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Optimization of Physio-chemical Conditions for Removal of Copper(II) Ions from Industrial Effluents Using Various Sorbents

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Removal of copper(II) ions from industrial effluents using different adsorbents such as activated carbon, brick kiln ash, tea waste, Ravi river sand and eggshells was studied to optimize the physicochemical conditions for maximum removal. The range of pH, temperature and concentration was so adjusted that it covers the physicochemical conditions of actual waste generated from industrial facilities. The initial and final concentration of copper was measured by atomic absorption spectroscopy. The residual concentration of copper in wastewater after adsorption was less than 1.0 mg/L, the released limit given in National Environment Quality Standards (NEQS). Maximum sorption (96–97%) of Cu(II) ions on activated carbon was achieved with (125 μm) particle size at 28°C temperature, pH 7. Under optimized conditions and temperature range of 301–315 K, ΔH, ΔS and $\Delta G_{301\ K}$ for 100 ppm solution are $-16.09 \pm .02$ to 85.46 ± 0.47 kJ/mol, -41.20 ± 0.07 to 246.93 ± 0.98 J/mol and -4.53 ± 0.62 to 11.26 ± 1.2 kJ/mol respectively and for 150 ppm solution the thermodynamic entities are $\Delta H = -10.78 \pm 0.09$ to 57.03 ± 0.62 kJ/mol, $\Delta S = -22.75 \pm 0.32$ to 162.99 ± 2.03 J/mol and $\Delta G_{301\ K} = -3.79 \pm 0.4$ to 8.15 ± 0.9 kJ/mol. Based on this study, the removal efficiency of various sorbents may be enhanced by optimizing certain specified physiochemical conditions.

Key Words: Physico-chemical conditions, Adsorption, Copper, Indigenous sorbents, Industrial release limit.

INTRODUCTION

The elements which have been identified from different effluents are heavy metals. Heavy metals are metallic elements, which have their atomic density greater than 6 g/cm^3. Heavy metals including chromium, copper, lead, nickel and zinc are either toxic themselves to biological organisms or induce deficiency in others. Considerable proportions of most heavy metal ions are toxic or carcinogenic and hence present a threat to human health and the environment when they are discharged into various water bodies. Copper being a heavy metal, is not biodegradable like other toxic pollutants and once in the environment, its potential toxicity is controlled by its physico-chemical form[1]. These elements when introduced into the soil are either dissolved in soil solution or leeched down with excess water or part of it is fixed temporarily or permanently on to soil colloidal complex. These elements which move downward through the soil contaminate the ground water which is often used for drinking purpose and may be injurious to humans and animals[2, 3].

Natural sources of copper exposure include windblown dust, volcanoes, decaying vegetation, forest fires and sea spray. Anthropogenic emissions include smelters, iron foundries, power stations and combustion sources such as municipal incinerators. The major release of copper to land is from tailings and overburdens from copper mines and sewage sludge. Agricultural use of copper products accounts for 2% of copper released to soil.

The lower limit of the acceptable range of oral intake (AROI) is 20 μg Cu/kg body weight per day. This figure is arrived at from the adult basal requirement with an allowance for variations in copper absorption, retention and storage. In infancy, this figure is 50 μg Cu/kg body weight per day. The upper limit of the AROI in adults is uncertain but it is most likely in the range of several but not many mg per day in adults (several meaning more than 2–3 mg/day). This evaluation is based solely on studies of gastrointestinal effects of copper contaminated drinking water. Physical conditions associated with copper imbalance in human beings include arthritis, fatigue, adrenal burnout, insomnia, scoliosis, osteoporosis, heart disease, cancer, migraine headaches, seizures, fungal and bacterial infections including yeast infection, gum disease, tooth decay, skin and hair problems and female organ conditions including uterine fibroids, endometriosis and others[4, 5].

There is need to treat the waste water to bring the concentration of toxic elements below the recommended release limit[6].

Adsorption is one of the methods commonly used to remove heavy metal ions from various aqueous solutions with relatively low metal ion concentrations. The efficiency of adsorption relies on the capability of the adsorbent to concentrate or adsorb metal ion from the solutions onto its surface. There are many types of adsorbents including activated carbon, oxide minerals, polymer fibres, resins and biosorbents that have been used to adsorb metal ions or to enrich trace amounts of metals from various aqueous solutions. Different naturally occurring adsorbents like activated carbon[7–10], tea waste[11], egg shells[12], mineral mixtures[13] and rice husk[14] are being used as adsorbents for industrial waste management.

