometals using plant extracts. In the present study to the 25 ml seed extract 100 ml of 0.01 M CuSO₄ solution was added and kept it in microwave oven at 180 watts for 10 minutes. Formations of copper nanoparticles were checked by using UV-vis spectrophotometer (Lambda Scientific Spectrophotometer) at regular intervals [24]. This naturally occurring nanoparticle is generated by the erosion and chemical degradation of plants.

Characterization of CuNp:

The characterization technique involves UV-vis absorption spectra (Figure-1), by color change (Figure-2),

C. Preparation of Standard Samples:

A 100 ppm stock solution of nitrite was prepared by dissolving 177 mg of Analytical grade sodium nitrite in 1000 ml standard flask and made up to the mark with double distilled water [25-27]. From the stock solution of Nitrite the working standards were prepared by taking appropriate quantities to get the desired concentration of

NO₂. The 0.1575 gm of sodium sulphite is dissolved in 1000 ml of distilled water to get 100 ppm SO₂ solution. The working standards are treated with copper nanoparticles and checked for percentage removal by using UV-Vis Spectrophotometer. Batch Adsorption Studies were carried out for the removal of SO₂ and NO₂. The percentage removal of NO₂ is calculated by using the following formula [28-30].

$$\% \text{ Removal} = \frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}} \times 100$$

D. Experimental Procedure:

In the present study an attempt has been made to prepare and use of green synthesized copper nanoparticles in air pollution controlling technologies. Batch adsorption experiments were adopted for the removal studies. The NO₂ analysis was carried by NEDA method and SO₂ by West Gaeke method [31-34]. The experiments are conducted with respect to contact time, effect of NO₂ and SO₂ concentrations and copper nanoparticles dosage.

Effects of Copper nanoparticle with respect to Contact time for SO₂ and NO₂

The initial (before adsorption) and the final (after adsorption) concentration is determined at regular intervals of 5, 10, 15, 20, 30, 40, 50, 60, 70 and 80 minutes. The results are given in Table and Fig.

Effect of initial aqueous SO₂ Concentration for SO₂ and NO₂

Different concentrations of aqueous solution of SO₂ are mixed with a fixed amount of adsorbent. The experiments are carried out with contact time that is fixed depending upon contact time experiments. The results are given in Table and Fig.

Effect of Copper nanoparticle Dosages for SO₂ and NO₂

Definite concentrations of aqueous solution of SO₂ are mixed with different amount of adsorbent dosages i.e. 0.01gms, 0.03gms, 0.04gms and 0.06gms respectively. The experiments are carried out with the contact time of one hr. is maintained.

Preparation of Copper Immobilized beads

Copper Immobilized beads are prepared by using Sodium alginate and Calcium chloride. An aqueous solution of sodium alginate was prepared by adding 1gm of sodium alginate to 100 ml of distilled water and 0.1M (1.1gm/100ml) of aqueous calcium chloride was prepared. When the sodium alginate was added drop wise to the calcium chloride solution, spherical, green-colored calcium alginate beads were formed. Both empty beads as well as beads containing Copper nanoparticles were prepared. (amount of CuNp is 5 mg/100ml of sodium alginate).

Effect of Copper Immobilized beads with respect to Contact time for SO₂ and NO₂

The initial (before adsorption) and the final (after adsorption) concentration is determined at regular intervals of Time i.e. 5, 30, 80, and 120 minutes. The results are given in Table and Fig.

Effect of initial aqueous SO₂ Concentration for SO₂ and NO₂

Different concentrations of aqueous solution of SO₂ are mixed with a fixed amount of adsorbent. The experiments

are carried out with contact time that is fixed depending upon contact time experiments. The results are given in Table and Fig.

Effect of Copper Immobilized beads Dosages for SO_2 and NO_2

Definite concentrations of aqueous solution of SO_2 are mixed with different amount of adsorbent dosages i.e. 0.5 gm, 1.0 gm, 1.5 gm and 2.0 gm respectively. The experiments are carried out with the contact time of one hour is maintained.

3. RESULTS AND DISCUSSION

A. UV-visible Analysis of Copper Nanoparticles:

The change of pure copper to copper nanoparticles was determined by measuring the UV-visible spectrum the most confirmatory device for detection of surface Plasmon resonance property of copper nanoparticles by diluting a small aliquot of the sample in distilled water, the results and adsorption maxima were shown in figure-1 & figure-2.

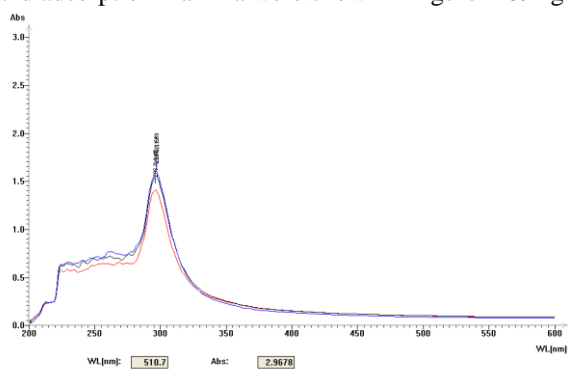


Figure-1: Graphical form of absorbance for synthesis of CuNp by using *Sesamum indicum* seeds extract



Figure-2: Change in colour of *Sesamum indicum* seeds extract during copper nanoparticles synthesis

