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Hydroxyapatite nanoparticle-modified apple pomace as a biosorbent for copper and iron removal: Isotherm and kinetic analysis

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The present study investigates the potential application of activated biomass waste decorated with hydroxyapatite nano-particles (HANP), i.e., HANP@AP, for decontamination of Cu and Fe metals from aqueous medium. We presumed that Cu and Fe ions can be removed from water contaminated with these ions efficiently owing to the electrostatic interaction provided by phosphate $(PO_4)^{3-}$ and (-OH) groups of HANP. Thus, the adsorption experiments have been designed to explore the potential of this HANP modified activated biomass waste. The influence of various factors like time (5-180 min), adsorbent dose (0.01-0.1 g), metal concentration (20-300 mg L^{-1}), and pH (2-8) on the adsorption process have also been investigated. The Langmuir adsorption isotherm is suited for the adsorption of both Cu and Fe showed that the maximum adsorption capacity of 76.3 mg g^{-1} for copper and 166.6 mg g^{-1} for iron when batch adsorption experiments are performed with initial metal ion concentration of 20-300 mg L^{-1} at pH 5 over the period of 180 min for Cu and 5 min for Fe using 0.1 and 0.04 g of adsorbent, respectively. It is observed that the pH plays quite an important role for the adsorption of Cu on to the surface of HANP@AP whereas the adsorption of iron on its surface remains unaffected by pH variations. Further, to understand the mechanism for the adsorption of copper and iron the surface of HANP@AP, kinetic studies are done in the time range of 20-180 min. The kinetics study data revealed that the Cu and Fe adsorption on activated waste following pseudo-second kinetics. Further, a comparison study with the previously reported biomass based biosorbents is also done which showed the superiority of HANP@AP for the decontamination of these heavy metal ions.

Keywords: Biosorbent, Copper removal, Hydroxyapatite nano-particles (HANP), Iron removal, Isotherms, Kinetics

Introduction

Copper (Cu) and iron (Fe) are vital trace elements for humans, animals, and plants. Copper is required for the various metabolic processes and the proper operation of the organs. It is known to have antimicrobial, antibacterial and antibiofouling properties, whereas iron is necessary for the growth and development of healthy muscles, bone marrow and organ functioning, etc. Apart from this iron is also required for the transportation of oxygen throughout the human body. Despite their importance and necessity, these elements have been classified as heavy metals, if they exceed their permissible limits as set by various organizations. Copper is regulated at 1.3 mg L^{-1} by USEPA, 2.0 mg L^{-1} by WHO, 0.05 mg L^{-1} by ISI, and 1.5 mg L^{-1} by ICMR and CPCB. Similarly, WHO and ISI recommend 0.1 mg L^{-1} and ICMR and CPCB recommend 1.0 mg L^{-1} limit of iron[4]. An excess amount of copper shows probable hazards to aquatic wildlife, several invertebrates and even plants. Excess intake of copper by humans causes damage to the liver, bone, immune and central nervous systems[5]. It also causes nausea, diarrhea and anemia. When large amount of copper gets accumulated in the human tissues it causes genetic disorder, Wilson's disease also called hepatolenticular degeneration, etc.[6] In the same way, excessive consumption of iron results in nausea, vomiting and diarrhea, along with iron poisoning in children causing serious health issues and even death[7]. Heavy metals are non-degradable, thereby gets accumulated in living beings showing health hazardous effect on them[8].

The main source of heavy metal ions entering within human or animal system is wastewater. Thus, nowadays, owing to their high toxicity, it is an obligation to take initiative for their removal from water bodies. Thereby, several technologies have been reported for their removal which includes electro-coagulation[9,10] flocculation, ultra-filtration, reverse osmosis, chemical precipitation, adsorption, ion-exchange, and membrane filtration[11,12,13]. It has been found that all these conventionally methods, except adsorptions, are less economical, often carries out

