

Evaluation of removal efficiency of cu (II) ion by activated carbon prepared from Nirgudi, Mudra and Gliricidia Sipium leaves from their aqueous solution

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Abstract

Present study deals with the removal of copper ions from aqueous solution by using activated carbon of natural leaves like Nirgudi (NAC), Mudra (MAC) and Gliricidia Sipium (GAC) leaves which is highly efficient, ecofriendly and locally available adsorbents. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of contact time, pH and the initial concentration of copper (II) solution were considered. The results show that the contact time 105 minutes for all adsorbent are sufficient to fit the equilibrium. The optimal adsorption pH for the adsorption of copper (II) ions is 7 for NAC, MAC and 8 for GAC adsorbents. The maximal quantities adsorbed by every adsorbent were 98.63 for NAC, 98.61 for MAC and 98.46 for GAC. Two isotherms models amongst which are Langmuir and Freundlich have been applied to the experimental data. The value of separation factor RL was found to be 0.01847, 0.02506 and 0.04477 for NAC, MAC and GAC respectively suggesting the isotherm to be favorable at the concentration studied. The Langmuir model best described the adsorption of copper (II) ions in aqueous solution by the selected adsorbents.

Keywords: Adsorption isotherms, gliricidia cipium, mudra and, nirgudi.

1. Introduction

Heavy metal ions are highly toxic for animals and human beings (Ansari et al. 2006). Heavy metal contaminates the environment and is a widespread problem (Ansari 2006). Toxic heavy metals in the aquatic ecosystem raise human health risks and cause harmful effect to living organism in water and also to the consumer of them (El-said et al. 2010). Among the heavy metal like cadmium, cobalt, zinc, copper, and iron ignition beyond permissible quantities causes psychological disorder in human beings (Prabakarani et al. 2011). The World Health Organization in 2006 recommended 2.0 mg/L as the maximum acceptable concentration of copper in drinking water. In human copper toxicity causes itching and dermatization, due to their toxicity, accumulation in food chain and keratinization of the hands and soles of feet (Banerjee et al. 2012). The removal of heavy metals from waste water has recently become the subject of considerable interest (Krishna et al. 2011). Therefore there is a growing need for the development of new, innovative and cost effective methods and the removal of metal (Sayeda et al. 2010).

A number of techniques used for the removal of metal ions from aqueous solutions have been reported mainly reduction, electrochemical precipitation, evaporation, solvent extraction, ion exchange, electrolysis, reverse osmosis, chemical precipitation are expensive and non-environmental friendly, as compared to adsorption (Muthusamy et al. 2012). Adsorption process is considered better as compared to other methods, because of convenience, easy operation and simplicity of design (Bhatanagar et al. 2006).

Activated carbon (AC) is a generic term for a family of highly carbonaceous materials none of which can be characterized by a structural formula (Verla et al. 2012). Activated carbon is amorphous solid adsorbent that can be produced from almost all carbon rich materials there are various carbon rich materials used as metal ion adsorbent (Nwabanne et al. 2012). Several adsorbents, such as dyed Senna uniflorora leaves (Nalini et al. 2013), Teak leaves (Goswami et al. 2013), Soybean hulls (Doglas et al. 2006), Cement kiln dust (Waly et al. 2010), Sugar beet pulp (Ozer et al. 2005), Sugar cane bagasse (Patil et al. 2010), polyaniline coated saw dust (Liu et al. 2012), Hebba clay (Shama et al. 2010), Henna leaves (Shanti et al. 2013), Waste tire rubber ash (Mausavi et al. 2010), Decanter cake (Dewayanto et al. 2010), Coconut bagasse (Sousa Neto et al. 2011), Chestnut shell, (Yao et al. 2010) Synthetic Geo-thite (Mertain et al. 2013), Zeolite NaX (Pandey et al. 2009), coconut pollen, (Agini et al. 2007) Mango leaf (Sethu et al. 2010) and Sorel's cement (Awwad et al. 2005).

The aim of this work is to study the removal of Cu (II) metal ions by Activated Carbon Prepared from Nirgudi, Mudra and Gliricidia Sipium leaves from synthetic waste water and to offer this adsorbent as local replacement for existing commercial adsorbent materials.

2. Experimental

2.1. Materials

The leaves of Nirgudi, Mudra and Gliricidia Cipium were collected from local field of Jalgaon District. These waste materials were

washed with water, dried in sunlight, then 60 °C for 24 h in hot air oven. The dried material was subjected for acid treatment (ratio 1:1) and kept at room temperature overnight, then screened through mesh sieve with different particle size range A) 500-850 micron B) 180-500 micron C) 45-180 micron and stored in a tight lid container for further studies.