EXPERIMENTAL

Adsorption material included brick kiln ash, river Ravi sand, egg shells and tea waste. Activated carbon (particle size 75 μm, M.B. value 25, Fe contents ≤ 0.05%, ash 5% and moisture 10%) was obtained from the local market. Brick kiln ash (collected from the vicinity of Lahore) was first treated with dilute HCl to remove soluble and leached impurities. It was then washed with distilled water to remove excess of HCl, washed brick kiln ash was air dried. The chemical composition of brick kiln ash was established by using analytical techniques and given in Table-1. Tea waste (supreme brand) was treated with H_2SO_4 to remove tannin and air dried. The tea waste mainly consists of carbon 48.60% wt/dm, hydrogen 5.50% wt/dm and nitrogen 0.50% wt/dm[15]. The brick kiln ash and tea waste in dried form is sieved into three size fractions using 35 (550 μm), 70 (225 μm) and 120 (125 μm) mesh sieves. Particle fractions were collected in polyethylene bags and stored. River Ravi sand was washed with dilute HCl then washed twice with distilled water and air dried. The composition of river Ravi sand was analyzed by using inductively couple plasma spectrometry (ICP) as given in Table-2. Egg shells [largely composed of calcium carbonate (about 94%) with small amount of magnesium carbonate, calcium phosphate and other organic matter including protein[16]] along with membrane were washed with water, air dried and ground powder, passed through 120 mesh sieve. All adsorbents were stored in polythene bags.

TABLE-1
CHEMICAL COMPOSITION OF
BRICK KILN ASH

Element	% age
Fe	34.0–41.0
MgO	6.3–11.5
Al	4.8–9.3
SiO_2	20.5–30
Zn	0.01–0.08
Ca	5.2–16.4

TABLE-2
CHEMICAL COMPOSITION
OF RIVER RAVI SAND

Oxides	Wt. (%)
SiO_2	83.361
Al_2O_3	5.301
CaO	4.369
Fe_2O_3	2.988
MgO	1.456
Na_2O	1.232
K_2O	1.101
MnO	0.053
ZnO	0.004

Samples of effluents from the various chemical industries situated in industrial area of Lahore (Punjab), expecting to release copper compounds in their wastewater, were collected and analyzed; it was observed that the average concentration of copper in these effluents was between 100–150 ppm. Therefore two samples (A) 100 ppm and (B) 150 ppm were prepared for copper to cover the observed concentration of copper present in actual industrial waste. Standard solution of 1000 ppm was prepared using extra pure $CuSO_4 \cdot 5H_4O$. From 1000 ppm standard solution different concentrations of copper sulphate solution were prepared by dilution.

An assembly of glass columns was used for the adsorption treatment. The dimensions of the column for samples was taken as: diameter 1.9 cm, bed height 24 cm, volume 68 cm^3.

The removal efficiency of adsorbents was checked by varying the particle size of adsorbents, pH of samples and temperature. For adsorption treatment the effluents were allowed to pass through the glass columns packed with suitable materials.

Adsorbents were carefully introduced from the top, continuous tapping ensured the uniform packing up to the desired level. The known volume of particular sample was then introduced at the top. The effluent was collected from the bottom in plastic bottles and again analyzed for the concentration of copper. The change in the concentration of copper after treatment was calculated by taking the difference between two concentrations. The concentration of copper in solutions was measured by atomic absorption using Varian (AA 1275) atomic absorption spectrophotometer equipped with hollow cathode lamps of copper.

The percentage sorption and distribution coefficient (K_d) was calculated using the following relationship:

$$(\% \text{ Sorption}) = [(C_i - C_t/C_i)] \times 100$$

$$K_d = C_i - C_t/C_i \times V/m = \text{cm}^3/\text{g}$$

where C_i is the initial concentration of the simulated solution and C_t the concentration of solution after treatment, V = volume of adsorbate (cm^3) and m = amount of adsorbent (g). The % sorption and the distribution coefficient can be correlated as:

$$(\% \text{ Sorption}) = 100\, K_d/(K_d + V/m)$$

RESULTS AND DISCUSSION

Table-3 shows the effect of particle size on the adsorption capacity of tea waste and brick kiln ash. Fine particles showed almost complete removal of the unwanted metals, as reported by[17, 18]. The removal efficiency of the particles is in the order: fine > medium > coarse. The fine particles provided maximum surface area for adsorption. The fine particles of 120 mesh of brick kiln ash provided excellent removal of copper as presented in Figs. 1 and 2.