partial removal of contaminants and even produces toxic by-products. However, adsorption is a method that is generally achieved by using natural waste materials or food and fruit industrial waste or even different bacteria, thus, provides an eco-friendly, economic, simple but efficient and flexible alternative process. Till now copper had been eliminated using various adsorbents like jatropha biomass[14], natural clay[15], Adenanthera pavonina seeds[16], Bengal gram husk and orange mesocarp[17], mussels shells[17], *Syzygium Cumini* L (Jamun)[18], leaf of pineapple[19], various bacteria[20], palm kernel shell[21], papaya wood[22], rice husk ash[23], banana peels and fish scales[24]. Removal of Iron was also done using various biomass-based adsorbents such as eggshells[25], and charcoal mixture[26], maize stalks[27]. The presence of various functional groups such as flavonoids, terpenoids, alkanes, calcium carbonate ($CaCO_3$), lignin, cellulose, hemicellulose, etc., on the surface of biomass makes them as suitable candidate to be used as adsorbent materials for adsorption phenomenon. Apart from this these bio-sorbents can also be chemically modified or used as a support for immobilization/stabilization of various nanoparticles on their surfaces to further improve their adsorption capacity and removal efficiency.

Of late application of nanoparticle has become one of the most studied and important subjects in a variety of fields, owing to their numerous implications and diverse properties such as fine particle size and large surface area which equip them with numerous active sites for various applications along with the added benefit of reusability and selectivity[28]. However, these nanoparticles forms agglomerates and settle to the bottom, an irreversible phenomenon that eventually makes them unstable, thereby makes them lose their activities. Thus, to avoid agglomeration and flocculation of nanoparticles, they must be impregnated on a solid surface. Lately several researchers explored the applicability of bio-sorbents as solid support for stabilization of nanoparticles such as pectin coated iron oxide magnetic nanocomposite[29], straw/Fe_3O_4 nanocomposite[30], alginate beads based on magnetite nanoparticles[31] and zero-valent iron-impregnated cashew nutshell (70 mg g^{-1}) on a nanoscale[32]. The applicability of apple pomace (AP), waste generated from apple juice industry, was explored for removal of Cu ions from wastewater by different researchers[33-36].

In the present study, we have shown the use of apple as a solid support for immobilization of hydroxyapatite nanoparticles (HANPs) for the removal of copper (Cu) and iron (Fe) ions from wastewater. We have surmised that immobilization of HANPs on the surface of AP can be achieved by virtue of electrostatic interaction imparted by various functional groups such as hydroxyl and carboxyl functional groups present on AP (essentially due to pectins, polysaccharides, cellulose, hemicellulose and lignin) with the calcium and phosphate groups of Hydroxyapatite NPs, i.e. $Ca_{10}(PO_4)_6(OH)^2$. The appended HANPs along with the functional group of AP will enhance the adsorption capacity and removal efficiency for toxic heavy metal ions like copper and iron owing to the electrostatic interaction between the electron deficient metal ions and electron rich surface of the modified biosorbent. Thus, HANPs we embedded on the surface of AP in a similar way as reported in our previous study where HANPs modified AP was exploited for effective removal of Lead (Pb) and Cadmium (Cd) ions from aqueous solutions and shown high adsorption capacity[37].

Thereby, considering the potential of HANP@AP towards the removal of Lead (Pb) and Cadmium (Cd), HANP@AP was used as bio-sorbent for the decontamination of Cu and Fe from aqueous medium. The parameters like pH, dose, concentration and time were optimized which strongly affects the adsorption phenomenon. The resulting data were further verified by applying isotherms to specify whether adsorption was single-layered or multilayered and kinetics to obtain the adsorption mechanism or rate of adsorption.

Experimental Section

Materials and chemicals

All chemical reagents employed in the present study were of analytical grade and used without further purification. Ammonia solution (30%), calcium hydroxide ($Ca(OH)_2$), and potassium dihydrogen phosphate (KH_2PO_4) were purchased from SDFCL, India. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Merck, 1-6-hexanediamine was purchased from MD Biomedical, France, copper nitrate ($Cu(NO_3)_2$) was acquired from Himedia, and ferric chloride ($FeCl_3$) was purchased from Fischer Scientific (Qualigens). The apple pomace (waste biomass) was obtained from apple juice industry in Parwanoo, district Solan, Himachal Pradesh, India. pH variation was measured by using pH meter (Orion state A214) where the pH was adjusted using 0.1 M of NaOH/HCl.

