

## Effective removal of $\text{Cu}^{2+}$ ions from polluted water using new bio-adsorbents

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### Abstract

Sorbents derived from stem powders of *Feronia limonia* (FLSP), *Amorphophallus paeoniifolius* (APSP) and *Pumpkin* (*Cucurbitapepo*) (PSP) plants are investigated for the removal of  $\text{Cu}^{2+}$  ions from polluted water by adopting batch methods of extraction. Extraction conditions are optimized for the effective removal of  $\text{Cu}^{2+}$  ions. High sorption capacities are observed: 175.5 mg/g for FLSP; 140.4 mg/g for APSP; 130.0 mg/g for PSP. Effective pH ranges are: 5 to 10 for FLSP; 6 to 10 for APSP and 7 to 10 for PSP. The three spent adsorbents can be regenerated and used. Thermodynamic parameters indicate that the adsorption process is spontaneous, endothermic and have positive change in entropy values. As  $\Delta H$  values are more than 25.0 kJ/mole, the adsorption may be due to surface complex formation between  $\text{Cu}^{2+}$  ions and functional groups of the adsorbents viz., -OH, -COOH etc. in the effective pH ranges. The good adsorption behaviour of FLSP even in acidic pHs may be due to the ion-exchange of  $\text{Cu}^{2+}$  ions for  $\text{H}^+$  ions of the functional groups of the adsorbent. The Langmuir adsorption isotherm and pseudo second-order model describe well the adsorption process. The sorbents are effectively applied to treat effluents from Cu-based industries and polluted lake water.

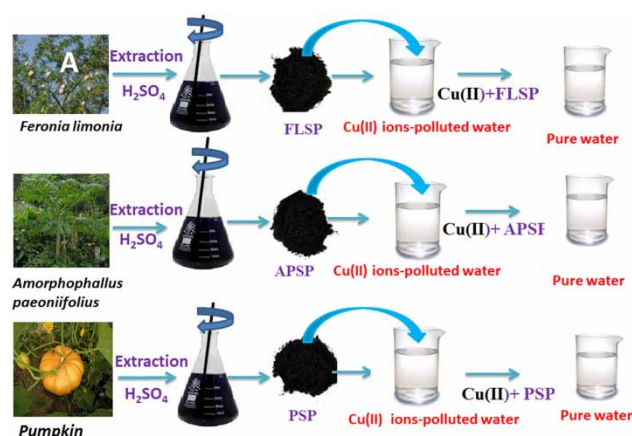
**Key words:** *Amorphophallus paeoniifolius*, applications,  $\text{Cu}^{2+}$  removal, bio-sorbents, *Feronia limonia*, *Pumpkin* (*Cucurbitapepo*)

### Highlights

- Stem powders of *Feronia limonia* (FLSP), *Amorphophallus paeoniifolius* (APSP) and *Pumpkin* (PSP) are identified for their strong affinity for  $\text{Cu}^{2+}$ .
- Sorbents derived from them show high sorption capacities for  $\text{Cu}^{2+}$ .
- Sorbents are effective in a wide pH range.
- Adsorption nature is analyzed by thermodynamic, adsorption isotherms and kinetic models.
- The adsorbents are successfully applied to treat Cu-polluted water.

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## Graphical Abstract



## INTRODUCTION

The detrimental effects of the contamination of water bodies with copper ions are well known (APHA 1998; Aydin *et al.* 2008). Intake of water containing copper ions causes many health ailments such as malfunctioning of the liver, gastroenterological problems, neurological problems, and so on. Even traces of copper ions in water bodies are objectionable as the copper ions undergo bio-amplification with lapse of time and eventually, the concentration reaches objectionable levels (APHA 1998; Aydin *et al.* 2008; Nassef & El-Tawee 2015; Al-Saydeh *et al.* 2017; Devi *et al.* 2019). Such enrichment of concentrations causes stress on aquatic life and as a result, eco-systems are disturbed (APHA 1998; Nassef & El-Tawee 2015). The maximum permissible limit of copper ions in water as per WHO is 2.0 mg/L (APHA 1998).

The discharges of un-treated or ill-treated effluents from copper-based industries are the main sources of water contamination (Nassef & El-Tawee 2015; Al-Saydeh *et al.* 2017). Further, the over use of Copper sulphate as fungicide in agricultural fields also contributes to the contamination of copper ions in water bodies near to the agricultural fields.

Hence, treatment of water or effluents from copper-based industries for the removal of copper ions assumes importance. Many procedures based on membrane filtration (Al-Saydeh *et al.* 2017), cementation (Ahmed *et al.* 2011; Gros *et al.* 2011), electro-dialysis (Caprarescu *et al.* 2015; Dong *et al.* 2017), photocatalysis (Satyro *et al.* 2014; Kanakaraju *et al.* 2017), electro-flotation (Nawel *et al.* 2018), and reverse osmosis (Al-Saydeh *et al.* 2017) are developed for the control of copper ions in polluted water/ industrial effluents. These methods produce good quality water but suffer from the fact that they are non-economical and need technical expertise to monitor the process.

In this context, adsorption methods based on adsorbents derived from biota are interesting to the researchers. These methods are simple, effective and eco-friendly. Further, the precursors used to generate the adsorbents are renewable plant materials. Active carbons of peanut hull (Zhu *et al.* 2009), *Phaseolus aureus* hulls (Rao *et al.* 2009) and *Ceiba pentandra* hulls (Madhava Rao *et al.* 2006) are investigated as adsorbents.

Bio-materials of vegetables (Myalowenkosi *et al.* 2019), *Limonia acidissima* plant barks (Devi *et al.* 2019), rice husk (Yahaya *et al.* 2011), *Hibiscus cannabinus* plant stems (Devi *et al.* 2019), potato and banana peels (Taralgatti 2016), sugar beet pulp (Aksuand & Alper Işoglu 2005), green algae (Gupta *et al.* 2006), wheat bran-dehydrated (Ozer & Ozer 2004) and coffee waste (Lovell Odili *et al.* 2016) are used as adsorbents for the removal of copper ions from water. Treated fly ash (Wang *et al.* 2006; Alinnor 2007), clay (Vengris *et al.* 2001), eggshells (Ahmad *et al.* 2012), chitosan-based adsorbent (Cao *et al.* 2001; Prakash & Arungalai Vendan 2016) are also investigated as adsorbents.

