Adsorption Efficiency of Synthetic Nano Iron Oxide and Commercial Activated Carbon Towards The Removal of Cu(Ii) Ions – Comparative Study

G.Kanthimathi[, 1], P.Kotteeswaran[1] and M.Kottaisamy[2]
[1]*Department of Chemistry, Ramco Institute of Technology, Rajapalayam, India – 626 1172*
[2]*Department of Chemistry, Thiagarajar College of Engineering, Madurai   India – 625 015*
Corresponding author: kanthi_somu@rediffmail.com

Abstract :- **The adsorbent Nano Iron Oxide (SNIO) was synthesized and essential characterstics were ascertained using FT-IR, SEM, and EDAX techniques. Commercially Available Carbon (CAC) was activated further by acid treatment to enhance its adsorption capacity. Adsorption experiments were carried out by using Batch method to compare the sorption behaviour of SNIO and CAC for the removal of Cu(II) ions. The study was conducted on the basis of parameters such as a function of initial concentration of the adsorbate, adsorbent dosage, contact time and pH. Freundlich and Langmuir isotherm models have been tested. The applicability of various first order kinetic equations like Natarajan-Khalaf, Lagergren, Elovich and Power functions equations were tested. The separation factor (R) was found to be between 0 and 1 for both the adsorbent, it clearly indicates the feasibility of adsorption.**

Keywords: SNIO, CAC, Adsorption

I.   Introduction

Copper is an essential micro-nutrient for all forms of life [1,2]. The daily requirement of copper is about 2.0 mg for an adult [3]. Eventhough copper is needed for all human beings, problems arise when it is deficient or in excess. The Environmental Protection Agency's (EPA) lead and copper rule promulgated, in 1991, that the maximum contaminant level goal (MCLG) for copper [4] is 13 mg L^{-1}. Researchers found that copper exerts a much more inhibitory effect on biological processes than zinc and nickel. The presence of excess of copper causes Wilson's disease [5] due to which the bio-synthesis of ceruloplasmin is suppressed. Other toxic effects of copper in humans include congestion of nasal mucous membranes and pharynx, ulceration of nasal septum, metal fume fever, kidney stone formation, etc. The ingestion of acute toxic levels of copper may result in nausea, vomiting, diarrhea, liver damage, hemoglobinuria and hematuria. Copper in water is extremely toxic to aquatic biota.
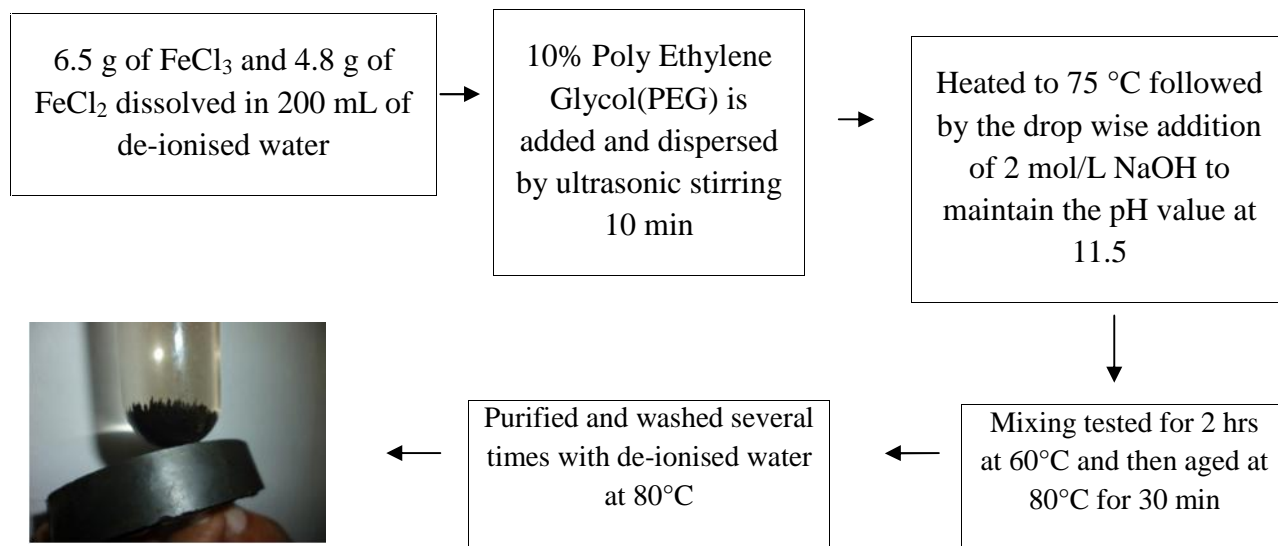
Fargasova and Salim et al [6,7] have proved the adverse effect caused by copper on plants, i.e., accumulation of copper in plants generates depression of short length. Bio accumulation of heavy metals including copper affects earth-worms also. Aluminium and copper seem to exert deleterious influence on benthic life forms [8]. A maximum concentration of 0.1 ppm copper has been prescribed for drinking water by the Indian Standards Institution. It has been estimated that total copper emission to the atmosphere is approximately 74,500 tonnes per year. Natural sources of copper pollution are windblown dusts, vegetation exudates, volcanic emission, etc. Anthropogenic sources include metal production, weed and fossil fuel combustion and waste incineration. Among industrial sources, the main contributors of copper are metal pickling baths, copper plating baths, waste waters from rayon process, pulp and paper mills, petroleum refining, metal work and foundries, mine water, etc[9, 10,11] .