Characterization of HANP@AP before and after adsorption

Functional groups characterization of synthesized material, i.e., HANP@AP, was done using Fourier-transform infrared spectroscopy (FTIR) analysis using Shimadzu-IR Affinity-1 working wavenumber range from 400 to 4000 cm^{-1}. The concentrations of Cu and Fe ions adsorbed during entire study were estimated by ICP-OES analysis by using Thermo Scientific (iCAP 7400 series) analyser with detection limit 0.04 to 9.36 µg/L. The multielement calibration standards were used for calibration.

Batch adsorption study

At room temperature, a sequence of experiments was performed to rationalize the adsorption efficiency of HANP@AP concerning removal of Cu and Fe. The variable factors influencing the adsorption capacity, such as pH (2-8), metal concentration (20-300 mg L^{-1}), HANP@AP (0.01-0.1 g) dose, and time (20-180 min.), was investigated. All experiments were conducted in conical flasks (250 mL) containing desired metal concentration in 50 mL distilled water in triplicate. To specify the maximum removal efficiency for metal ions by HANP@AP, a single parameter was changed at a time while the others remained constant. To achieve equilibrium and proper adsorption, the conical flasks were agitated for a set amount of time on a mechanical shaker, followed by filtration. ICP-OES was used to analyze the filtrate for metal ions concentration in the liquid medium. For Cu and Fe, q_{max} (maximum adsorption capacity) was also calculated using adsorption isotherms.

Synthesis of HANP modified apple pomace (HANP@AP)

AP collected from apple juice industry was washed and dried at room temperature. The completely dried AP was then ground to very fine particles using mortar and pestle. Prior to the impregnation and adsorption studies, this fine powder was sieved through 0.45 mm sieve and stored in an air tight container to avoid any moisture entrapment within its pores. The synthesis and impregnation of HANP on AP was carried out in the same manner as described previously[37]. In a flat bottom flask, potassium KH_2PO_4 (2.5 g, 18.7 mmol) was mixed with $Ca(OH)_2$ (2.0 g, 26.99 mmol) along with 30 mL of distilled water. Thereafter, 1-6-hexadiamine (8.0 g, 68.84 mmol) was added to the above reaction mixture and then the whole reaction mixture was allowed to react for 30 min. at 70°C for complete dissolution. Further, the reaction mixture was cooled to room temperature and then 30% ammonia solution was added drop-wise to maintain the pH of 10. To impregnate AP with HANP, 10.0 g of AP was added to the above mixture along with NaOH and then allowed to react for 30 min. at 80°C. The finished product was cooled, filtered and washed for further process. At the end, HANP@AP was oven dried at 80°C and used it for further adsorption studies.

Results and Discussion

Characterization of HANP@AP, Cu onto HANP@AP and Fe onto HANP@AP

The FTIR spectra not only provide information about the functional groups involved in the binding of metal ions to the adsorbent's active sites but also about the adsorption process. Herein, the successful immobilization of HANP on AP, i.e., HANP@AP, and confirmation of copper/iron ions removal by HANP@AP was confirmed by FTIR analysis (Fig. 1). The FTIR spectrum of HANP@AP[39] showed a wide absorption band at 3370.9 cm^{-1} and narrow peaks at 2925.5 and 2848.8 cm^{-1} corresponding to –OH and –CH stretching frequency of $–CH_2$ groups, respectively. Furthermore, an extreme peak at 1033.6 cm^{-1} indicates towards the symmetric bending mode of O–P–O of PO_4^{3-} encompassing the biomass network[38]. Also, small peaks 435.4 and 602.9 cm^{-1} corroborates to stretching and bending of the phosphate group of HANP@AP [39]. Further, the removal of Cu/Fe ions from aqueous solution was also confirmed from FTIR analysis. The emergence of a less extreme PO_4^{3-} peak and a slight shift in –OH absorptions bands from 3370.9 cm^{-1} to 3403.4 cm^{-1} and 3396.5 cm^{-1} for Cu onto HANP@AP and Fe onto HANP@AP, respectively confirms the adsorption of copper and iron metal ions on HANP@AP from wastewater.