2.2. Preparation of activated carbon from adsorbent

Carbon was prepared by treating air dried adsorbent with sulphuric acid in a weight ration 1:1 for 24 h. the resulting black product was kept in an oven maintained at 500 °C for 12 h followed by washing with NaHCO₃ and water until free from excess acid, the pH of washing becomes 7.0 and dried at 150 ± 5°C to obtain sulphuric acid treated activated carbon of Nirgudi, Mudra and Gliricidia Cipium and its physical properties were analyzed by usual standard methodologies.

2.3. Preparation of cu (II) solution

The stock solution of Cu (II) ion was prepared by dissolving 0.3929 gm of CuSO₄ · 5H₂O in 1000 ml volumetric flask and made up to the mark with double distilled water. All the required working solutions were prepared by diluting the stock solution with double distilled water. Batch adsorption studies were performed at room temperature.

2.4. Experimental methods and measurement

The adsorption experiments were carried out by agitating the carbon with 50, 75, 100 mg/l metal ion solution of desired concentration at pH 7.0 and at room temperature in a mechanical Shaker (120 rpm) after a defined time interval, samples were withdrawn from the shaker, filtered by Whatman filter paper No. 1 and the supernat solution was analyzed for Cu (II) ion concentration using an Atomic Absorption Spectrometer (Thermo scientific S-series AA Spectrometer) at 324.8 nm.

3. Results and discussion

The four natural easily available adsorbents were selected from local area. The Table 1 shows selected adsorbents from natural waste.

Table 1: Selected adsorbents from natural waste:

Sr.No.	Adsorbent Name	Botanical name	Abbreviation
1	Nirgudi	Vitex Nigundo	NAC
2	Mudra	Abutilan Indicum	MAC
3	Gliricidia	Gliricidia Sipium	GAC

3.1. Characteristics of the adsorbent

The physico-chemical properties of the prepared activated carbon were determined by standard methods (Table 2).

Table 2: Characteristics of adsorbents

Sr No	Properties	NAC	MAC	GAC
1	Density (g/cm ³)	0.4408	0.2092	0.3692
2	pH	6.8	7.1	6.8
3	Moisture content (%)	0.8	10.2	12.8
4	Ash Content (%)	6.4	10	11.7

3.2. Effect of contact time

Figure 1 showed the percentage removal of the Cu (II) metal ions by the NAC, MAC and GAC as adsorbent. The effect of contact time was studied in the range of 15, 30, 45, 60, 75, 90, and 120 min. It reveals that the Cu (II) metal ion present in the synthetic wastewater, there was a progression in the percentage removal of metal ion present in the synthetic wastewater with time on all

selected adsorbents. The results also showed that, the adsorption was fast at initial stage of contact period and after that near the equilibrium it became slower. Adsorptions reach equilibrium within 120 min for all selected adsorbent. From the result of the adsorption experiment Cu²⁺ ions had the highest percent removal of 98.63 at the end of 105 min by the NAC, followed by MAC and GAC with 98.61 and 98.46 respectively. These results are important, as equilibrium time is one of the important parameters in adsorption, and the time consumed for industrial wastewater disposal should be considered. The fast metal uptake by the adsorbent may be attributed to their highly porous and mesh structure, which provide a large surface area for the adsorption of Cu (II) onto the binding sites (Pankaj P et al. 2009). Thus for subsequent experiments, an equilibrium time of 120 minutes was chosen for the sake of convenience.

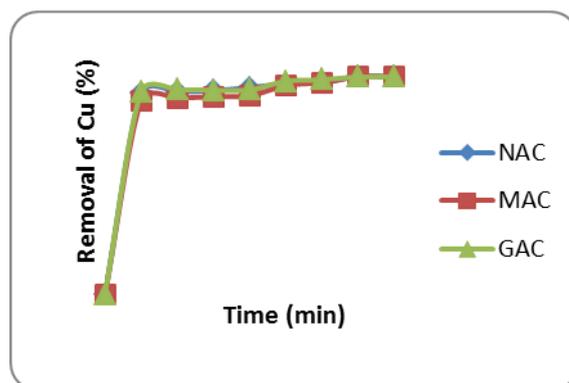


Fig. 1: Effect of contact time on the removal of copper by the NAC, MAC and GAC as adsorbent at 50 ppm, pH 7, 0.4 g/100ml adsorbent dose and particle size 45-180 micron.