B. Effect of Contact time:

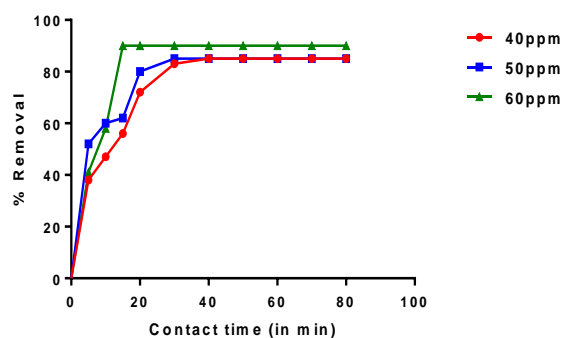


Figure-3: Effect of Contact Time between Copper Nano particle and SO_2

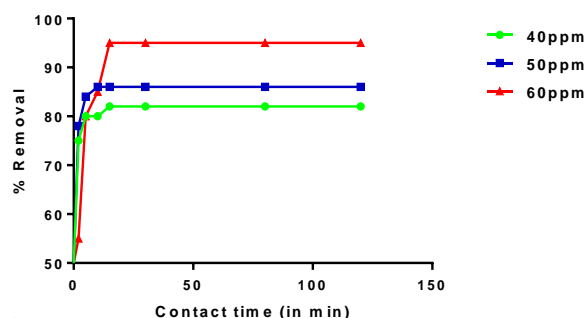
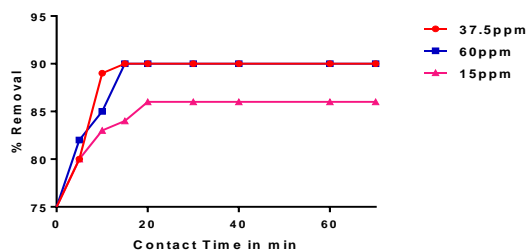
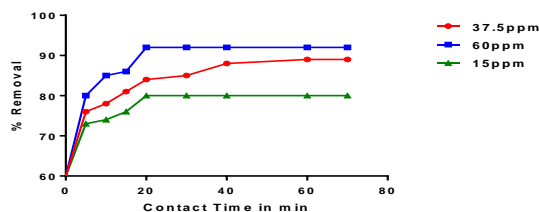


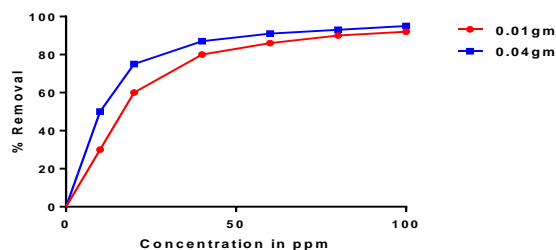
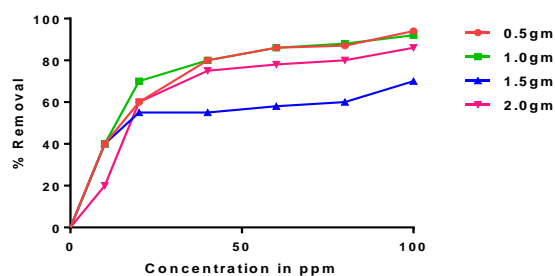
Figure-4: Effect of Contact Time between Immobilized CuNp beads and SO_2

The adsorption of SO_2 by Copper nanoparticles at different concentrations increased with increase in contact time. The percentage removal of SO_2 is rapid at the beginning and became stable after short interval of time indicating a favourable condition for controlling SO_2 by copper Nanoparticles. The optimum contact time for 40 ppm, 50 ppm and 60 ppm are 40 min, 30 min and 15 min, with 85%, 85% and 90% removal respectively. The nanoparticles have a unique property such as high surface area which immediately adsorbs the SO_2 molecules which are more even at higher concentration. However, the same experiments were conducted with immobilized copper nanoparticles (Ca- alginate + CuNP), observed a rapid adsorption process and adsorbed with in 10 -15 minutes for all three concentration performed in present study. There was no significant change observed in percentage removal of SO_2 (Fig-4). From the results it can be concluded that the percentage removal of SO_2 in both conditions are identical, but immobilized copper nanoparticles has taken less contact time for removal of aqueous SO_2 compared to copper Nanoparticles. The reason behind this structural variability increases by the process of immobilization, which leads to difference in structure of green synthesized copper nanoparticles [35-36].

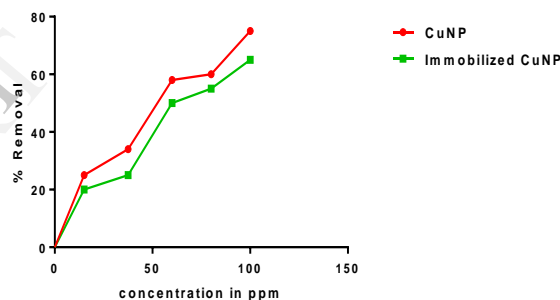
Figure-5: Effect of Contact Time between Copper Nano particle and NO₂.Figure-6: Effect of Contact Time between Immobilized CuNP beads and NO₂

The adsorption of NO₂ by Copper nanoparticles at different concentrations increased with increase in contact time. The percentage removal of aqueous NO₂ is high at higher concentration and taken less optimum contact time compared to lower concentration in both conditions i.e. CuNp and immobilized CuNp. The results are shown in Fig- 5 & 6, which indicates that immobilized copper nanoparticles has the more adsorption capacity compare to mobilized CuNp with a lesser contact time period. The reason behind this, the immobilized copper nanoparticles may have high catalytic properties and show more capacity of adsorption than uniformly functionalized nanoparticles [37]. From the above experiments it can be report that the both immobilized and non immobilized copper nanoparticles which is prepared by using *Sesamumindicum* seed extract has the efficiency to remove aqueous SO₂ and SO₂ from a liquid media. However, the percentage removal of aqueous NO₂ and SO₂ are identical (85-90%) when the experiments are performed with Copper nanoparticles, where a significant change was observed in percentage removal of aqueous SO₂ and NO₂ when the experiments conducted with respect to immobilized copper nanoparticles. It indicates that the immobilized copper nanoparticles attracts more towards aqueous NO₂ compared to SO₂.

C. Effect of Initial SO₂ and NO₂ Concentrations on Adsorption process:

Figure-7: Effect of Concentration between Copper Nano particle and SO₂Figure-8: Effect of Concentration between Immobilized CuNP beads and SO₂

The percentage removal of aqueous SO₂ is increased with increase in SO₂ concentration in both conditions i.e. CuNp and Immobilized CuNp, because the mobility of adsorbate molecules low at higher concentrations and interaction between adsorbate molecules towards adsorbent is high at higher concentration due to less dilution of water molecules (Debye-Hukel's theory). From the results (Fig- 7 & 8) it can be concluded that both mobilized and immobilized copper nanoparticles has the capacity to removal aqueous SO₂ even at higher concentration. Although the degradation was same for both cases, but with the immobilized copper nanoparticles more dosage is required which was due to reductive surface area for adsorption [38-40].