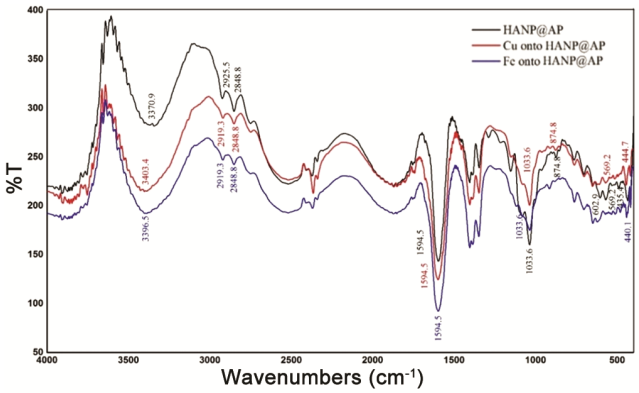

Fig. 1 — FTIR spectra of HANP@AP before and after Cu and Fe adsorption

Effect of various parameters

Dose variation

The adsorption of metal ions from their synthetic solutions is highly affected by the dose of HANP@AP use. To evaluate the precise dose of adsorbent, an experiment was performed in which the dose of HANP@AP was varied from 0.01 to 0.1 g at initial concentration of 50 mg L^{-1} for a period of 120 min. As can be seen in Fig. 2, the adsorption potentials of both the metal ions were increased as the dose of the adsorbent HANP@AP increased. This can be ascribed to increase in the amount of available surface area thereby the number of binding sites on adsorbent[40]. It was observed that the adsorption of Cu was significantly increased from 39.47% to 82.26% when dose of HANP@AP was increased from 0.04 g to 0.06 g, whereas for Fe the absorption was 99.97% when 0.04 g of HANP@AP was used. However, the adsorption rate remained nearly constant, and no further increase in adsorption capacity was observed beyond 0.06 g for Cu and 0.04 g for Fe even when 0.1 g of adsorbent was used. This indicates that maximum adsorption had been reached. For further adsorption experiments, the adsorbent doses were fixed at 0.10 g and 0.04 g, respectively, for Cu and Fe.

pH variation

Metal ion adsorption capacity is observed to be greatly influenced by pH changes. The pH of the aqueous solutions was maintained in the range 2-8 using 0.1 M of NaOH/HCl. It was found that Cu removal efficiency was low in pH ranging from 2-3 which can be attributed to the presence of excess H^+ ions in the aqueous solution that competes with the inorganic pollutants (metal ions) for binding to the adsorbent site[41]. However, adsorption was found to increase as the pH was increased from 3-5 which can be corroborated to decrease in H^+ ion concentration (Fig. 3). However, the adsorption efficiency was found to be constant in the range pH 5 to 8. Above pH 8, the adsorption phenomenon was not studied because of the possibility of formation of metal hydroxide, which causes precipitation and thus decreases adsorption capacity[42]. As can be seen in Fig. 3, iron removal efficiency by HANP@AP is completely independent of pH. The percent removal was nearly 100% throughout the pH range. As a result, the optimal pH for Cu was determined to be 5 and same pH was considered for Fe.

Effect of contact time

Time has a noticeable effect on adsorption like adsorbent dose and pH. It is critical to define an optimal agitation time for the adsorption process, as prolonged shaking increases processing time and, consequently, reduces the economic and commercial feasibility of the method. To understand the effect of time on the adsorption efficiency of HANP@AP, experiments were conducted at different time interval. Thus, conical flasks with 50 mL synthetic solutions of 50 mg L^{-1} of Cu and Fe with optimized adsorbent doses of 0.06 g and 0.04 g, respectively, were agitated for time intervals ranging from 5 to 180 min. It was observed that Cu adsorption was low initially but as time passes adsorption increases and reaches to equilibrium at nearly 80 min with a removal efficiency of 96%, (Fig. 4), and beyond this time the adsorption remains constant once equilibrium is reached. As time passes, Cu is more effectively adsorbed on unoccupied binding sites of HANP@AP which leads to increase in adsorption level [43]. As a result, an agitation time of 80 min was chosen for further copper adsorption studies. Iron, on the other

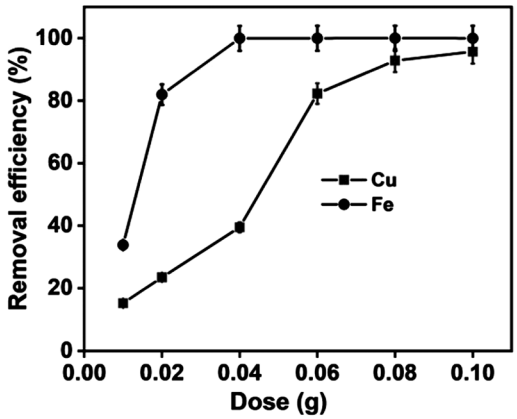

Fig. 2 — Effect of dose (0.01-0.1 g) on adsorption of Cu and Fe onto HANP@AP (Initial metal ion conc. 50 mg L^{-1})