3.3. Effect of particle size

Surface area of the adsorbent is an important parameter for adsorption. Exposure of adsorbent sites for solid metal ion interaction is high if the surface area of adsorbent is high¹². Hence to study this parameter batch adsorption studies were done by using three different particle sizes of NAC, MAC and GAC such as A= 500 -850, B= 180-500, C= 45-180 micron. The relationship between the size of the particles of the adsorbent and the copper metal ion removal percentage is illustrated in Fig 2.

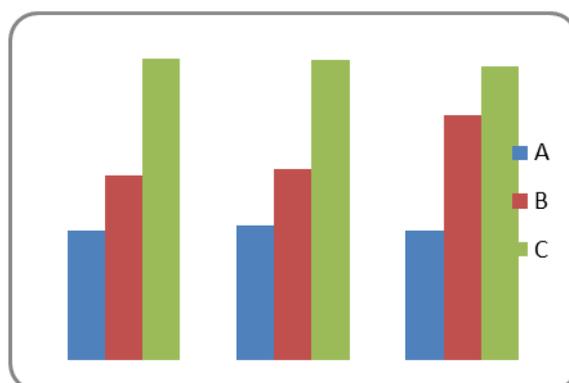


Fig. 2: Effect of particle size on the adsorption of Cu (II) ions (Initial concentration: 50 mg/ l, contact time: 120 min, pH: 7.0, temperature: 301 ± 1 K, adsorbent dosage: 0.4 g/100 ml, Particle size: A= 500 -850, B= 180-500, C= 45-180 micron).

Fig 2 indicates that the percentage Cu (II) ion removal has increased with the decrease in particle size. As the particle size is smaller, the surface area per unit weight of adsorbent is larger and consequently the higher percentage of metal removal is noted⁵. The maximum percentage of Cu (II) ions were removed by taking the adsorbent size of 45-180 micron. Hence for the entire study

NAC, MAC and GAC of 45-180 micron were used in order to produce effective adsorption process.

3.4. Effect of pH

The pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions. For this the role of hydrogen ion concentration was examined at different pH. The effect of initial pH on the extent of removal of Cu (II) ions by adsorption on NAC, MAC and GAC at 28°C is given in Fig.3. The adsorptions of Cu (II) ions on the adsorbents are found to be highly pH dependent. As pH increases, the extent of removal increases, reaches a maximum value and then decreases further increased up to optimum pH. The optimum pH for removal of Cu²⁺ ions is fixed as 7.0 for NAC and MAC. The optimum pH for removal of Cu²⁺ ions is 8 for GAC⁵. The neutral pH is found to be favorable. This suggests the Copper adsorption was very low at pH<2 and at pH>8.0, metal removal was due to precipitation caused when OH⁻ ions formed complex with copper (Mamatha et al. 2013).

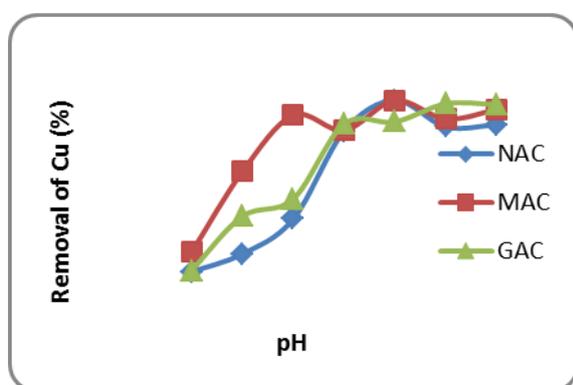


Fig. 3: Effect of pH on copper adsorption by NAC, MAC and GAC at an initial concentration of 50 ppm, 120 min, and 0.4 g/100 ml adsorbent dose

3.5. Effect of initial concentration of cu (II)

In batch adsorption processes, the initial metal ion concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the solution and solid phase. The effect of initial metal ion concentration ranging from 50-100 mg/l on NAC, MAC and GAC was studied by taking different concentrations of Cu (II) solutions at pH 7, while keeping the dosage of the adsorbent 0.4g/100 ml constant and temperature at 28 °C. The results are tabulated in Table 3.

Table 3: Effect of initial metal concentration on the adsorption of Cu (II) ion by NAC, MAC and GAC (contact time = 120 min, pH 7.0, temperature = 28 °C and adsorbent dosage = 0.4 g/100 ml, V =100 ml, Time: 120 mins W= 400 mg)

Ci	Ce			Qe			% of Cu removed		
	NAC	MAC	GAC	NAC	MAC	GAC	NAC	MAC	GAC
50	0.68	0.69	0.76	12.32	12.32	12.30	98.63	98.61	98.46
75	1.70	1.44	1.09	18.32	18.38	18.47	97.73	98.07	98.54
100	4.51	2.90	2.41	23.87	24.27	24.39	95.48	97.09	97.58

It is indicated from the Table 3 that the percent adsorption decreases with the increase of initial metal ion concentration. As a result of the above observations, it is indicated that the adsorption process of Cu (II) ions on NAC, MAC and GAC has to be dependent on concentration of the metal ion solution up to some extent.