II.   Experimental Procedure

2.1 Preparation of Nano Fe_3O_4

Acid – Base hydrolysis of Ferrous and Ferric chloride is used for the synthesis of Synthetic nano iron oxide (SNIO). The flow diagram for the preparation of the nano iron oxide is given below.

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \quad Fe_3O_4 + 4H_2O$$

6.5 g of $FeCl_3$ and 4.8 g of $FeCl_2$ dissolved in 200 mL of de-ionised water → 10% Poly Ethylene Glycol(PEG) is added and dispersed by ultrasonic stirring 10 min → Heated to 75 °C followed by the drop wise addition of 2 mol/L NaOH to maintain the pH value at 11.5

Purified and washed several times with de-ionised water at 80°C ← Mixing tested for 2 hrs at 60°C and then aged at 80°C for 30 min

III.   Results and Discussion

3.1.1. X-ray Analysis

   X-Ray diffraction pattern of the commercial macro Fe_3O_4 and chemically synthesized Fe_3O_4 particles was shown in Fig. 1a and 1b. The curve shows all the diffraction peaks of the Fe_3O_4 (JCPDS -75-1609) and the broadening of the diffracted peaks of the chemically synthesized Fe_3O_4 shows a growth of nanocrystalline phase with an average size of 20nm calculated using the Debye-Scherer formula.
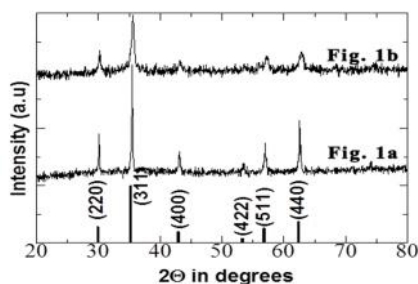

Fig.1.XRD pattern of Commercial micro(a) and synthesized Nano Fe_3O_4 (b)

3.1.2 SEM Analysis

   Fig. 2a   shows the high resolution scanning electron microscope (HRSEM) image of Fe_3O_4 after adsorption of Cu(II) ions. After treating with copper solution, the particle are showing an increased agglomeration and surface of the particles appears to be smooth and it is shown in Fig. 2a. A X-ray energy dispersion analysis (EDAX) of Fe_3O_4 after adsorption of the Cu(II) ions is depicted in Fig. 2b. From the EDAX spectrum, it is observed that there is major component of Fe and O due to Fe_3O_4 and presence of Cu adsorbed on it.
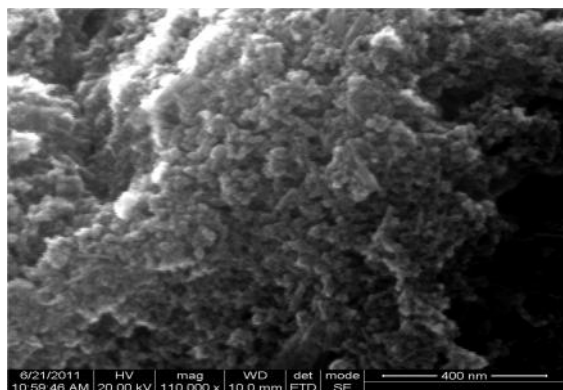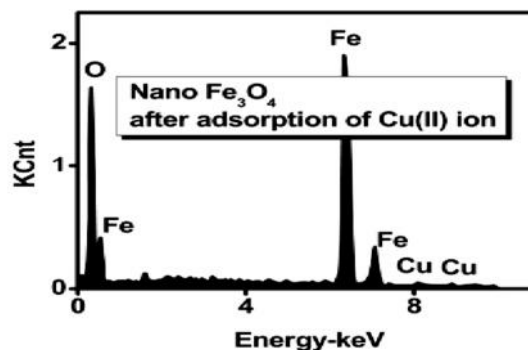
Fig. 2a SEM Micrograph of Copper adsorbed in nano Fe₃O₄