An effective review describing various methods of treating water for remediation of copper ions is reported (Al-Saydeh *et al.* 2017). In spite of these, intensive investigations are being pursued to develop simple, cost effective and eco-friendly methods for the removal of copper ions from polluted water using sorbents derived from bio-materials.

Copper exists in its stable divalent oxidation state in water. The speciation of divalent copper depends upon pH of water/polluted water. Below pH 3, copper exists as  $\text{Cu}^{2+}$  ions. Above pH:3, hydroxo species,  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}(\text{OH})_2$ ,  $[\text{Cu}(\text{OH})_3]^-$  &  $[\text{Cu}(\text{OH})_4]^{2-}$ , are formed (Cuppert *et al.* 2006; Albert Cotton *et al.* 2007). These hydroxo species as well as  $\text{Cu}^{2+}$  ions have a tendency to form surface complexes with the functional groups of the bio-adsorbents. Further, the redox potentials of  $\text{Cu}^{2+}/\text{Cu}^+$ :0.153 V and  $\text{Cu}^{2+}/\text{Cu}$ : 0.337 V (Vogel 1961) permit some naturally available functional groups to reduce  $\text{Cu}^{2+}$  to  $\text{Cu}^+/\text{Cu}$  (Sujitha & Ravindhranath 2017). The lower oxidation states of copper are insoluble in water and thereby enhance the removal of copper ions from water. Thus, by evoking the complex nature of  $\text{Cu}^{2+}$  ions and/or causing reduction of  $\text{Cu}^{2+}$  ions to  $\text{Cu}^+/\text{Cu}$ , the removal of copper ions from water may be aimed. The present work is in this direction.

## MATERIALS AND METHODS

Various plant materials were investigated for their affinity towards  $\text{Cu}^{2+}$  ions. It was observed that stem powders of *Feronia limonia*, *Amorphophallus paeoniifolius* and *Pumpkin (Cucurbitapepo)* plants had affinity for  $\text{Cu}^{2+}$  ions. The present investigation pertains to use these materials as adsorbents for the removal of  $\text{Cu}^{2+}$  ions from polluted waters.

### Chemicals

All chemicals used in this work (Copper Sulphate, HCl, NaOH) of A.R. quality were purchased from Merck. India Pvt. Ltd. Throughout the experiment, double distilled water was used. The standard solutions and reagents were prepared as described in the literature (APHA 1998).

### Adsorbents

#### Plants

*Feronia limonia* plant is known as the wood apple plant; it belongs to the family *Rutaceae* in the plant kingdom and it grows well in India. Fruits of this plant are called 'poor man food' and the bio-materials of this plant are used in the treatment of liver and cardiac problems and diarrhoea. *Amorphophallus paeoniifolius* is known as *elephant foot yam* plant, which grows well in Africa and South Asia. It belongs to the *Araceaeacead* family of the plant kingdom. The fruit of this plant is grown in soils; it is a popular vegetable food and is used in various cuisines' items. *Pumpkin (Cucurbitapepo)* is an old domestic plant that is widely grown in many parts of the world. Its fruit has a thick shell containing pulp and seeds. The fruit is used in making many varieties of vegetable curries.

### Preparation of adsorbents

Stems of *Feronia limonia*, *Amorphophallus paeoniifolius* and *Pumpkin (Cucurbitapepo)* plants were cut, washed with distilled water and dried in hot air at 105 °C for four hours. The dried materials were crushed to powder. The powdered particles were sieved to pass through 75  $\mu\text{m}$  (ASTM) mesh. The obtained adsorbents were preserved in brown bottles. The prepared stem powders of *Feronia limonia*, *Amorphophallus paeoniifolius* and *Pumpkin* plants were named FLSP, APSP and PSP respectively. These were used in the present investigations.

## Adsorption experiment

Batch modes of extractions were employed (Trivedy 1995; Metcalf & Eddy 2003; Sujitha & Ravindhranath 2018a, 2018b) using simulated  $\text{Cu}^{2+}$  solutions of different known concentrations. General procedure: known amounts of FLSP, APSP or PSP were added to 100 ml  $\text{Cu}^{2+}$  solution taken in 250 ml stoppered iodine flasks. Initial pHs of solutions were adjusted to desired values using dil HCl/NaOH. The flasks were placed in mechanical shakers and agitated at 350 rpm for the desired period. The solution was filtered through G3 crucibles and assayed for residual  $\text{Cu}^{2+}$  content by the AAS method as described in the literature (APHA 1998). AA 500 instrument with features: flame absorption; slit: 0.4; fuel flow rate: 1,200 (mL/min); lamp current: 5.0 amp; high voltage: 416.25 V wavelength: 217.00 nm, was used.

Percentage removal of copper ions and adsorption capacities of adsorbents ( $q_e$ ) were calculated by using the following equations.

$$\% \text{removal} = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

where  $m$  = mass of adsorbent (g);  $V$  = volume of the solution (L);  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of copper ions.

The effect of various parameters, viz., pH, dosage of FLSP, APSP or PSP, initial  $\text{Cu}^{2+}$  ions concentration and agitation time, on the percentage removal of  $\text{Cu}^{2+}$  ions were investigated and optimized. The adsorption experiment with the present adsorbents was studied by varying the pH of the agitating solution in the range 2–10, dosage of the adsorbents from 0.25 g to 3.00 g/L, initial  $\text{Cu}^{2+}$  ions concentration from 5 to 50 mg/L, contact time from 15 to 120 min, and optimized. In these investigations, the aimed parameter was varied while maintaining all other parameters at optimum levels.

Interference caused by naturally existing co-ions was also investigated by conducting extraction experiments for  $\text{Cu}^{2+}$  ions in the presence of a two-fold excess of co-ions. The effect of interference was studied in the presence of co-cations, namely:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and in the presence of co-anions, namely: sulphate, nitrate, phosphate, chloride, fluoride, bicarbonate. The effect of solution temperature on the extraction of  $\text{Cu}^{2+}$  ions was also investigated at 303, 313 and 323 K. Adsorption isotherms and kinetics were studied. The results are presented in Figures 1–11 and Tables 1 and 2. Regeneration of spent adsorbents was also investigated. The results are presented in Figure 12. The applicability of these adsorbents was investigated by treating samples collected from the effluents of copper-based industries and also lakes polluted due to excessive use of copper salts in intensive agricultural cultivation. The results are presented in Table 3.