Figure-9: Effect of Initial NO₂ concentration on CuNP and Immobilized CuNP.

NO₂ is a reddish brown gas with pungent and irritating odour. It absorbs light and leads to the yellow haze seen hanging over cities. It is one of the important components of smog. The removal NO₂ is increased with increase in NO₂ concentration indicates the adsorption rate increase as the NO₂ concentration increases. This can be attributed to greater driving force and consequently higher adsorption rate is observed. Polar covalent bonds present in NO₂ enhance the adsorption process by binding towards active sites on copper nanoparticles, where this attraction is low with immobilized copper nanoparticles which results lower percentage removal of NO₂. The Copper nanoparticles react with NO₂ very fast and sharp compared to SO₂, because of the reactivity difference between SO₂ and NO₂ with Copper nanoparticles. The molecules of NO₂ and SO₂ are said to be good and strong oxidizing agents but SO₂ acts as reducing agent in presence of water due to amphoteric nature [40], due to this reason the overall percentage removal of NO₂ is high compared to SO₂.

D. Effect of Adsorbent Dosage:

The percentage removal of NO₂ and SO₂ increases with increase in the dosage of the nano copper particles and

immobilized copper nanoparticles. The amount of copper nanoparticles required for removal of NO₂ and SO₂ is very less compared to the amount of immobilized copper nanoparticles. The percentage removal of SO₂ and NO₂ in both conditions (CuNp & immobilized CuNp) is low at lower concentration and high at higher concentrations. The reason behind this, the number of gas molecules is low at lower concentration and they are highly mobile due to high dilution factor. Due to this reason interaction between adsorbate and adsorbent is low at lower concentration compared to higher concentration. The removal efficiency of immobilized copper nanoparticles is low for the removal aqueous SO₂ and NO₂ compared to copper nanoparticles, even though the immobilized copper nanoparticles are more suitable adsorbent for the removal of aqueous SO₂ and NO₂ because separation, purification and storage of copper nanoparticles is very expensive. However, immobilization by using calcium chloride and sodium alginate is a cost effective process. Even though the dosage of the immobilized copper nanoparticles is more which provides meso porous structures with high surface area, which are able to provide simple accessibility and more chances for guest molecules and light to receive by the active sites. From economic point of view, the usage of copper nanoparticles for the removal SO₂ and NO₂ is not suitable. Due to high recovery cost and toxicity of nanoparticles, the immobilized nanoparticles are preferred (easy recovery) for removal.

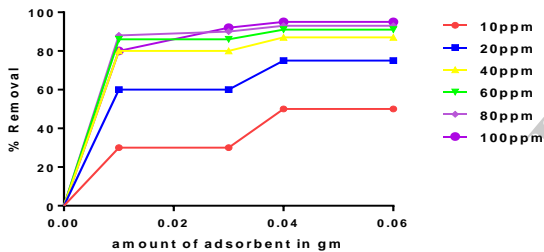


Figure-10: Effect of Dosage between Copper Nano particles and SO₂

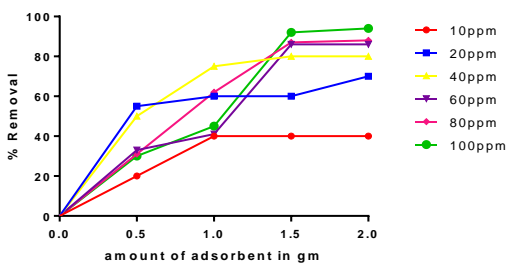


Figure-11: Effect of Dosage between Immobilized CuNP beads and SO₂

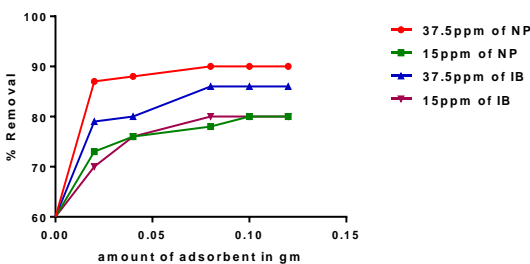


Figure-12: Effect of Dosage between CopperNano particles and Immobilized CuNP beads NO₂. (NP= Nanoparticle, IB= immobilized nanoparticles)

E. Kinetic Models:

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The mechanism of adsorption involves the chemical reaction of functional groups present on the surface of the adsorbent and adsorbate. In present study the experimental data were tested with Pseudo first order, Pseudo Second order, Elovich model and intra particle diffusion models [41].

Pseudo first order equation:

A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [42-44].

$$dq_t/dt = k_1 (q_e - q_t)$$

Where k₁ is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions q_t = 0 at t = 0 and q_t = q_t at t = t, the linear equation is as follows

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

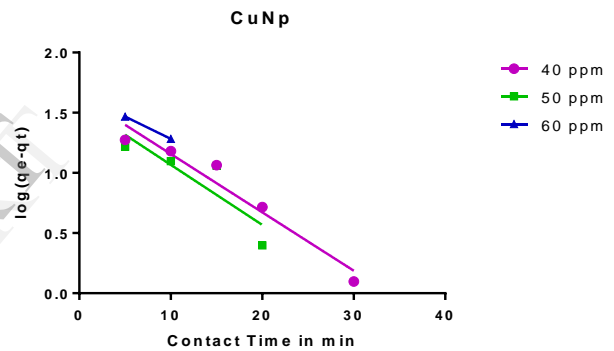


Figure-13: Pseudo Forst Order Kinetic Model for removal of SO₂ with CuNp

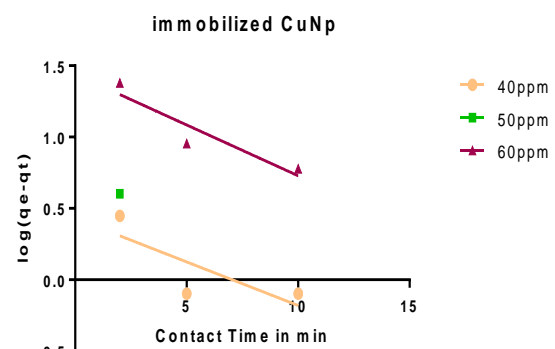


Figure-14: Pseudo First Order Kinetic model for SO₂ removal with immobilized CuNp

The plots of log (q_e - q_t) versus t at different time intervals are represented in figure-13 for both SO₂ and NO₂. The results are shown in figure-13 -16 for both CuNp and Immobilized CuNp. The graphs indicating that adsorption process is not validity of Lagergren rate equation of first order kinetics for the removal of aqueous SO₂ with immobilized CuNp (IB-CuNp) as adsorbent compare to CuNp. Where the kinetic data for removal of SO₂ by CuNp

is shown higher correlation coefficient values. It indicates that removal of SO₂ by CuNp as adsorbent follows Pseudo First order Kinetic model. The adsorption rate value k₁ is calculated from the slope and shown in table-1.