Fig. 2b EDAX for nano Fe₃O₄ after adsorption of Cu(II) ions

3.2 Effect of Initial Concentration of the metal ions

Adsorption studies of Cu(II) ions on SNIO and CAC at a fixed dose of adsorbent (1.07 g/L for SNIO and 13.3 g/L for CAC) at different initial concentrations of the metal ions (range : Cu(II) ions 50- 95 ppm) and constant contact time (60 min),   pH 5-6 for SNIO and pH 6-6.5 for CAC at temperature $28 \pm 1°C$ were carried out. The variations in the percentage removal of Cu(II) ions with its concentration are shown diagrammatically in Fig.3. In both cases of adsorbents, it was observed that the percentage removal of Cu(II) ions is low at higher concentration and gradually increases as the concentration of Cu(II) ions decreases. This is due to the fact that after the formation of mono-ionic layer at lower concentration over the adsorbent surface, further formation of the layer is highly hindered at higher concentration due to the interaction between Cu(II) ions present on the surface and in the solution. In addition to that, at low concentration of the Cu(II) ions, the ratio of the initial number of moles of the Cu(II) ions to the available surface area of the adsorbent is large and subsequently, the fraction of the adsorption becomes independent of the initial concentration of the metal ion. But at higher concentration, the adsorption sites available for the adsorption become lesser, and hence, the percentage removal of the metal ions at higher concentration decreases. The optimum concentration of the Cu(II) ions is found to be 50ppm for its efficient removal by adsorption on the SNIO. For CAC the optimum concentration of the Cu(II) ions is found to be 60.2 ppm. The percentage removal of the Cu(II) ions by SNIO at 50 ppm level is found to be 97.8 %, whereas the CAC removes only 84.2 % of the Cu(II) ions at 60.2 ppm concentration of the Cu(II) ions. The higher adsorptive power of the SNIO over the CAC may be attributed to the nanosize of the SNIO. When a particle decreases to the nanometer range, an increasing fraction of the atoms are exposed to the surface, giving rise to excess surface energy compared to macro molecules. Therefore, nanoparticles with a higher total energy should be prone to adsorb molecules onto their surfaces in order to decrease the total free energy [12].
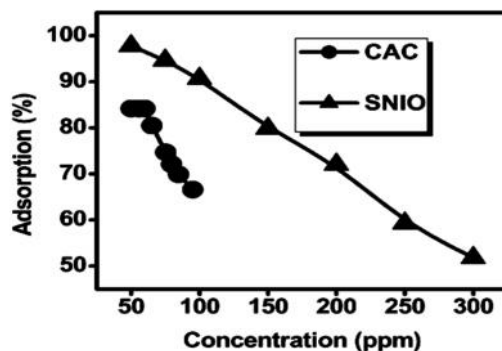

Fig.3. Effect of concentration on the percentage removal of the Cu(II) ions by adsorption on CAC and SNIO

3.3 Effect of the dose rate

The removal of the Cu(II) ions was studied with different doses of the SNIO and activated CAC at optimum concentrations of the Cu(II) ions 50ppm for SNIO and 60.2ppm for CAC with fixed contact time 60 minutes, pH 5-6 for SNIO and pH 6-6.5 for CAC and temperature 28± 1 ℃. The results are pictorially represented in Fig.4.