## RESULTS AND DISCUSSION

### Effect of various physicochemical factors on adsorption

#### Solution pH effect

The pH of the agitating solution was found to influence the adsorption of  $\text{Cu}^{2+}$  ions (Figure 2). A maximum % removal of 91.0% at pH:5 for FLSP; 86.0% at pH:6 for APSP and 80.0% at pH:7 for PSP was observed. The results are presented in Figure 1. These are important findings because this study facilitates the application of FLSP, APSP and PSP adsorbents for treating a variety of effluents with varied pHs 2 to 10.

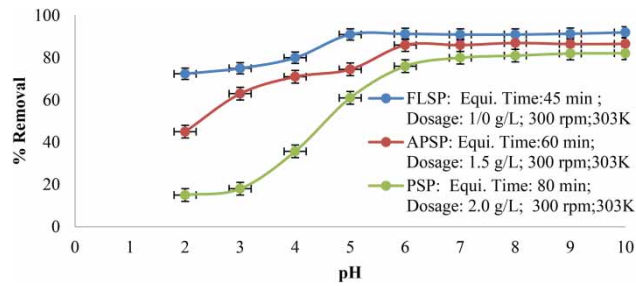


Figure 1 | Effect of pH on % removal of Cu<sup>2+</sup> ions.

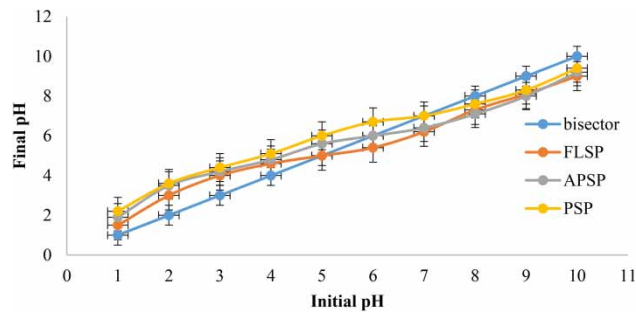


Figure 2 | Evaluation of pH<sub>PZC</sub> for FLSP, APSP and PSP.

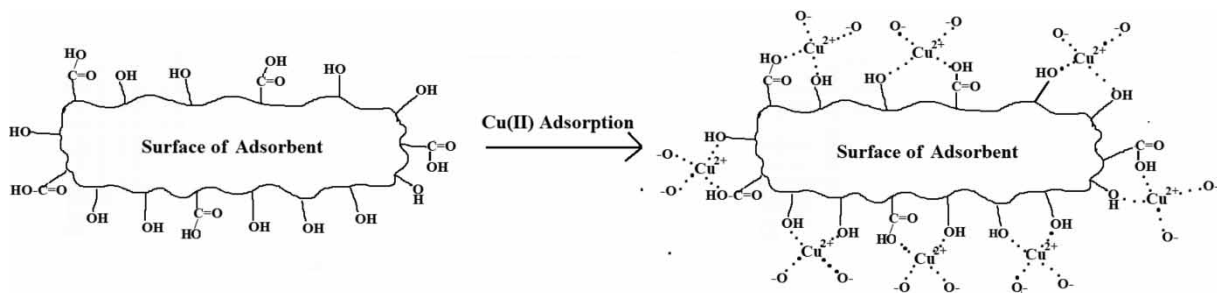


Figure 3 | Mechanism for the adsorption of Cu<sup>2+</sup> ions on to the surface of adsorbents.

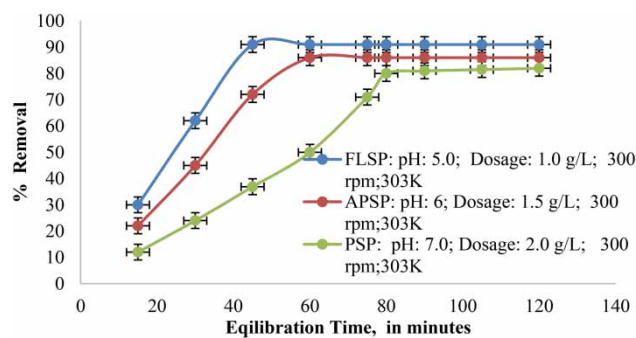
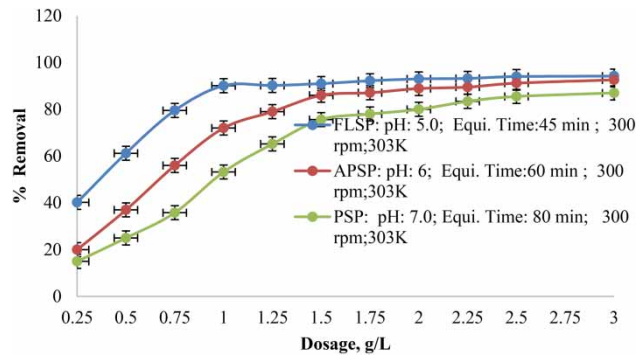


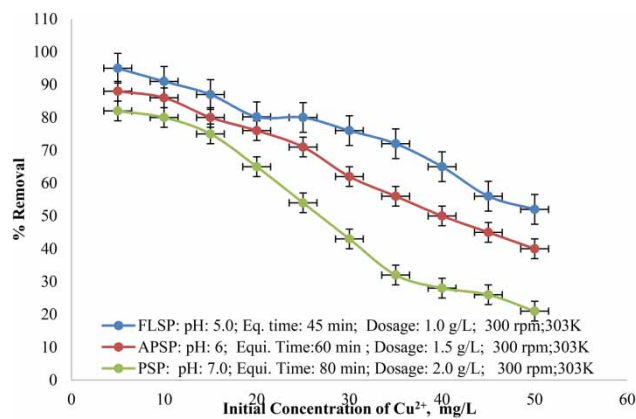
Figure 4 | Effect of equilibration time on % removal of Cu<sup>2+</sup> ions.