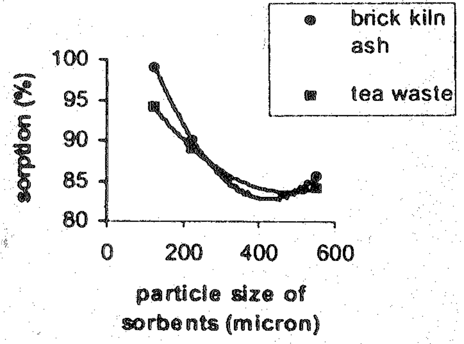

Fig. 1. Sorption of 100 ppm solution of Cu(II) ions on to sorbents

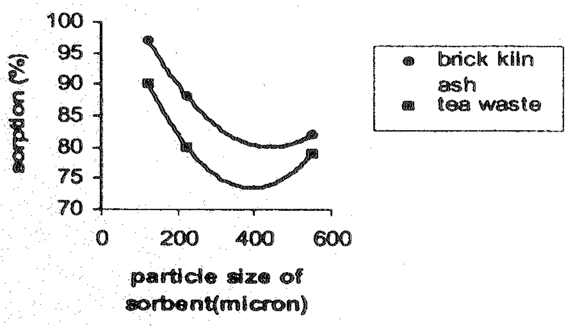

Fig. 2. Sorption of 150 ppm solution of Cu(II) ions on to sorbents

TABLE-3
EFFECT OF PARTICLE SIZE ON THE REMOVAL OF Cu(II) IONS

Adsorbing material (packed in 1.9 cm Φ × 24 cm column)	Concentration of Cu (ppm)	Cu removal (%) on mesh		
		35	70	120
Brick kiln ash	100	85.5	90.0	99.0
	150	80.0	88.0	97.0
Tea waste	100	84.0	89.0	94.0
	150	79.0	80.0	90.0

Table-4 explains the effect of temperature on adsorption of adsorbents (brick kiln ash, activated carbon, river Ravi sand, egg shells and tea waste), each sample solution with different temperature, *i.e.*, 28°, 32° and 42°C, was passed through the adsorbents. It was observed that the adsorption of copper increases with the decrease in temperature, as reported in literature[19, 20]. Low temperature gave maximum adsorption and adsorption increased in the order 28°C > 32°C > 40°C.

TABLE-4
EFFECT OF TEMPERATURE ON THE REMOVAL OF Cu(II) IONS

Adsorbing material (packed in 1.9 cm Φ × 24 cm column)	Concentration of Cu (ppm)	Cu removal (%)		
		28°C	32°C	42°C
Brick kiln ash	100	86.0	84.0	82.8
	150	83.0	81.7	80.0
Tea waste	100	90.0	86.0	81.0
	150	88.7	83.0	80.0
Activated carbon	100	98.9	98.7	95.0
	150	96.3	94.0	94.0
Egg shells	100	88.0	84.0	78.0
	150	85.7	80.0	76.5
River Ravi sand	100	87.5	77.5	75.0
	150	82.0	80.0	70.0

Tea waste, activated carbon and egg shells gave better adsorption for copper at low temperature as compared to kiln ash and river Ravi sand. Amongst these adsorbents activated carbon provided maximum adsorption for copper at low temperature (28°C). The values ΔH, ΔS were calculated from the slope and intercept of the linear Van't Hoff plot of log K_c *vs.* 1/T where $K_c = F/(1 - F)$ and T is absolute temperature in kelvin and F represents the fraction sorbed at equilibrium; a straight line with correlation factor of 0.94–0.99 was obtained (Figs. 3–12). The values of ΔH and ΔS were computed using the relations:

$$\log K_c = -\Delta H/2.303\ RT + \Delta S/2.303R$$

The free energy of adsorption ΔG was calculated using equation

$$\Delta G = -RT \ln K_c$$

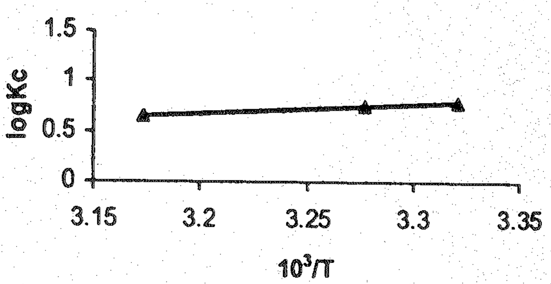

Fig. 3. Sorption of 100 ppm solution of Cu(II) ions on to brick kiln ash

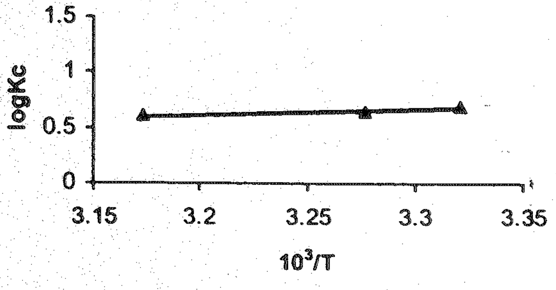

Fig. 4. Sorption of 150 ppm solution of Cu(II) ions on to brick kiln ash

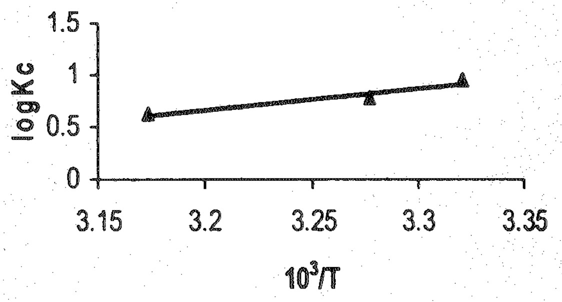

Fig. 5. Sorption of 100 ppm solution of Cu(II) ions on to tea waste

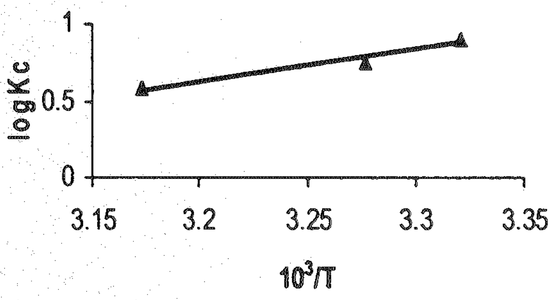

Fig. 6. Sorption of 150 ppm solution of Cu(II) ions on to tea waste

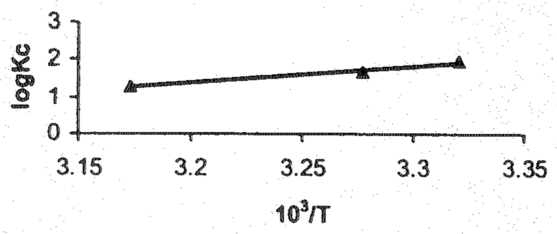

Fig. 7. Sorption of 100 ppm solution of Cu(II) ions on to activated carbon

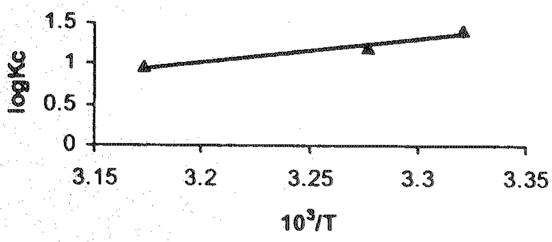

Fig. 8. Sorption of 150 ppm solution of Cu(II) ions on to activated carbon

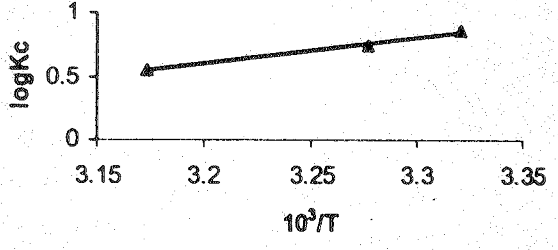

Fig. 9. Sorption of 100 ppm solution of Cu(II) ions on to egg shells

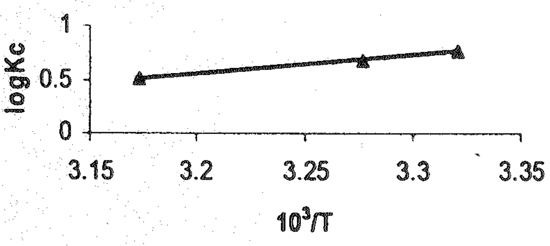

Fig. 10. Sorption of 150 ppm solution of Cu(II) ions on to egg shells

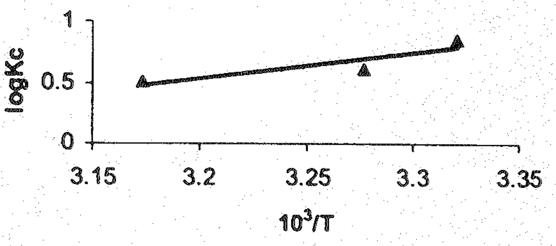

Fig. 11. Sorption of 100 ppm solution of Cu(II) ions on to river Ravi sand

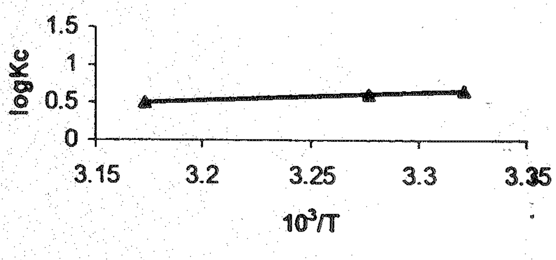

Fig. 12. Sorption of 150 ppm solution of Cu(II) ions on to river Ravi sand