It is noted that the percentage removal of the Cu(II) ions increases as the adsorbent concentration increases owing to the enhanced total surface area of the adsorbent. The removal of the Cu(II) ions increases slightly with increase in the dose of the SNIO and CAC. This means that the toxic ions can be removed effectively from the contaminated water with the proper amount of the adsorbent, which would possess more adsorption sites available for the metal ion uptake from the solution [13,14]. The SNIO shows higher adsorption capacity (97.8%) with the optimum dose of 1.07 g/L which is nearly thirteen times less than the CAC (84.2% at 13.3 g/L), because the nanoparticles possess more number of micropores and mesopores and higher total surface energy than macroparticles which are more prone to adsorb the Cu(II) ions on to the surface of the adsorbent in order to decrease the total free energy [12].
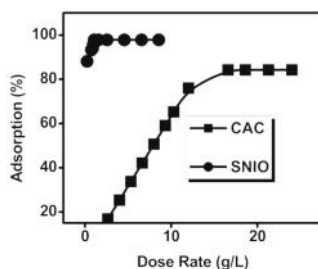

Fig. 4   Effect of the dose rate in the percentage removal of the Cu(II) ions by adsorption on SNIO and CAC.

3.4 Effect of Contact time

In order to study the effect of the contact time on the removal of Cu(II) ions, the adsorption experiments were carried out at different contact times at optimum concentrations of the metal ion with the respective dose of the SNIO and CAC. The relevant experimental data are graphically represented in Fig.5.
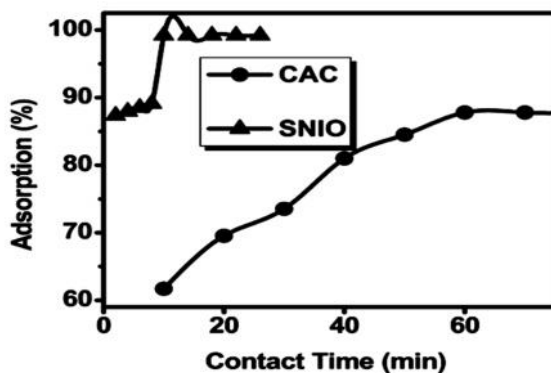

Fig.5.   Effect of Contact time in the percentage removal of the Cu(II) ions by adsorption on SNIO and CAC

The extent of removal of the Cu(II) ions increases initially and then becomes stagnant after the optimum contact time. The equilibrium time for the maximum removal of the Cu(II) ion is found to be 60 min for SNIO with the effective adsorption of 97.8%, for CAC 60 min with the effective adsorption of 84.2%. Both the adsorbents require same time but SNIO shows a higher adsorption capacity than CAC because the former possesses large surface area (63.87 m^2/g), whereas the latter possesses small surface area (1.37 m^2/g).

3.5 Effect of pH of the solution

The adsorption potential of the SNIO and CAC is found at various pH values, keeping the system at the optimum conditions of the initial concentration of the Cu(II) ions, adsorbent dose and contact time. The relevant experimental data are graphically represented in Fig.6. The removal of the Cu(II) ions through adsorption by the SNIO and CAC is effective in slightly acidic medium and the optimum pH range observed for SNIO is 5.98 and CAC 6.0. The percentage removal of metal ions is low at low pH and increases with the increase in pH. This observation reveals that the adsorption process is pH dependent. At low pH, because of the higher concentration of the H$^+$ ion and its higher mobility due to smaller size, the H$^+$ ions are preferentially adsorbed. At optimum pH (5.91 for SNIO, 6 for CAC), the concentration of the H$^+$ ions is lowered and consequently, the adsorption of the Cu(II) ions increases. At higher pH than the optimum, the OH$^-$ ion concentration is increased and preferentially adsorbed on the adsorbent and the surface of the adsorbent becomes negatively charged. Moreover at higher pH, the Cu(II) ions form various complex anion, hydroxide complexes, etc. which are retarded by the negatively charged surface of the adsorbent[15]. At optimum pH the SNIO shows higher adsorption capacity of 97.8% whereas the CAC shows only 84.2%.
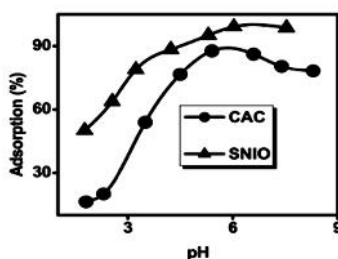

Fig.6 Variation in the percentage removal of the Cu(II) ions by adsorption on SNIO and CAC

3.7 Kinetics of adsorption

In order to study the kinetics of adsorption of the metal ions, the batch type adsorption experiments were carried out by varying the contact time at optimum initial concentration of the metal ions and fixed dose of adsorbent (1.07 g/L of SNIO and 13.3g/L of CAC) at 28 ± 1°C. The boundary layer resistance will affect the rate of adsorption. Increase in contact time will reduce this resistance and increase the mobility of the adsorbate (metal ions) in the adsorption system.   The applicability of various first order kinetic equations like Natarajan-Khalaf, Lagergren, Elovich and Power functions equations were tested. The values of rate constant from the above rate equations are collected in Table 1.