3.6. Adsorption isotherms

The adsorption data was analyzed with the help of the Freundlich and Langmuir isotherms:

The Langmuir isotherm is represented by the following equation

$$(C_e/q_e) = (1/b Q_0) + (C_e/Q_0) \quad (1)$$

Where,

q_e = amount of dye adsorbed at equilibrium (mg/g),

C_e = equilibrium concentration of dye (mg/L),

Q_0 = Langmuir Constant related to adsorption efficiency (mg/g) and

b = Langmuir Constant related to energy of adsorption (L/mg) [4].

The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms (Figure 4-6) NAC, MAC and GAC respectively. The values of Q_0 and b were determined from the slope and intercept of the plots (Table 4). The high value of correlation coefficient r^2 from Table 4 indicates that the adsorption of Cu(II) ion by NAC, MAC and GAC follows Langmuir isotherm model. The Table 4 also gives information about the adsorption capacity (Q_0) and energy of adsorption b of NAC, MAC and GAC adsorbents.

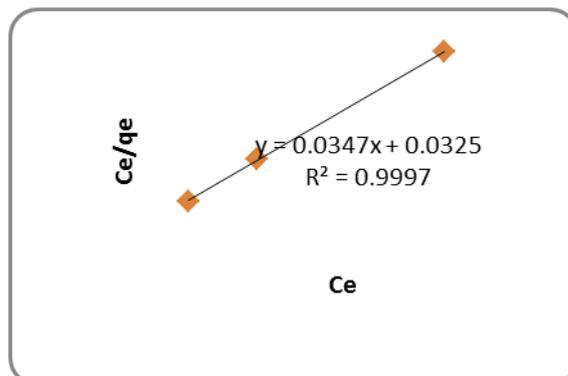


Fig. 4: Langmuir isotherm for removal of copper by NAC

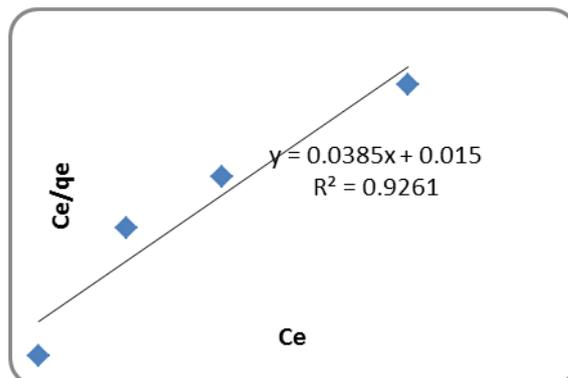


Fig. 5: Langmuir isotherm for removal of copper by MAC

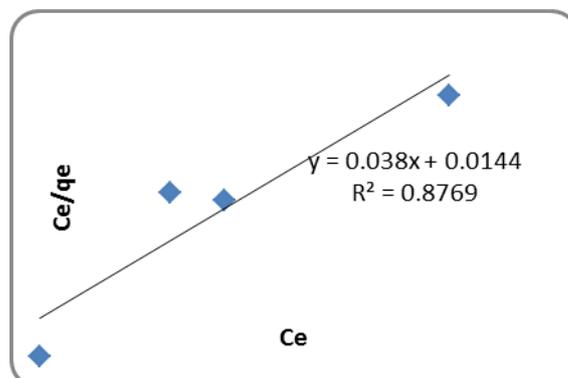


Fig. 6: Langmuir isotherm for removal of copper by GAC

To confirm favorability of the adsorption process, the separation factor (R_L) is calculated and presented in Table 4. The values are found to be between 0 and 1 and confirmed that the ongoing adsorption process is favorable.

$$R_L = 1 / (1 + bC_i) \quad (2)$$

Here, b is the Langmuir constant and C_i is the initial concentration of Cu (II).

The Freundlich isotherm is also employed for the adsorption of Cu (II) on the adsorbent. The Freundlich isotherm is represented by the following equation

$$\log q_e = \log k_f + (1/n) \log c_e \quad (3)$$

Here, q_e is the amount of Cu (II) adsorbed (mg/l), c_e is the equilibrium concentration of Cu (II) in the solution (mg/l) and k_f and n are constant incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. The plot of $\log q_e$ versus $\log c_e$ (Fig. 7-9) suggest that applicability of Freundlich isotherm for NAC, MAC and GAC. The values of k_f and n were determined from the slope and intercept of the plots (Table 4).