pH<sub>PZC</sub> values for the three adsorbents were evaluated and found to be: 5.0 for FESP; 6.0 for APSP and 7.0 for PSP (Figure 2). At these pHs, the said adsorbents' surfaces are neutral and above these values, the surfaces are negatively charged due to dissociation of functional groups and at lower

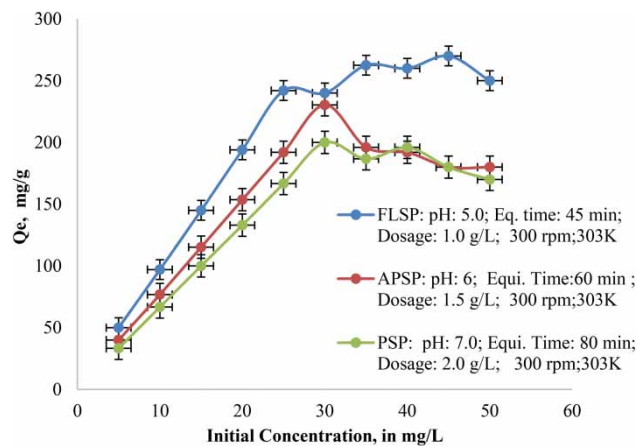




**Figure 5** | Effect of adsorbent dosage on % removal of  $\text{Cu}^{2+}$  ions.



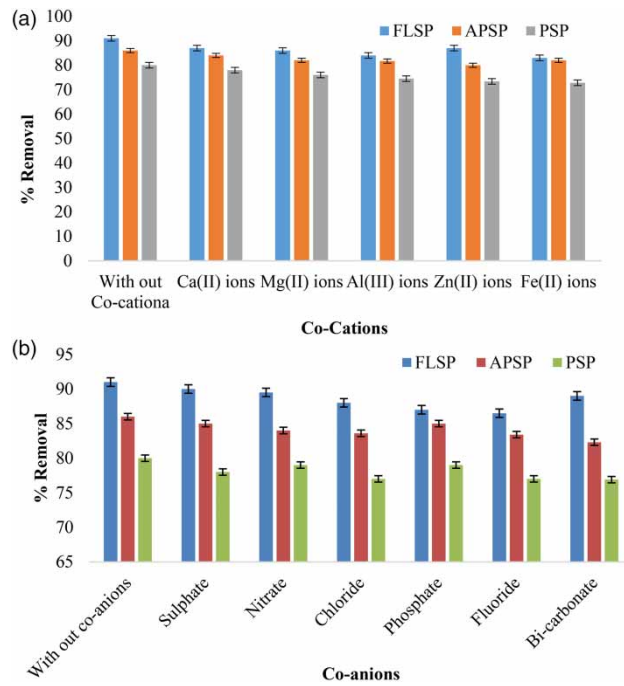
**Figure 6** | Effect of initial concentration on % removal of  $\text{Cu}^{2+}$  ions.



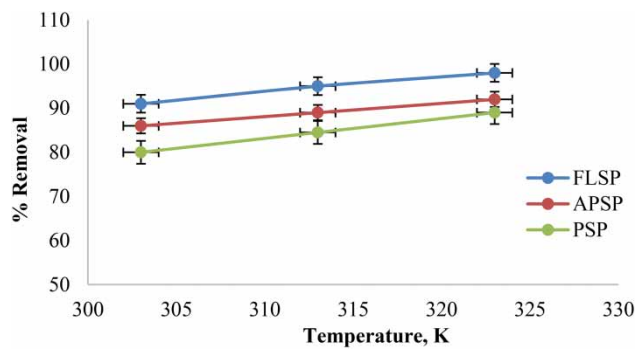
**Figure 7** | Effect of initial concentration on adsorption capacities,  $q_e$ , of adsorbents.

pHs, the surface of the adsorbents is positively charged due to protonation (Suneetha *et al.* 2015a; Krishna Mohan *et al.* 2019). The speciation of  $\text{Cu(II)}$  ions are:  $\text{Cu}^{2+}$ - below pH:3;  $\text{Cu(OH)}^+$ - between 3 and 6;  $\text{Cu(OH)}_2$  -between 6 to 11; and  $[\text{Cu(OH)}_3]^-$  and  $[\text{Cu(OH)}_4]^{2-}$  - above 11 (Cuppert *et al.* 2006; Cotton *et al.* 2007).

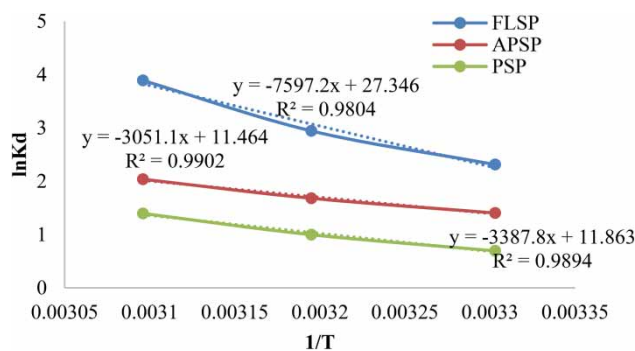
The adsorptions were lower at pHs below 5.0 for FESP, 6.0 for APSP and 7.0 for PSP. At lower pH values, there is a competition between  $\text{H}^+$  ions and  $\text{Cu}^{2+}$  ions for the active sites on the surface of the



**Figure 8** | (a) Effect of co-cations on % removal of Cu<sup>2+</sup> ions. (b) Effect of co-anions on % removal of Cu<sup>2+</sup> ions.