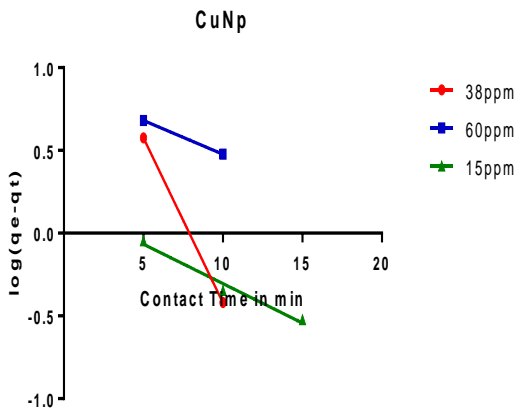


Figure-15: Pseudo First Order Kinetic model for removal of NO₂ with CuNp.

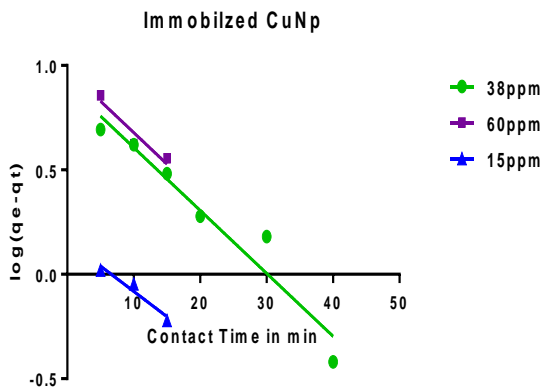


Figure-16: Pseudo First Order Kinetic model for removal of NO₂ with immobilized CuNp

The removal of aqueous NO₂ by CuNp and immobilized CuNp is perfectly fitted into both Pseudo first order kinetic and Pseudo Second order kinetic models but the correlation coefficient values of pseudo second order kinetic model, slightly more compare to pseudo first order kinetic model in both cases (CuNp & IB-CuNp). The statistical data concluding that removal of NO₂ follows Pseudo second order kinetic model. The adsorption rate value k₁ is calculated from the slope and shown in table-2.

Pseudo Second order equation:

Pseudo-second order model is derived on the basis of adsorption capacity of the solid phase, expressed as:

$$t/q_t = \frac{1}{k_2 q_e^2} + t/q_e$$

Where k₂ is the rate constant of pseudo second order adsorption (g/mg min) and q_e is the equilibrium adsorption capacity (mg/gm) [45].

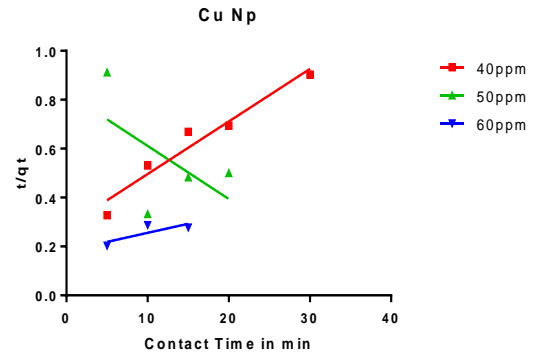


Figure-17: Pseudo Second Order Kinetic Model for removal of SO₂ with CuNp

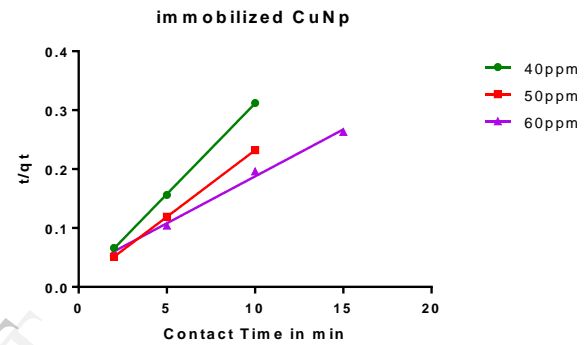


Figure-18: Pseudo second Order kinetic model for SO₂ removal with immobilized CuNp

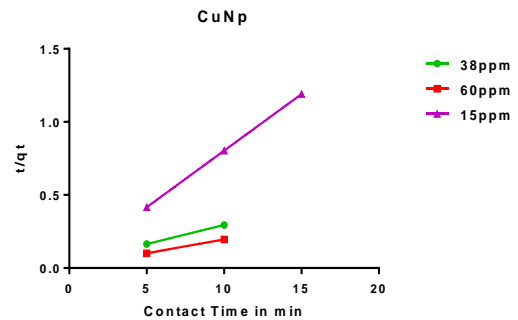


Figure-19: Pseudo Second Order Kinetic Model for removal of NO₂ with CuNp

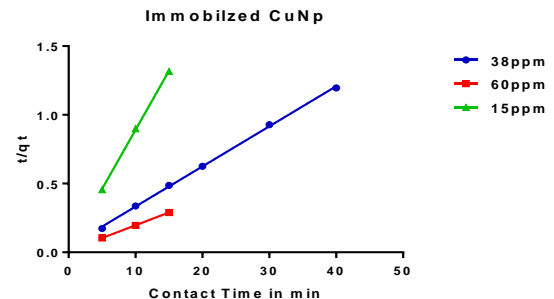


Figure-20: Pseudo Second Order Kinetic model for NO₂ removal with immobilized CuNp

The plots of t/q_t versus t at different time intervals are represented in figure- 17 -20. From the figure-18-20, it was observed that the relationship is linear and R² values are very high compared to pseudo first order kinetics. The graph indicating that adsorption process is following

pseudo second order kinetics for the removal of SO₂ and NO₂ using both CuNp and IB-CuNp, except the removal process of SO₂ by CuNp. The correlation coefficient values of pseudo second order kinetic model is lesser than pseudo first order in this condition. The adsorption rate value K₂ is calculated from the slope and shown in table 1 & 2. The CuNp follows pseudo first order kinetic model with SO₂ as adsorbate, where as both pseudo first and second order kinetic models were fitted with NO₂ as adsorbate indicating that the difference in reactivity due to the nature of adsorbate molecules present in liquid medium.