The slope and intercept of Fig. 3–12 gave thermodynamic entities for 100 ppm and 150 ppm solution. The values of thermodynamic entities are given in Table-5.

The negative enthalpy and negative free energy reflect the exothermic and spontaneous nature of sorption respectively.

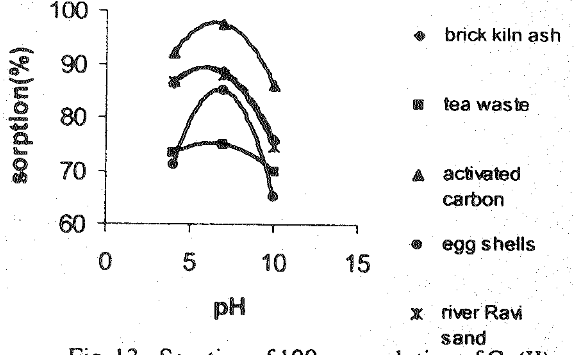

Fig. 13. Sorption of 100 ppm solution of Cu(II) ions on to sorbents

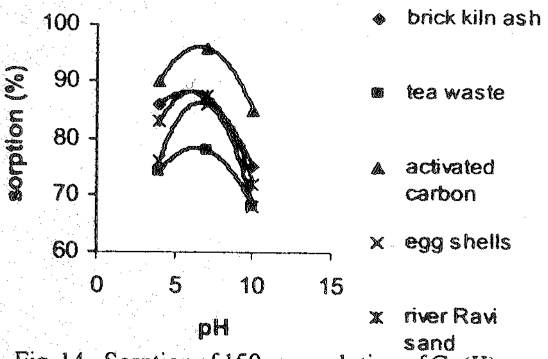

Fig. 14. Sorption of 150 ppm solution of Cu(II) ions on to sorbents

TABLE-5
THERMODYNAMIC QUANTITIES FOR ADSORPTION OF Cu(II) IONS

Adsorbing material (packed in 1.9 cm Φ × 24 cm column)	Concentration of Cu (ppm)	Thermodynamic quantities		
		ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Brick kiln ash	100	–16.09 ± 0.02	–41.20 ± 0.07	–4.53 ± 0.62
	150	–10.78 ± 0.09	–22.75 ± 0.32	–3.95 ± 0.83
Tea waste	100	–39.77 ± 0.51	–114.38 ± 1.69	–5.50 ± 0.9
	150	–39.87 ± 0.35	–115.68 ± 1.14	–5.15 ± 0.7
Activated carbon	100	–85.46 ± 0.47	–246.93 ± 0.98	–11.26 ± 1.2
	150	–57.03 ± 0.62	–162.99 ± 2.03	–8.15 ± 0.9
Egg shells	100	–40.34 ± 0.13	–117.54 ± 0.45	–4.98 ± 0.6
	150	–33.94 ± 0.10	–97.92 ± 0.33	–4.48 ± 0.5
River Ravi sand	100	–40.43 ± 0.94	–119.15 ± 3.08	–4.87 ± 0.6
	150	–20.17 ± 0.07	–54.44 ± 0.23	–3.79 ± 0.4