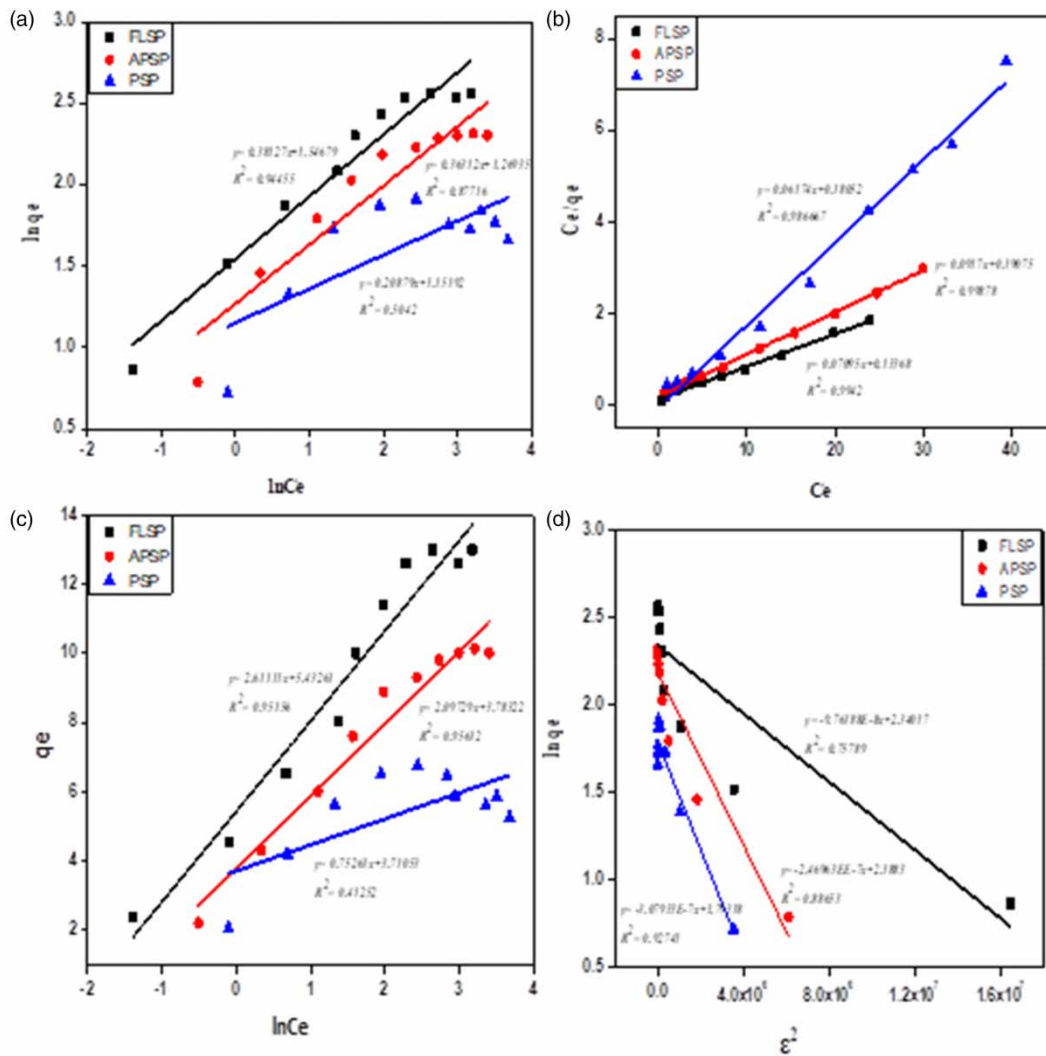


**Figure 9** | Effect of solution temperature on % removal of Cu<sup>2+</sup> ions.



**Figure 10** | Van't Hoff plot.

adsorbent and this electrostatic repulsion decreases the adsorption of Cu<sup>2+</sup> ions onto the adsorbent's surface (Zujin *et al.* 2019). The maximum adsorption at these pH<sub>PZC</sub> values when the surface is neutral is due to the decrease in protonation and hence, the adsorption of Cu<sup>2+</sup> ions onto the surface of



**Figure 11** | Application of various adsorption isotherm models: (a) Freundlich; (b) Langmuir; (c) Temkin; (d) Dubinin-Radushkevich.

**Table 1** | Evaluated thermodynamic parameters for  $\text{Cu}^{2+}$  adsorption 'onto' FLSP, APSP and PSP

Adsorbent	$\Delta H$ (KJ/mole)	$\Delta S$ (J/mole)	$\Delta G$ (KJ/mole)			$R^2$
			303 K	313 K	323 K	
FLSP	63.166	227.37	-5.7265	-8.001	-10.3240	0.9804
APSP	25.368	95.32	-3.5140	-4.4672	-5.4204	0.9902
PSP	28.168	98.635	-1.7185	-2.705	-3.69	0.9894

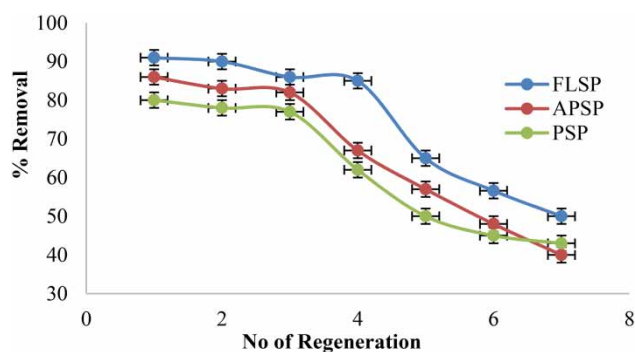
adsorbents increases due to a sort of complex formation between the surface groups of the adsorbents and hydrated copper ions (Zujin *et al.* 2019), Figure 3.

The free hydrated  $\text{Cu}^{2+}$  ions in aqueous solution are adsorbed by the fibrous adsorbent. The extent of adsorption depends on the pH of the solution. The adsorption mechanism is as shown in Figure 3. Each  $\text{Cu}^{2+}$  ion is coordinated with four oxygen atoms and the copper ion is in square-planar configuration. The  $-\text{OH}/-\text{COOH}$  groups on the adsorbent are well situated to form a five-membered chelating structure. This is a three-dimensional lattice of  $\text{Cu}^{2+}$ -bridging structure (Norkus *et al.* 2002). In basic solutions, the insoluble aggregates of  $\text{Cu}(\text{II})$ -hydroxyl species are formed, resulting in high  $\text{Cu}^{2+}$  removal (Zujin *et al.* 2019).