Elovich Model:

Adsorption data can also be analyzed using the Elovich equation at the following linear form

$$dq_t/dt = \alpha \exp(-\beta q_t)$$

Where, α is the initial adsorption rate (mg·g⁻¹·min⁻¹) and β is the desorption constant (g·mg⁻¹) during any one experiment. If the adsorption of aqueous solutions of SO₂ and NO₂ by CuNp and immobilized CuNp, fits to the Elovich model, a plot of q_t versus ln(t) should give a linear relationship with a slope of (1/β) and an intercept of 1/β ln(αβ). The results for Elovich model represented in figure-21-24 for both SO₂ and NO₂ removal process with both adsorbents.

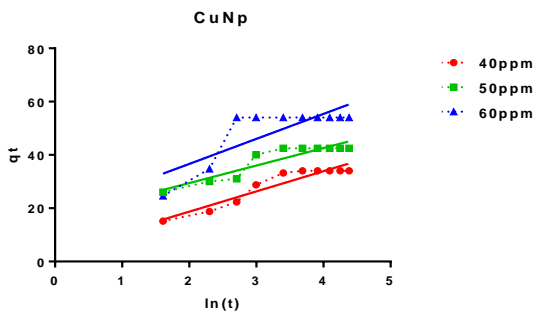


Figure-21: Elovich Model for removal of SO₂ with CuNp

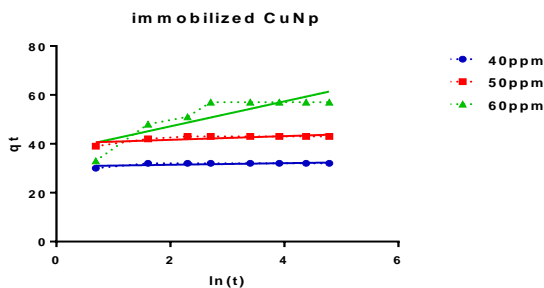


Figure-22: Elovich Model for removal of SO₂ with immobilized CuNp

It was evident from the figure-21 and 24, the adsorption process fits for Elovich model for the removal of SO₂ with CuNp and NO₂ with IB-CuNp as adsorbents. A significant change was observed in correlation coefficient values with increase in concentration of adsorbate molecules in both conditions. This result concluding that the elovich model for SO₂ (CuNp as adsorbent) and NO₂ (IB-CuNp as adsorbent) removal follows Elovich model at lower concentrations. The R² and ASS (Absolute Sum of Squares) values were given in table- 1 & 2 [46].

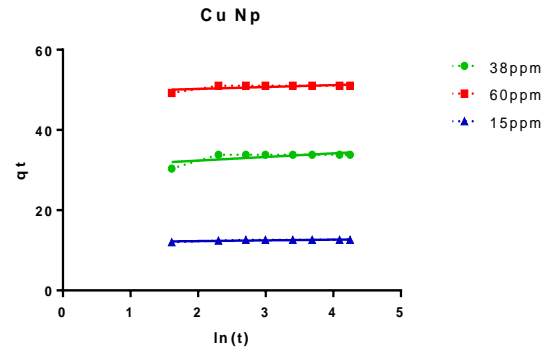


Figure-23: Elovich Model for removal of NO₂ with CuNp

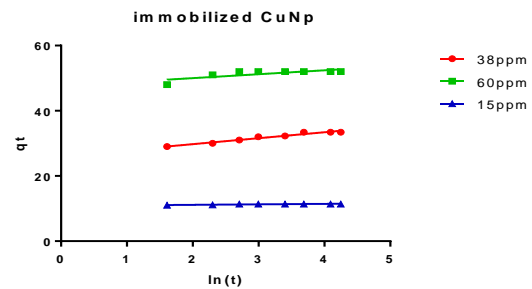


Figure-24: Elovich Model for removal of NO₂ with immobilized CuNp

Intraparticle diffusion Model:

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form of functions of the geometry of the sorbent particle. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half power of time rather than time t. Assuming that the rate is controlled by pore and intraparticle diffusion, the amount adsorbed (q_t) is proportional to the t^{1/2}, as shown below

$$q_t = k_{id}t^{1/2} + I$$

Where q_t is the amount of adsorbed (mg/g) at time t (min), and I is the intercept (mg/g). k_{id} and I values are obtained from the slopes and intercept of the linear plot.

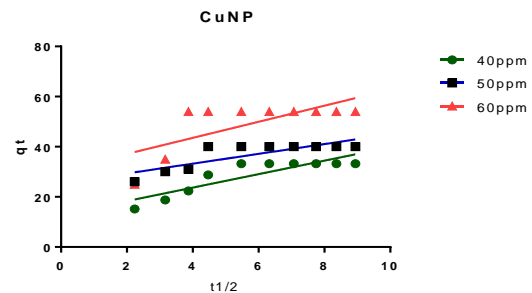


Figure-25: Intraparticle Diffusion Model for removal of SO₂ with CuNp

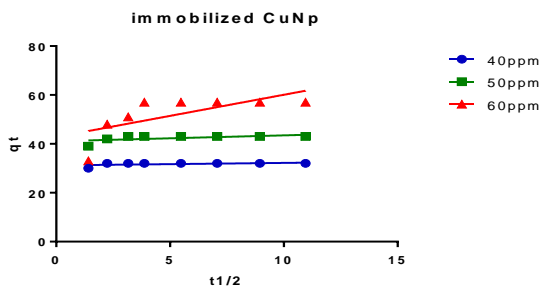


Figure-26: Intraparticle Diffusion Model for removal of SO₂ with immobilized CuNp

Figure-25 and 26 represents the plots of q_t versus t^{1/2} for adsorption of SO₂ by CuNp and immobilized CuNp, at various initial concentrations. From the figures and table-1 & 2 it can conclude that the adsorption mechanism is not fits to intra particle diffusion model [47].