The linear kinetic plots Figs. 7.1, 7.2, 7.3, 7.4 observed and the computed (correlation coefficient) values which are very close to unity indicate the applicability of these first order kinetic equations and the first order nature of the adsorption process of the metal ions. The rate of adsorption of Cu(II) ions on the SNIO is found to be higher than CAC. The reason for this may be due to the large surface area and the highly active surface sites present in the SNIO than in CAC. Apart from the adsorption at the outer surface of the adsorbent, there also exists a possibility of inter-particle diffusion of the adsorbate molecule from the bulk of the outer surface into the internal pores of the adsorbent. The possibility was explored by plotting the amount of Cu(II) ions adsorbed (x/m) per unit mass of the adsorbent against time$^{1/2}$. The linear plots was observed and shown in Fig. 7.4, indicate that the intra-particle diffusion is the rate limiting step.
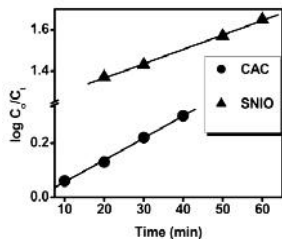
Fig.7.1   **Application of the Natarajan and Khalaf equation for the removal of Cu(II) ions by adsorption on SNIO and CAC.**
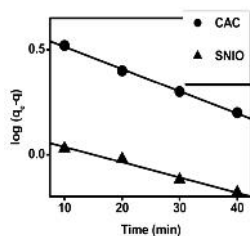

Fig.7.2 Application of the Legregren equation for the removal of Cu(II) ions by adsorption on SNIO and CAC.
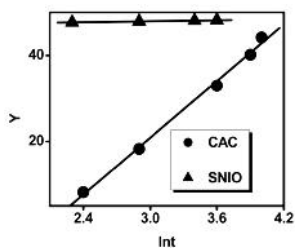

Fig.7.3 Application of Elovich equation for the removal of Cu(II) ions by adsorption on SNIO and CAC.
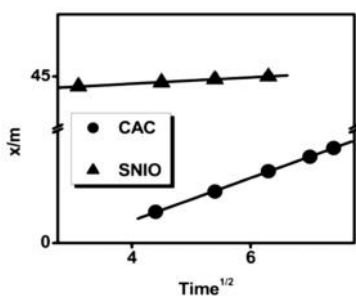

Fig.7.4 Application of the Intra particle equation for the removal of Cu(II) ions by adsorption on SNIO and CAC.

Table 1.   Rate constants of the adsorption of the Cu(II) ions at different contact time

	Rate constant of the adsorption (10^{-2})					Intra- particle diffusion coefficient (10^{-2} min$^{-1/2}$)
	K_a	K_b	K_c	K_d	Average	
CAC	0.8	2.0	4.0	99	26	12
SNIO	0.7	2	263	1	66	73

The rate constant for the adsorption of Cu(II) ions on SNIO is found to be greater than CAC. The reason for this may be due to the large surface area and the highly active surface sites present in the SNIO than in CAC. The possibility of inter-particle diffusion of the adsorbate molecule from the bulk of the outer surface into the internal pores of the adsorbent was explored by plotting the amount of Cu(II) ion adsorbed (x/m) per unit mass of the adsorbent against time$^{1/2}$. The linear plots was observed and shown in Figure 7.4, indicate that the intra-particle diffusion is the rate limiting step. The greater the intra-particle diffusion co-efficient, greater is the rate of adsorption. The rate of adsorption is higher in the case of SNIO than CAC.

3.8 Adsorption Isotherm

The study of adsorption isotherm has been of importance and significance in the water and waste water treatment by the adsorption technique, as they provide an approximate estimation of the adsorption capacities of the adsorbents. The data obtained for the removal of the Cu(II) ions on the SNIO and CAC at optimum conditions are modeled with Freundlich isotherm $\log x/m = \log k + 1/n \log C_e$ and Langmuir isotherm $C_e/Q_e = C_e/Q_o + 1/Q_o b$.