**Table 2** | (A) Evaluated parameters of various adsorption Isotherms for the  $\text{Cu}^{2+}$  adsorption 'onto' FLSP, APSP and PSP.  
(B) Kinetics of adsorption

(A)					
Adsorbents	Parameters	Freundlich isotherm	Langmuir isotherm	Temkin isotherm	Dubinin-Radushkevich isotherm
FLSP	Slope	0.38127	0.06174	2.61111	$-9.8 \times 10^{-8}$
	Intercept	1.54679	0.18052	5.43261	2.34017
	$R^2$	0.94445	0.986667	0.95156	0.75789
	$R_L/1/n/B/E$	$1/n = 0.381$	$R_L = 3.1$	$B = 2.61$	$E = 1.6$
APSP	Slope	0.36312	0.19075	2.09729	$-2.5 \times 10^{-7}$
	Intercept	1.26935	0.0917	3.78322	2.1883
	$R^2$	0.87716	0.99878	0.95612	0.88683
	$R_L/1/n/B/E$	$1/n = 0.363$	$R_L = 1.13$	$B = 2.09729$	$E = 0.9$
PSP	Slope	0.20879	0.07095	0.75261	$-3.1 \times 10^{-7}$
	Intercept	1.15192	0.13368	3.71053	1.79318
	$R^2$	0.5042	0.9942	0.41252	0.92741
	$R_L/1/n/B/E$	$1/n = 0.208$	$R_L = 0.7$	$B = 0.7526$	$0.7$
(B)					
Adsorbents	Parameters	Pseudo 1st order	Pseudo 2nd order	Elovich	Bangham's pore diffusion
FLSP	$R^2$	0.8211	0.9839	0.77858	0.7454
APSP	$R^2$	0.8684	0.9718	0.82913	0.84447
PSP	$R^2$	0.89465	0.9867	0.87942	0.86834

**Figure 12** | Regeneration of spent adsorbents

### Contact time

The time of contact between adsorbents and  $\text{Cu}^{2+}$  ions solution was investigated and the findings are presented in Figure 4.

Copper removal was linearly increased with the progress of time initially. The increase in adsorption rate is due to the greater attraction of copper ions towards the surface active sites of the adsorbent (Al Moharbi *et al.* 2020). But after a certain time, a steady state was observed. The steady state was reached after 45 min for FESP and percentage removal was observed as 91% at that time and even after 100 min also have the same percentage removal. Similarly, 86% at 60 min for APSP and 80% at 80 min for PSP also have the same percentage removals even after 100 min.

Initially, many surface active sites were available for adsorption but with progress of time, they were used up by the copper ions. As the dosage of adsorbents was fixed, steady state was resulted when all active sites were saturated with the adsorption of copper ions. A similar trend was reported in the literature for the adsorbent derived from stems of Senna Occidentalis plant. The maximum percentage removal was 87.3% at 50 min and no noticeable change (steady-state) was observed even after 90 min (87.8%) (Suneetha *et al.* 2015b).

**Table 3** | Applications

Adsorbents									
Samples	FLSP* (pH:5; Equi. Time: 45 min; Dosage: 1.0 g/L; 300 rpm; 303 K)			APSP* (pH:6; Equi. Time: 60 min; Dosage: 1.5 g/L; 300 rpm; 303 K)			PSP* (pH:7; Equi. Time: 80 min; Dosage: 2.0 g/L; 300 rpm; 303 K)		
<b>1. Effluent samples from industries</b>									
	Copper ions Concentration			Copper ions Concentration			Copper ions Concentration		
	Ci mg/L	Ce mg/L	Percentage of extraction	Ci mg/L	Ce mg/L	Percentage of extraction	Ci mg/L	Ce mg/L	Percentage of extraction
1	6.5	0.3	95.4	6.5	0.18	97.2	6.5	0.36	94.5
2	7.0	0.5	92.9	7.0	0.37	94.7	7.0	0.88	97.4
3	8.4	1.0	88.1	8.4	0.90	89.3	8.4	0.90	89.3
<b>2. Contaminated lake-water samples</b>									
1	1.0	0	100	1.0	0	100	1.0	0	100
2	2.1	0	100	2.1	0	100	2.1	0	100
3	3.2	0.1	96.9	3.2	0	100	3.2	0	100

Average of five estimations; SD  $\pm$  0.13.

### Sorbents concentration

The minimum needed concentration of FLSP, APSP or PSP for the maximum copper removal was investigated by conducting the extraction experiments with the change in concentration of the said adsorbents from 0.25 g to 3.00 g/L. The other extraction conditions were maintained constant as noted in Figure 5. The results (Figure 5) showed that optimum amount of sorbent concentration needed was 1.0 g/L for FLSP, 1.5 g/L for APSP and 2.0 g/L for PSP.

At the lower dosage of adsorbents, more surface-active sites were exposed for the adsorbate ions and have increased adsorption rate. As the dosage increases, the percent removal also increases. But, at certain dosage, there is no noticeable change in percent removal. This is due to blocking of some surface-active sites by aggregation of the adsorbent particles (Sujitha & Ravindhranath 2019). Hence, for all further experiments the dosage values of present adsorbents were fixed at 1.0 g/L for FLSP, 1.5 g/L for APSP and 2.0 g/L for PSP. The ability of an adsorbent depends upon its porous structure, surface area and also the size of adsorbate to be adsorbed. So, the optimum dosage of the adsorbent depends upon its own characteristics (Nageeb Rashed 2013).

### Initial concentration of Cu<sup>2+</sup>

The variations of adsorption capacities of FLSP, APSP and PSP with respect to initial Cu<sup>2+</sup> ions concentration was investigated by treating various concentrations of Cu<sup>2+</sup> solutions (ranging from 5 to 50 ppm) with the said adsorbents at the optimum conditions of extraction established in this investigation. The observed results are depicted in Figures 6 and 7.

As the initial Cu<sup>2+</sup> ions concentration raises, the percentage of extraction of copper ions decreases (Figure 6). For a fixed amount of sorbent dosage, only a fixed number of active sites are available. With the increase in concentration of copper ions, the demand for active sites is also increased. But only a limited number of active sites are available and hence, % removal decreases as the concentration is increased. A similar trend was observed in the literature (Suneetha *et al.* 2015a).

It is interesting to note the increase in adsorption capacity,  $q_e$ , of the adsorbents with increase in initial concentration Cu<sup>2+</sup> ions (Figure 7). The increase in  $q_e$  values with increase in concentration may be due to the difference in concentrations between the copper ions on the sorbent surface and copper ions in the bulk of the solution. This concentration differences drifts more copper ions towards

the surface of the adsorbent, resulting the increase in  $q_e$  values (Sujitha & Ravindhranath 2017, 2018a, 2018b).