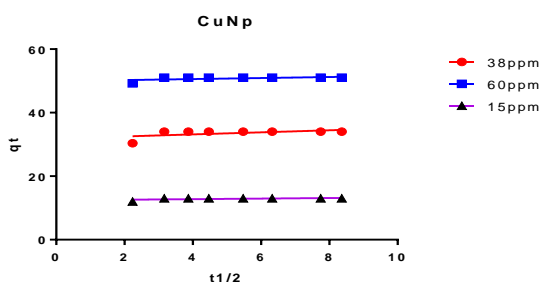


Figure-27: Intraparticle Diffusion Model for removal of NO₂ with CuNp

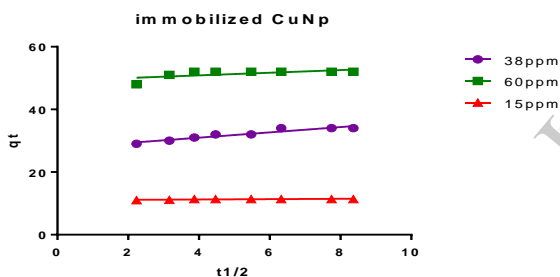


Figure-28: Intraparticle Diffusion Model for removal of NO₂ with immobilized CuNp

The adsorptive removal of aqueous NO₂ by CuNp showing high correlation coefficient values at lower concentrations compare to higher concentration. This observation concluding that removal of NO₂ by copper nanoparticles follows intraparticle diffusion model at lower concentrations and deviates at higher concentrations.

Pore Diffusion Model:

In pore diffusion model it is assumed that the adsorbate diffuses into the pores in the fluid phase and it is taken up by adsorption on walls of pores. The molecules cannot diffuse along the walls of the pores in the adsorbed state, that can migrate only by desorbing first. The linear formula for pore diffusion as follows

$$\epsilon\rho + \rho_p \frac{\delta q}{\delta t} = \frac{\epsilon\rho}{r^2} \frac{\delta}{\delta r} (r^2 D_p \frac{\delta c_p}{\delta r})$$

$$k_f (c - c_p) = \epsilon\rho D_p \frac{\delta c_p}{\delta r}$$

$$k_f = \frac{R_p \rho_p V_L}{3 W A t} \ln \left[\frac{C_t}{C_0} \right]$$

$$W A = \frac{V_L (C_0 - C_\epsilon)}{q}$$

- Where D_p = Pore diffusion coefficient
- C_p = Initial solution Concentration
- K_f = Fluid to particle transfer coefficient
- R_p = Radius of the particle
- P_p = Density of media
- V_L = volume of the sample

The rate of the pore diffusion coefficient and other functional kinetic parameters calculated by respective formula is represented in table-3.

Solid Diffusion Model:

The solid diffusivity D_s is a very complicated parameter to evaluate due to large number of factors that control the solid diffusion rate. Some of these factors are type of adsorbent, its internal structure and particle size, particle loading, the solid-liquid ratio in the system and the initial concentration in solution. All these factors and many other factors interfere with evaluating D_s from the classical diffusivity equation. Therefore starting value of k_f and D_s can be input in the model. The corrected values are obtained by super position of experimental and theoretical data such that they yield congruent curve. The linear formula for solid diffusion is as follows

$$k_f (C_b - C_\epsilon) = D_s \rho_s \frac{\delta q_p}{\delta r}$$

Combined Diffusion Model:

Adsorbent particles are heterogenous systems formed by the porous solid phase and fluid phase filling the void fraction of the solid. The internal diffusion can be expressed by two simultaneous mechanisms of diffusion, including molecular or knudson diffusion and surface diffusion. If one combines and considers this combined parallel resistance within the adsorbent pellet, a material balance for spherical particle results in the following partial differential equations [48].

$$\epsilon p \frac{\delta c_p}{\delta t} + \rho_p \frac{\delta q}{\delta t} = \frac{1}{r^2} \frac{\delta}{\delta r} (r^2 \epsilon p D_p \frac{\delta c_p}{\delta r} + D_s \rho_p \frac{\delta q}{\delta r})$$

$$k_f (c - c_p) = D_s \rho_p \frac{\delta q}{\delta r} + \epsilon p D_p \frac{\delta c_p}{\delta r}$$

4. CONCLUSIONS:

Copper nanoparticles (CuNp) and immobilized copper (IB-CuNp), were successfully employed as adsorbent for removal of SO₂ and NO₂ from aqueous solutions of SO₂ and NO₂ respectively. The obtained results indicated a demonstration

S.No	Parameters	Aqueous SO ₂ concentration (40 ppm)	Aqueous SO ₂ concentration (50ppm)	Aqueous SO ₂ concentration (60 ppm)
	Pseudo first order kinetic model			
	COPPER NANOPARTICLES			
01	R ²	0.947	0.759	0.999
	ASS	0.048	0.098	0.000
	K ₁	0.118	0.191	0.121
02	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.617	0.000	0.863
	ASS	0.075	0.000	0.026
	K ₁	0.743	0.752	0.368
	Pseudo Second order kinetic model			
	COPPER NANOPARTICLES			
03	R ²	0.944	0.318	0.650
	ASS	0.009	0.126	0.001
	K ₂	0.021	0.021	0.007
04	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.999	0.999	0.995
	ASS	0.0008	0.0003	0.0004
	K ₂	0.030	0.022	0.015
	Elovich model			
	COPPER NANOPARTICLES			
03	R ²	0.901	0.849	0.663
	ASS	47.32	57.64	335.6
	α	0.886	1.442	-0.050
	β	0.131	0.152	0.106
	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.427	0.569	0.721
	ASS	2.005	5.970	140.0
	α	4.555	3.986	1.817
	β	3.058	1.328	0.195
	Intraparticle diffusion model			
	COPPER NANOPARTICLES			
04	R ²	0.775	0.674	0.501
	ASS	99.12	87.36	484.7
	kid	2.685	1.953	3.206
	I	12.95	25.44	30.71
	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.227	0.329	0.471
	ASS	2.704	9.300	265.8
	kid	0.1001	0.2400	1.7270
	I	31.21	41.08	42.81

adsorption activity even nanoparticles were immobilized. The highest efficiency of immobilized nanoparticles is explained on the basis of surface chemistry of the nanoparticles. A detailed kinetic investigative studies have been carried out and indicated the adsorption of NO₂ by copper nanoparticles followed both Pseudo first order kinetic model and pseudo second order kinetic model, where adsorption of SO₂ by CuNp followed Pseudo second order kinetic model in comparison. Elovich model and intraparticle diffusion models were followed by NO₂ at low concentration