Table-6 shows the effect of pH of sample on adsorption. Three different samples were prepared with different pH values which are as, 4, 7, and 10 using buffer solutions of acetic acid/sodium acetate and ammonium hydroxide/ammonium chloride respectively. The removal of copper by adsorbents is highly dependent on the pH of the solution which affects the surface charge of the adsorbents, degree of ionization and speciation of the adsorbates. Three different samples were passed through columns filled with adsorbents (brick kiln ash, tea waste, activated carbon, egg shells and river Ravi sand). Change in adsorption efficiency with change in pH of samples is found to be significant. All adsorbents showed maximum adsorption[21–25] efficiently at pH 7. In acidic or basic solutions the adsorption was less as compared to that in neutral solution. So at pH 7 comparatively more activated carbon proved to be the best adsorbent for removal of copper. River Ravi sand and brick kiln ash were of the same efficiency. Tea waste and egg shells were of poor efficiency.

TABLE-6
EFFECT OF pH ON THE REMOVAL OF Cu(II) IONS

Adsorbing material (packed in 1.9 cm Φ × 24 cm column)	Concentration of Cu (ppm)	Cu removal (%) at pH		
		7	4	10
Brick kiln ash	100	88.5	86.2	76.0
	150	87.0	86.0	75.0
Tea waste	100	75.0	73.7	70.0
	150	78.0	74.0	68.0
Activated carbon	100	97.5	92.0	86.0
	150	96.0	90.0	85.0
Egg shells	100	85.0	71.2	65.0
	150	76.0	86.0	68.0
River Ravi sand	100	88.0	86.7	74.5
	150	87.5	83.0	72.0

The results of copper concentration dependence study on adsorbents were also subjected to analysis in terms of Langmuir and Freundlich adsorption isotherms. The data do not fit for Langmuir equation. However, Freundlich adsorption isotherm was capable of describing the data over the concentration range studied. The Freundlich isotherm was tested in the following linearized form:

$$\log C_{ads} = \log A + 1/n \log C_e$$

where C_{ads} = Amount of copper ions adsorbed at equilibrium (mol/g)

C_e = Equilibrium concentration of copper in the solution (mol/L)

A and 1/n = Freundlich constant

Almost all this adsorptive separation process depends on physical adsorption rather than chemisorption and this therefore is the focus of the present review. The heat of adsorption provides a direct measure of the strength of the bonding between sorbate and surface. Physical adsorption from the liquid phase is invariably exothermic, although there are very small heat changes, as may be shown by a simple thermodynamic argument. Since the adsorbed molecule has at most two degrees of translational freedom on the surface and since the rotational freedom of the adsorbed species must always be less than that of the liquid phase molecule, the entropy change on adsorption $\Delta S = S_{ads} - S_{gas}$ is necessarily negative. In order for significant adsorption to occur, the free energy change on adsorption, ΔG, must also be negative and since $\Delta G = \Delta H - T\,\Delta S$, this requires ΔH negative or exothermic adsorption. Therefore maximum sorption at low temperature (28°C) is exactly according to this theory.

Conclusion

Activated carbon proved to be an excellent adsorbent for adsorption of copper from aqueous solutions. The maximum adsorption can be obtained by using particle size of 120 mesh and adopting physico-chemical conditions of temperature at 28°C in neutral media (pH 7).

The negative value of ΔH and negative value of ΔG show the exothermic and spontaneous nature of sorption respectively. The maximum sorption at 28°C also supports the exothermic nature of sorption. The lower sorption at higher acidic concentrations and lower pH values may be due to the competition between the positively charged Cu^{2+} and H^+. The lower sorption at higher pH might be due to the surface complexation phenomenon, which is facilitated by the dissociation of surface functional groups.

A comparative experimental data obtained in this study reveals that activated carbon may be employed for the removal of copper from aqueous industrial effluents before discharging them into water bodies. Recyclization of used activated carbon may be achieved under certain conditions.

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