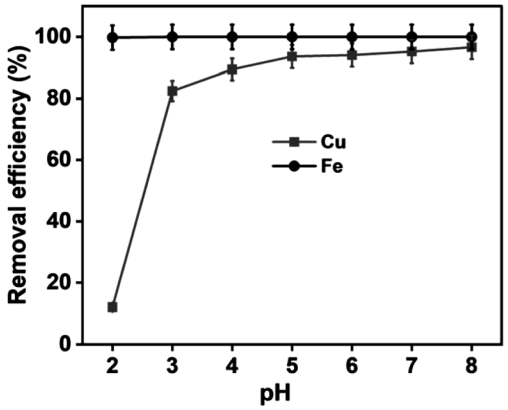

Fig. 3 — Effect of pH (2-8) on adsorption of Cu and Fe onto HANP@AP

hand was adsorbed on HANP@AP within 5 min and its adsorption capacity remains unaffected by the time factor.

Effect of concentration

Apart from adsorbent dose, pH, and contact time, the concentration of metal ion also plays a significant role on the adsorption potential of HANP@AP. The metal ion concentration was varied from 20 to 300 mg L^{-1}. For Cu and Fe, the adsorbent doses were 0.06 g and 0.04 g, with contact times of 80 and 20 min, respectively. To optimize initial concentration, a graph was plotted between percent removal and concentration. According to Fig. 5, the adsorption rate of Cu increases with increasing metal ion concentration till 50 mg L^{-1}, whereas Fe showed adsorption up to 130 mg L^{-1}. After reaching equilibrium, the adsorption capacity gradually decreases. This decrease in adsorption rate indicates that the active sites of bio-sorbents became saturated after certain initial concentration[44]. With a 0.06 g adsorbent dose, sufficient binding sites were available for Cu ions, so adsorption capacity increased with increasing concentration. Eventually, all of the sites become occupied with metal, and a further increase in concentration leads to the non-availability of binding sites for the extra metal ions, resulting in a lower probability of adsorption[45]. As a result, the optimal concentration for Cu ions was considered to be 50 mg L^{-1} whereas for Fe ions the optimal concentration observed was 130 mg L^{-1}.

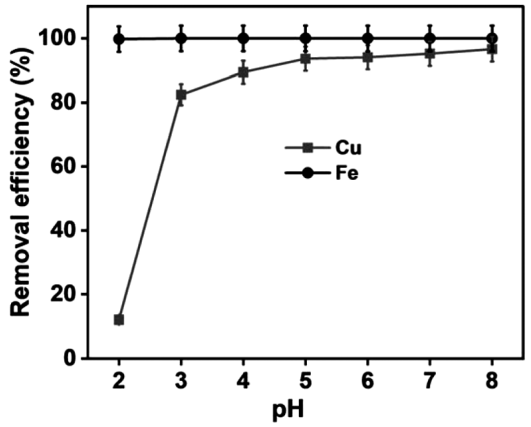

Fig. 4 — Effect of contact time (5-180 min) on adsorption of Cu and Fe onto HANP@AP

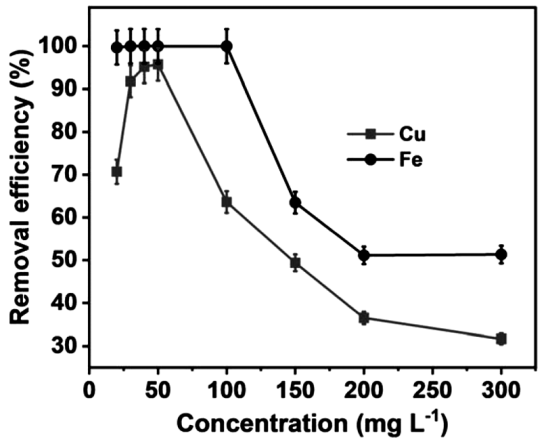

Fig. 5 — Effect of initial concentration of metal ions (20-300 mg L^{-1}) on adsorption of Cu and Fe onto HANP@AP