### Effect of co-ions

Simulated solutions containing two-fold excess of co-ions than  $\text{Cu}^{2+}$  were prepared. These solutions were treated with FLSP, APSP and PSP at the optimum conditions established in this investigation. The results were presented in Figure 8(a) and 8(b). It can be inferred that fluoride,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  interfered to some extent. Other co-ions were least interfered.

Some cations and anions, namely Ca(II), Mg(II), Al(III), Zn(II), Fe (II) and chloride, sulphate, nitrate, phosphate, bicarbonate and fluoride were considered as co-ions to study the absorption capacity of present adsorbents, FLSP, APSP and PSP for  $\text{Cu}^{2+}$  ions. Simulated solutions containing two-fold excess of co-ions than  $\text{Cu}^{2+}$  were prepared. These solutions were treated with FLSP, APSP and PSP at the optimum conditions established in this investigation. The results were presented in Figure 8(a) and 8(b).

The percent removal of  $\text{Cu}^{2+}$  ions decreases with the presence of co-ions because the co-ions have shown some significant influence on the adsorbate-adsorbent interaction at the solid/liquid interface. This is due to the competition between the co-ions and  $\text{Cu}^{2+}$  ions for surface active sites to adsorb on the adsorbents (He *et al.* 2015; Zhang *et al.* 2020).

The competition capability of co-ions depends on the different properties of co-ions, such as electric charge, ionic potential, electronegativity, ionic radii, position in the Irving-Williams series, atomic weight, highest standard reduction potential etc. The extent of decrease in percent removal depends on these properties of co-ions (He *et al.* 2015; Ouyang *et al.* 2019). Hence, the percent removal of  $\text{Cu}^{2+}$  ions with the present adsorbents: FLSP, APSP and PSP decreases in the presence of co-ions.

### Thermodynamic studies

The effect of temperature on the sorption of  $\text{Cu}^{2+}$  on FLSP, APSP and PSP were investigated. Solution temperature has good effect on the % removal.  $\text{Cu}^{2+}$  ions adsorptivities of the three adsorbents, FLSP, APSP and PSP, were studied at 303, 313 and 323 K. At these temperatures, the extraction experiments were conducted at the optimum conditions established in this work. The findings are presented in Figures 9 and 10.

As the temperature increases, the adsorption also increases. With the increase in temperature, the surface functional groups of the adsorbents undergo enhancement in vibrational motions. This results in decrease in the density of the surface layers of the adsorbent and as a consequence, some new pores on the surface are generated. Further, the increase in temperature increases the kinetic energy of the migrating adsorbate ions. These two factors result in the penetration of adsorbate ions deeper into the surface layers of the adsorbents and attains more access to the deeper laying adsorption sites in the sorbents (Sujitha & Ravindhranath 2018a, 2018b). The cumulative effect of these factors enhances the adsorption of  $\text{Cu}^{2+}$  ions 'onto' the surface of the adsorbents.

Thermodynamic parameters:  $\Delta G^0$  (kJ/mole),  $\Delta H^0$  (kJ/mole) and  $\Delta S^0$  (J/K. mole) were evaluated with equations:  $\Delta G^0 = -RT \ln K_d$ ;  $\ln K_d = \Delta S^0/R - \Delta H^0/RT$ ;  $K_d = q_e/C_e$  and  $\Delta G^0 = \Delta H^0 - T \Delta S^0$ , where  $K_d$  = distribution coefficient;  $q_e$  = amount of  $\text{Cu}^{2+}$  sorbed;  $C_e$  = equilibrium  $\text{Cu}^{2+}$  concentration;  $T$  = temperature (Kelvin),  $R$  = gas constant. The results are presented in Table 1.

The endothermic nature of the process is due to the strong attractions between the surface functional groups of the adsorbent and the  $\text{Cu}^{2+}$  ions. To this energy is needed for desorbing the  $\text{Cu}^{2+}$  ions from their hydration shells (Zhao *et al.* 2010). Another possible mechanism is the exchange of  $\text{Cu}^{2+}$  ions with  $\text{H}^+$  ions. To this process also, an amount of energy is required to cleave the hydroxyl group hydrogen bonds before to the cation exchange (Sandy *et al.* 2012).

Positive  $\Delta H$  values indicate endothermic nature of adsorption for all the three sorbents. As the values are more than 25.0 kJ/mole, the adsorption is not simple 'Physisorption' involving electrostatic interactions and it may be due to some kind of complex formation between  $\text{Cu}^{2+}$  ions and surface functional groups of the adsorbents viz., -OH, -COOH etc. or Ion-exchange at low pHs especially with FLSP as adsorbent. The similar study was observed in the literature (Sandy *et al.* 2012).

The positive  $\Delta S$  values indicate the disorder at the solid-liquid interface (Sujitha & Ravindhranath 2018a, 2018b) and it is a good condition for the  $\text{Cu}^{2+}$  to crossover the solution/solid interfaces and thereby resulting more adsorptivities. Among the three adsorbents, FLSP has  $\Delta S$  value of the order of 227.37 J/mole, indicating the strong tendency of  $\text{Cu}^{2+}$  ions to cross over the interface. The negative  $\Delta G$  values and their increase with temperature confirm the spontaneity of the sorption process.

### Adsorption isotherms

Adsorption nature was analyzed by applying various isotherms; namely, Freundlich, Langmuir, Temkin and Dubinin-Radushkevich models (Naga Babu *et al.* 2018; Sujitha & Ravindhranath 2019). The pertaining equations employed are:

Freundlich:  $\log(q_e) = \log k_f + (1/n) \log C_e$ ;

Langmuir  $L(C_e/q_e) = (a_L/k_L) C_e + 1/k_L$ ;  $RL = 1/(1 + a_L C_i)$

Temkin linear equation:  $q_e = B \ln C_e + B \ln A$ ,  $RT/b = B$ ;

Dubinin – Radushkevich equation:  $\ln q_e = -\beta \varepsilon^2 + \ln q_m$ ,  $\varepsilon = RT \ln(1 + 1/C_e)$ ,

where  $C_i$  and  $C_e$  are the initial and final concentration of adsorbate;  $q_e$  = adsorption capacity;  $k_L$  and  $a_L$  are the Langmuir constants;  $R_L$  = dimensionless separation factor,  $A$  = Temkin isotherm constant (L/g),  $B$  = heat of sorption;  $\beta$  = constant related to energy and  $q_m$  = Dubinin-Radushkevich adsorption capacity (mono layer) (mol/g). The results are presented in Figure 11 and Table 2(A).