Table 4: Langmuir and Freundlich parameters of adsorption isotherms

adsorbents	Langmuir isotherm results				Freundlich isotherm results		
	Q ₀	b	r ²	R _L	K _f	1/n	r ²
NAC	29.4	1.062	0.99	0.0184	1.16	0.34	0.98
	1	5	9	7	0	8	2
MAC	35.7	0.777	0.99	0.0250	1.17	0.47	0.99
	1	8	9	6	3	3	2
GAC	61.6	0.426	0.93	0.0447	1.19	0.55	0.89
	6	7	4	7	1	3	6

From the Table (4), the Freundlich constant, $1/n$ denoting the intensity of adsorption indicates a favorable adsorption since $1/n < 1$. The adsorptions of Cu (II) ions onto NAC, MAC and GAC studied had been more favorable. The same result of R_L that is ($0 < R_L < 1$) for the adsorption of copper was investigated by Akai M Awwad (Awwad et al. 2012). The adsorption capacity (k_f) obtained for different adsorbents has been comparable, among them GAC shows highest value of adsorption capacity.

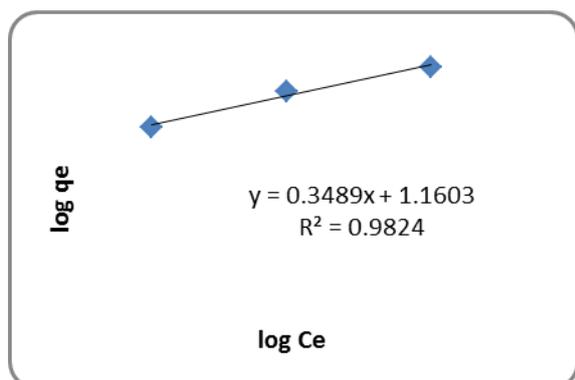


Fig. 7: Freundlich isotherm for removal of copper by NAC

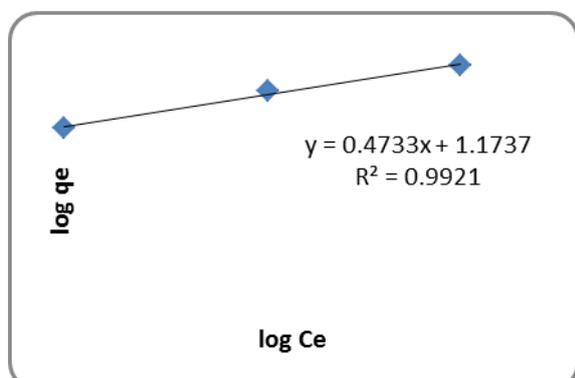


Fig. 8: Freundlich isotherm for removal of copper by MAC

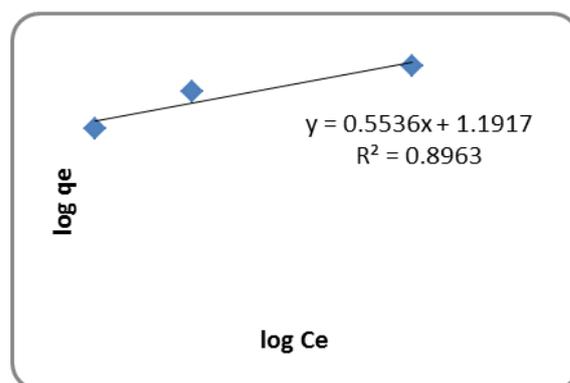


Fig. 9: Freundlich isotherm for removal of copper by GAC

4. Conclusion

This work clearly indicates the potential of using NAC, MAC and GAC as an excellent adsorbents for the removal of Cu (II) ions from aqueous solutions. The amount of Cu (II) ions adsorbed onto the NAC, MAC and GAC increased with an increase in pH. The optimum pH was found as pH 7 for the removal of Cu (II) ions by NAC and MAC while pH=8 for except GAC (pH= 8). The NAC, MAC and GAC of particle size 45-180 micron were identified to bring about maximum adsorption percentage of Cu (II) ions. The equilibrium data was analyzed for the Langmuir and Freundlich isotherm model. Among these two isotherms, Langmuir isotherm fitted well with the experimental data than Freundlich isotherm. This confirms the monolayer adsorption process. Taking into consideration of the above results, it can be concluded that the NAC, MAC and GAC were a suitable adsorbents for the removal of Cu (II) ions from aqueous solution in terms of low cost, natural and abundant availability.

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