When the pertaining parameters for each isotherm are plotted, linear plots are observed Figures 8a and 8b. The linearity indicates the applicability of all the isotherms for the Cu(II) ions on the SNIO and CAC. Various useful parameters like adsorption capacities of the SNIO and CAC, energy of adsorption, separation factor and correlation co-efficient obtained from various models are collected in Table 2. Adsorption capacity is found to be high for SNIO (Q_o =200) than CAC (Q_o =25), and the energy of the adsorption is found to be less for SNIO (b=0.008) than CAC (b=0.01). The low energy of the adsorption for the SNIO may be due to the larger surface area and the highly active surface sites present in the SNIO than CAC. The separation factor R obtained for the removal of Cu(II) ions by the SNIO (0.7) and the CAC (0.6) are found to be between 0 and 1 indicating the feasibility of the adsorption . The adsorption intensity 1/n values for the SNIO and the CAC are > 0.05 indicating a strong bond formation between the adsorbate and the adsorbent during the adsorption.
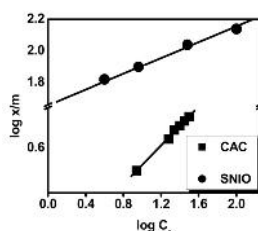

Fig. 8a Application of Freunlich isotherm for the removal of the Cu(II) ions by adsorption on CAC and SNIO.
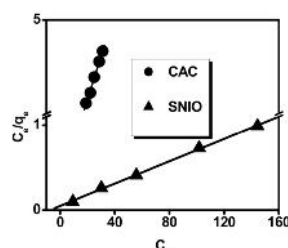

Fig.8b Application of Langmuir isotherm for the removal of the Cu(II) ions by adsorption on CAC and SNIO

Table 2.   Freundlich and Langmuir constants derived from the simultaneous removal of Cu(II) ion by using CAC and SNIO.

Adsorbent	Freundlich constant			Langmuir constant			
	K	1/n	r ^{2}	Q_0(mgg^{-1})	B(Lmg^{-1})	R	r ^{2}
CAC	2.23	0.2	0.99	25	0.01	0.6	0.99
SNIO	44.6	0.25	0.99	200	0.008	0.7	0.99

In the present study, the efficiency of the SNIO towards the removal of the Cu(II) ion was examined and compared with that of the CAC. The optimum conditions of the various factors for the maximum removal of the Cu(II) ions arrived at from the studies are given in Table 3. The kinetic study showed that the removal of the Cu(II) ions on the SNIO and CAC followed first-order kinetics and the rate constant were found to be 66×10^{-2} and 26×10^{-2} min^{-1} respectively. The energy of the adsorption for the SNIO was found to be lower compared to the CAC. The higher adsorption capacity, higher rate constant of adsorption and lower energy of the adsorption of the SNIO compared to the CAC attributed to the large surface area and higher active surface sites of the SNIO. Hence, the SNIO may be considered to be a better alternative adsorbent for the removal of the Cu(II) ions than for CAC.

Table 3.   The optimum conditions of the various factors for the maximum removal of the Cu(II) ions arrived at from the studies

Parameter	SNIO	CAC
Initial concentration of the Cu(II)ion (ppm)	50	60.2
Dose rate (g/L)	**1.07**	**13.3**
Contact time (min)	60	60
pH	5-6	6-6.5
Stirring Speed (rpm)	120 ± 5	120 ±5
Percentage Removal (%)	**97.8**	**84.2**
Adsorption capacity (mg/g)	**200**	**25**
Energy of adsorption (L/mg)	**0.008**	**0.01**
Amount adsorbed per unit mass of the adsorbent (q_e) (mg g^{-1})	**45.74**	**3.81**

IV.   Conclusion

The synthetic nano Fe_3O_4 with an average size of 20 - 25 nm may be considered to be a superior, more effective and efficient alternative adsorbent than commercial activated carbon (CAC) for the removal of Cu(II) ions from aqueous solutions due to the following advantages.

1. Synthesis of nano Fe_3O_4 is less expensive than CAC
2. It requires less dosage for the removal of Cu(II) ions (Table 3)
3. Higher percentage removal than CAC (Table 3)
4. Higher Adsorption capacity (Table 3)
5. Greater amount of metal ions are adsorbed per unit mass of the adsorbent (Table 3)
6. Rate of the reaction is faster (Table 3)

As per Table 3, we infer that synthetic nano Fe_3O_4 is more suitable for the removal of Cu(IIions than Commercial Activated Carbon (CAC).

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