Adsorption Isotherms

Adsorption isotherms are normally used to investigate the equilibrium relationship that exists between the number of metal ions adsorbed on the adsorbent surface and the number of metal ions remaining in the solution. The existence of adsorption isotherms provides knowledge about adsorption modes[46]. The results of varying the initial concentrations were subjected to Langmuir and Freundlich adsorption isotherms. The equations involved are:

Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L . q_{max}}$$

Freundlich isotherm:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

Where, q_e = mass of metal ions adsorbed (mg g^{-1}), C_e = concentration of metal ions in the solution when mass adsorbed is q_e (mg L^{-1}), K_L = Langmuir constant, q_{max} = maximum adsorption capacity (mg g^{-1}), K_F and n = Freundlich constants.

Table 1 — Langmuir and Freundlich adsorption isotherms for copper and iron adsorption onto HANP@AP

Metal	Langmuir					Freundlich			
	Equation	R^2	Q_{max} (mg g^{-1})	K_L	R_L	Equation	R^2	n	K_F
Cu	Y=0.013x + 0.127	0.97	76.33	0.102	0.003-0.048	Y=0.19 x +3.27	0.83	5.24	1905
Fe	Y=0.006x + 0.024	0.94	166.66	0.25	0.00-0.032	Y=0.13 x +4.39	0.62	7.56	24837

A graph of C_e/q_e vs C_e was used to calculate the maximum adsorption capacity (q_{max}). Cu and Fe linear graphs indicated that the Langmuir equation was obeyed, with R^2 value of 0.97 and 0.94, respectively (Table 1). The resulting values were also subjected to the Freundlich isotherm, but it did not fit well with the adsorption data well. It shows that the adsorbent's surface (HANP@AP) was homogeneous, with each binding site capable of binding one adsorbate molecule, implying the occurrence of monolayer adsorption. It also suggested that the adjacent adsorbed adsorbates have no interactions with one another[47]. The maximum adsorption capacity of HANP@AP for Cu and Fe was found to be 76.33 and 166.66 mg g^{-1}, respectively, with Langmuir constant (K_L) of 0.102 and 0.25, respectively (Table 1).

The adsorption capacities of HANP@AP for Cu and Fe are compared with the other reported modified biosorbent (Table 2 & 3). The adsorption capacity of HANP@AP was found to be higher than the reported modified bio-sorbent for both the metal ions.

The dimensionless equilibrium constant (R_L) was calculated to evaluate the favourability of the adsorption process. R_L values ranging between 0 and 1 indicate favourable adsorption and support the applicability of the Langmuir isotherm model. The calculated R_L values for both metals are summarized in Table 1. The results show that all R_L values fall within the range of 0 to 1 at all studied concentrations, confirming that the adsorption process is favourable and follows the Langmuir adsorption isotherm model.

Kinetic study

Using Lagergren's pseudo-first-order reaction mechanism and Ho's pseudo-second-order reaction mechanism, the kinetics of batch adsorption studies can be calculated. These models calculate the reaction rate as well as the time it takes to reach equilibrium.

Pseudo-first order:

$$\ln (q_e - q_t) = \ln q_e - k_1 . t$$

Pseudo-second order:

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

Where, q_e = amount adsorbed at equilibrium (mg g^{-1}), q_t = amount adsorbed at time, t, k_1 = rate constant (min^{-1}), k_2 = rate constant (g (mg $min)^{-1}$).

To establish the kinetics of metal ion adsorption by HANP@AP, solutions with concentrations ranging from 20 to 60 mg L^{-1} were agitated for 10-80 minutes with an optimized dose of HANP@AP. The concentration of residual metal ions in the filtrate was then calculated by plotting the graphs of ln (q_e-q_t) and t/q_t against time for pseudo-first and second-order, respectively. The data were subjected by both kinetic models. Table 4, shows the values of rate constants as well as their R^2 equivalents. For the adsorption of Cu and Fe ions, the second-order kinetics process was found to be more accurate, implying chemisorption[57]. Figure 6 shows kinetics fitting of pseudo-second order for copper and iron ions.