S.No	Parameters	Aqueous NO ₂ concentration (40 ppm)	Aqueous NO ₂ concentration (50ppm)	Aqueous NO ₂ concentration (60 ppm)
	Pseudo first order kinetic model			
	COPPER NANOPARTICLES			
01	R ²	0.999	0.999	0.977
	ASS	0.000	0.000	0.000
	K ₁	0.445	0.484	0.534
02	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.936	0.906	0.935
	ASS	0.052	0.004	0.002
	K ₁	0.385	0.407	0.487
	Pseudo Second order kinetic model			
	COPPER NANOPARTICLES			
03	R ²	0.999	0.999	0.999
	ASS	0.000	0.000	0.000
	K ₂	0.026	0.019	0.077
04	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.999	0.999	0.999
	ASS	0.005	0.0006	0.0001
	K ₂	0.029	0.018	0.085
	Elovich model			
	COPPER NANOPARTICLES			
03	R ²	0.459	0.459	0.598
	ASS	5.532	1.532	0.125
	α	3.464	4.617	4.148
	β	1.107	2.105	5.555
	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.958	0.598	0.676
	ASS	0.839	5.572	0.061
	α	2.699	3.651	4.260
	β	0.547	0.832	6.756
	Intraparticle diffusion model			
	COPPER NANOPARTICLES			
04	R ²	0.305	0.305	0.305
	ASS	7.88	1.970	0.608
	kid	0.323	0.161	0.089
	I	31.87	49.93	12.41
	IMMOBILIZED COPPER NANOPARTICLES			
	R ²	0.909	0.422	0.520
	ASS	2.352	8.010	0.090
	kid	0.845	0.421	0.054
	I	27.60	49.18	11.03

and deviation is observed at higher concentrations with immobilized copper nanoparticles as adsorbent. The obtained result concluding that rate determining step for removal of aqueous NO₂ by immobilized CuNp is through intraparticle diffusion. Kinetic data tends to fit well for pseudo second order kinetic model for SO₂ removal by immobilized CuNp confirming the chemisorption of SO₂. Kinetic data did not fit into Elovich model and Intraparticle diffusion model (IB-CuNp as adsorbent for removal of SO₂) indicating that adsorption is controlled by pore surface only. The interesting feature in the immobilization of nanoparticles enables effective removal of toxic gases by adsorption process. This approach should find relevant industrial application in different sectors of industry. This report on adsorbent activity opens up new opportunities for the development of new nano adsorbent systems, despite a number of challenges and difficulties, there is a great potential for application of immobilized nanoparticles.

Parameter	Pore Diffusion (SO ₂)		Pore Diffusion (NO ₂)		Solid Diffusion (NO ₂)	
	CuNp	IB-CuN P	CuNp	IB-CuN P	Cu Np	IB-CuN P
Cp	40 ppm	40 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Dp	2.469 X 10 ⁻³ m ² /sec	7.054 X 10 ⁻³ m ² /sec	8.426 X 10 ⁻³ m ² /sec	6.662 X 10 ⁻³ m ² /sec	Nil	
Pp	0.99823 gm/cm ³					