The adsorption of copper ion onto FLSP and APSP are described well by Langmuir and other isotherm models falls in the order Temkin isotherm > Freundlich > Dubinin-Radushkevich isotherm. For PSP, the order is: Langmuir followed by Dubinin-Radushkevich and the other models least fit.

### Kinetics of adsorption

The kinetics of adsorption were analysed by using pseudo first-order, pseudo second-order, Elovich and Bangham's pore diffusion models. The results were presented in Table 2(B).  $R^2$  values falls in the order: pseudo second-order > pseudo first-order > Elovich > Bangham's pore diffusion models.

The correlation coefficient ( $R^2$ ) values decides the kinetic model for the adsorption process. The kinetic model which has high correlation coefficient values was well fitted with the experimental data of an adsorbent (Suneetha *et al.* 2015a). So, the pseudo second-order model explains well the kinetics for all the three adsorbents, which was confirmed by higher correlation coefficient values ( $R^2$ ). The similar studies were observed in the literature (Suneetha *et al.* 2015a). The experimental data, which was fitted to the pseudo second-order model, indicates the strong interactions between the metal ions and surface functional groups of the adsorbent (Afrodita *et al.* 2015).

### Regeneration and reuse of spent FLSP, APSP and PSP

The spent FLSP, APSP and PSP were investigated to regenerate and reuse using various acids/ bases/ salts. 0.1N HCl was found to be successful. The spent adsorbents were soaked in 0.1 N HCl overnight, filtered, washed with distilled water for their neutrality and then dried at 105 °C. Thus, regenerated

FLSP, APSP and PSP were employed for treating simulated  $\text{Cu}^{2+}$  solutions. The findings are presented in Figure 12.

It may be inferred from Figure 12, upto 4 cycles of regenerated FLSP can be used. APSP and PSP can be used as adsorbent for up to 3 cycles of regeneration with marginal loss of adsorptivities.

### Applications

In order to assess the applicability of the FLSP, APSP or PSP for treating real polluted water, experiments were conducted with the samples collected from the effluents of copper-based industries and polluted lake waters. The samples were treated with FLSP, APSP or PSP as adsorbents at the optimum extraction conditions established in this investigation (as cited in Table 3). The results are tabulated in Table 3.

It can be inferred from the table that FLSP, APSP and PSP can be successfully applied for treating polluted water for the removal of  $\text{Cu}^{2+}$  ions.

### Comparison of present investigation with previous works

The developed sorbents in the present investigation viz., FLSP, APSP and PSP, are contrasted with other adsorbents investigated previously relating to adsorption capacities and effective pH of solutions. The results are presented in Table 4.

**Table 4** | Comparison with hitherto existing good works

S. No.	Sorbents	$\text{Cu}^{2+}$ -sorption capacity, mg/g	pH	References
1	<i>Hibiscus cannabinus</i> stems	15.0	4	Devi <i>et al.</i> (2019)
2	<i>Phaseolus aureus</i> hulls A.C.	20.0	7	Rao <i>et al.</i> (2009)
3	Bio materials of <i>Limonia acidissima</i> plant	13.5	4	Devi <i>et al.</i> (2019)
4	<i>Ceiba pentandra</i> hulls A.C.	21.0	7	Madhava Rao <i>et al.</i> (2006)
5	Fly ash-HCl treated	21.5	7	Alinnor (2007)
6	Clay/HCl-treated	83.3	5	Vengris <i>et al.</i> (2011)
7	Sea food processing waste sludge	20.9	3	Lee & Davis (2001)
8	Biomass of Rose waste	56.0	5	Iftikhar <i>et al.</i> (2009)
9	Eggshells powder-coated with $\text{Fe}_3\text{O}_4$	44.0	6	Ahmad <i>et al.</i> (2012)
10	Chitosan/chitosan-cross linked	88.43/200	4.5/5.6	Cao <i>et al.</i> (2001); Prakash & Arungalai Vendan (2016)
11	Green alga	133.0	5	Gupta <i>et al.</i> (2006)
12	Fly ash/NaOH-treated	64.0	6.2	Wang <i>et al.</i> (2006)
13	FLSP	175.5	5 to 10	Present work
14	APSP	140.4	6. to 10	
15	PSP	130.0	7 to 10	

It can be seen from Table 4 that FLSP, APSP and PSP have more adsorption capacities than many reported in the literature. Further, the effective pH ranges for all the three adsorbents are greater. This permits the direct applicability of the adsorbents to treat effluents from industries which generally have varied pHs.

## CONCLUSIONS

Sorbents derived from stem powders of *Feronia limonia* (FLSP), *Amorphophallus paeoniifolius* (APSP) and Pumpkin (*Cucurbitapepo*) (PSP) plants were investigated as adsorbents for the removal of  $\text{Cu}^{2+}$  ions from polluted water by batch methods of extraction. Different extraction conditions such as pH, dosage, initial concentration of  $\text{Cu}^{2+}$  ions, and contact time were optimized for the maximum possible removal of  $\text{Cu}^{2+}$  ions from water. The adsorption capacities were found to be high: 175.5 mg/g for FLSP; 140.4 mg/g for APSP; and 130.0 mg/g for PSP. The positive and negative values of thermodynamic parameters,  $\Delta H$  and  $\Delta G$ , indicate the endothermic and spontaneous nature of the adsorption for all three sorbents respectively. The positive  $\Delta S$  values indicate disorder at the solid-liquid interface. The three spent adsorbents can be regenerated and used.

The adsorption nature was analysed by adopting various isotherm and kinetic models. It is observed that the Langmuir isotherm and pseudo second-order models have described well the adsorption of copper ions onto the FLSP, APSP and PSP. The adsorbents developed in this investigation are applied effectively to treat effluents from copper-based industries and contaminated waters from lakes.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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