5. REFECENCES:

- C.S. Rao, Environmental pollution control engineering (new age international(pvt) ltd) 31,1997.
- T. Shivaji Rao, Airpollution and its contrling technologies, (vani printer,Visakhapatnam) 16, 1998.
- J.O.M. Bockers. environmental chemistry(plenum pree,NewYork),1997, pp-122-137.
- P.J. Baxter, 2000 gases in :P.J. Baxter, P.h Adams, T.C.AW, A.Cokcraft.
- A.Well burn. Air pollution and climate changes the biological impact (addision wesely longmen limited), harlow, 1994,268.
- Ganggolli.Sm(Ed), the Dictionary of substance and then effects, Royal society of chemistry, Cambridge, 1999.
- E. Robbinson and R Robinson. 'sources, abundance and fate of gaseous atmospheric pollutants' final report, Standard Res. Inst, Project PR-675(Amer petrol. Inst., New York), 1968.
- H.F Jhonston, and D.R. Coughanowr "Adsorption of SO₂ from Air" Ind. Eng.chem.50,1958,1169.
- P.A. Leighton, "Photochemistry of air pollution" (Academic press, New York), 1961.
- P.Brimblecombe. "Air composition and chemistry", (Cambridge university press).. Cambridge, 1996.
- B.J. Finlayson-pitts and J.N.pitts, "Atmospheric chemistry fundamentals and experimental techniques", (Wiley Inter sciences publication) New York,1986.
- J.N. Porter, K.A. Horton, Mougini-Mark, P.J. Lienert.b, S.k. Sharma and e.Lau. Sutton.A.j., Elias and appenhiemer.C2002. Geophysical research letters 29(16). 2002, 14744.
- E.A. Patty Inter science vol.11, Newyork, 1962, 892-895.
- H.W. De Koing, "Hand book of air pollution Analysis 11nd edition , 1986, Editiors Harrison R.M and perry. A.chapman and Hall, London, UK), 563-578.
- M.V. Sefton, American industrial Hygiene Association Journal, 44(7), 1983, 514-520.
- A .Lam, Canx, Einsinthal and R. huddle, J.Enzyme microb,Technol.,29(1),28(2001)
- A. Lam ,CarX, Einsinthal, and R. Hubble, J.,Enzyme microl,Technol.,29,28-38 (2001)
- DingFang.J.Liu John and M.sansoline,ASCE and Frum Cart Ledge,J.Env.Eng.,130,374(2002).
- T. Nakamura, M. Kawasaki, Mastsamoto, k.Tannand, Skchand enkyu,16,57-62(2003).
- B.S. Chu, B.S. Baharin, Y.B. cheman, and S.Y. Quck, 2005. "Comparison of selected adsorbent for adsorption and desorption of vitamin Efrom palm fatty acid distillate".Journal of food lipids,12(1):1-23.
- Feng n c,Guo x y , Liang s. Adsorption study of copper(II) by chemical modified orange peel[J]. Journal of Hazardous Materials, 2009,164(2/3);1286-1292.
- Vijayaraghavan Kuppusamy, Joseph Raj Kandasamy Palanivelu and Manickam Velan copper removal from aqueous solution by gren alga Ulva reticulata. Elcctronic J.biotechnology 7(1):61-71
- Liang s, Guo x y , Feng nc, tian q h. Application of orange peel xanthate for the adsorption of pb²⁺ from aqueous solution[J]. Journal of hazardous Materials,2009,170(1);425-429.
- N. Gandhi, D. Sirisha and K.B. Chadra Shekar. "Adsorption of Chromium (VI) from aqueous solution by using brick powder". Asian Academic Research Journal of Multidisciplinary, 1(15), 112-137, 2013.
- A. Nevine Kamal, "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith," Water treatment solutions desalination Vol. 223, pp. 152-161, 2008.
- N. Gandhi, D. Sirisha and K.B. Chadra Shekar. "Adsorption of Chromium (VI) from aqueous solution by using Multani miti". International journal of research in pharmacy and chemistry, 4(1), 168-180, 2014
- N. Gandhi, D. Sirisha and K.B. Chadra Shekar. "Adsorption of Fluoride from aqueous solution by using Chalk powder", World Journal of Pharmacy and Pharmaceutical Sciences, 2(5), 3897-3914, 2013
- G.Suresh and B.V. Babu. "Experimental investigation and theoretical modeling aspects in column studies for removal of Cr(VI) from aqueous solution using activated Tamarind seeds". Journal of Water Resource and Protection, 2 (1), 706-716, 2010.
- N. Gandhi, D. Sirisha and Vikas Chandra Sharma. "Microwave mediated green synthesis of silver nanoparticles using Ficus elastic leaf extract and application in air pollution controlling studies". International journal of Engineering Research and Applications. 2014, 4(1), 1-12.
- N. Gandhi, D. Sirisha, V. Mary Priyanka and S.R. Arthiisree. "Adsorption Studies on Mixed algae to control SO₂ and NO₂ pollution" International Journal of Pharma and Bio sciences, Vol. 3(4) B; pp 304-310, 2012.
- V. Marry priyanka, D. Sirisha and N. Gandhi. "Sulphur dioxide adsorption using *Macryloma uniflorum* Lam. Seed powder". Proceedings of the International Academy of Ecology and Environmental Sciences, vol. 2(4); pp 251-254, 2012.
- D. Sirisha, K. Mukkanti and N. Gandhi. "Adsorption Studies on Alum Sludge" Advances in Applied Science Research, vol. 3(5); pp 3362-3366, 2012.
- V. Mary Priyanka, D. Sirisha and N. Gandhi. "Adsorption studies on *Mangifera indica* controlling of SO₂ pollution" Journal of Chemical and Pharmaceutical Research, Vol. 4(3); pp 1768-1771, 2012.
- D. Sirisha, K. Mukkanti and N. Gandhi. "Adsorption of SO₂ by Marble chips". International Journal of Chemical Sciences, Vol. 10(2); pp 847-854, 2012.
- K. Mamatha, N. Gandhi and D. Sirisha. "Adsorption of aqueous solution of NO₂ by certain waste materials". Asian Journal of Research in Chemistry, Vol. 5(1); pp 143-145, 2012.
- P. Wst, W. ond Cleke, G. C.Anal.Om<. 28, 1,816,19\$.6,
- SIUml", R. V., w.o.. P, W" Tron, F, Ind Gleke. C.c. Anal. 0""...32,1,3(17,1960.
- Lod~e, J. P. Jr.. P.te, J. B., Ammons. B. E. ond 5"">11\$0'1. G. A, J. AirPol Control A..."" , 16,197.1966.
- O'Keeffe, A. E, Ind Orlm." G (.4""". Qlem.. 3&. 'J60, 1966,
- M.S. Onses, C.C Liu, C.J. Thodo, P.F Nealey, "Lanmuir," 2012, 28, 7299-7307
- K. Gilles, L. Kaulen, M. Polst, U. Simon, A. Offen hausser, D. Mayer, "Nanotechnology", 2011, 22, 295-301.
- ColmT. Mallon, Elaine Spain, Tiae Keyes and Robert.J.Forster; DNA mediated immobilization of electro catalytic nanoparticles in gold nanocavity arrays, Chem. Commun. 49, 1380-1382, 2013.
- T. Peng, D. Zho, K.D.W. Shi and K. Hirao, J.Phys.Chem.B 109, 4947 (2005)
- S.M. Paek, H.Jung, Y.L.Lee, M. Park, S.J. Hwang and J.H. Choy, Chem.Mater, 18, 1134 (2006)
- N.M. Mahamoodi, M. Arani, N.Yousefi Limaee, K.Gharajig and F. Nour Mohammadian, Mater. Research Bulletin, 42, 797 (2007).
- J. Raffiea Baseri, P. N. Palanisamy, and P. Siva kumar, "Adsorption of basic dyes from synthetic textile effluent by activated carbon prepared from Thevetia peruviana," Indian Journal of Chemical Technology, Vol. 19, pp. 311-321, 2012.
- Y. S. Ho and G. McKay, "A comparison of chemisorption kinetic models applied to pollutant re-moval on various sorbents," Trans. Inst. ChemEng. Vol. 76B, pp. 332-340, 1998.
- Y. S. Ho and G. McKay, "Comparative sorption kinetic studies of dyes and aromatic compounds onto yash," J. Environ. Sci. Health-A, Vol. 34, pp. 1179-1204, 1999.