Table 2 — Adsorption capacity of Cu (II) ion in solutions using modified waste biomass

S. No	Modified biosorbent	Adsorption capacity q_{max} (mg g^{-1})	Reference
1	Activate watermelon	31.25	43
2	Calcium hydroxide treated watermelon	27.02	43
3	Thiourea modified Sorhum bicolor agrowaste	15.15	48
4	NaOH and HCL modified Hizikia fusiformis (Algae)	45.09	49
5	carbonaceous material from grapefruit peel	48.22	50
6	Modified pomegranate peel	30.12	51
7	Nano-particle activated Apple Juice industry waste	76	Present Study

Table 3 — Adsorption capacity of Fe ion in solutions using modified waste biomass

S. No	Modified biosorbent	Adsorption capacity q_{max} (mg g^{-1})	Reference
1	Rice husk Ash	6.2	23
2	hazelnut hull	13.59	52
3	activated carbon from olive stone waste	50	53
4	biochar from oil palm	75.47	54
5	Pomegranate peel carbon	18.52	55
6	chemically pretreated oil palm	115	56
7	Apple Juice industry waste activated with nanoparticle	166	Present study

Table 4 — Pseudo-second order of kinetics for copper and iron onto HANP@AP at various initial concentrations from 20-60 mg L^{-1}

Conc. (mg/L)	Copper (Cu)				Iron (Fe)			
	Equation	R^2	q_e (mg g^{-1})	K_2	Equation	R^2	q_e (mg g^{-1})	K_2
20	y=0.1415x+0.01	0.99	7.06	1.75	Y=0.040 x +1	1	25	8
30	y=0.0578x+0.19	0.99	17.3	1.70	Y=0.0267x +0.00009	1	37.5	7.9
40	y=0.0424x+0.12	0.97	23.58	0.015	y=0.025x+0.0002	1	40	3.12
50	y=0.033x+0.024	0.99	30.3	0.045	y=0.016x+0.00007	1	62.5	3.65
60	y=0.0272x+0.08	0.99	36.76	0.009	y=0.0133x+0.0003	1	75.18	0.58

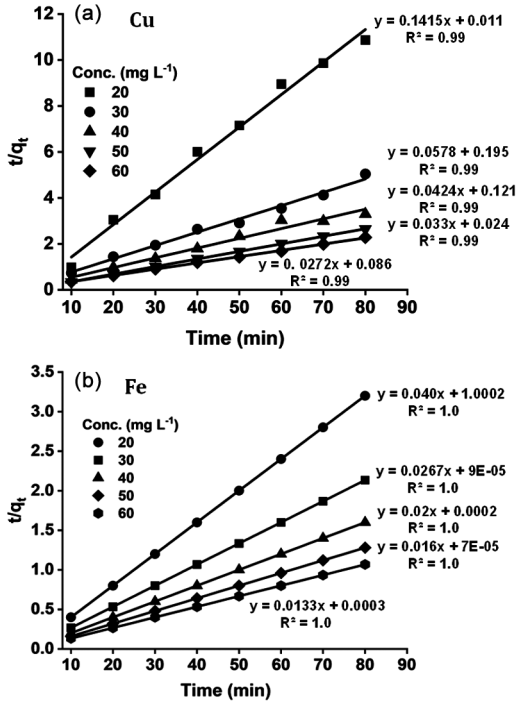

Fig. 6 — Pseudo-second order of kinetics for copper (a) and iron (b)

Conclusion

The present investigation showed that HANP@AP is an effective bio-sorbent for the removal of Cu and Fe from aqueous media. The adsorption of Cu was found to be pH dependent and whereas for Fe it's independent of pH. The removal of Cu and Fe increases with increased in HANP@AP dose and decrease with increasing concentrations of Cu and Fe. The equilibrium data were evaluated using Langmuir isotherm and rate of adsorption with time was analyzed using kinetics study. The experimental data results fit excellently with the Langmuir isotherm with adsorption capacity of 76.66 and 166.66 mg g^{-1} for Cu and Fe, respectively. The use of low-cost biomass waste functionalized with hydroxyapatite nanoparticles not only offers a sustainable and eco-friendly solution for decontamination of wastewater but also cleaned the industrial dumping sites. The high adsorption capacities suggest strong potential for application in large-scale wastewater treatment operations. Despite of advantages, there are many challenges such as better understanding of interactives mechanism between biosorbent and metal ions, scale-up, cost feasibility and treatment of huge volume of industrial wastewater. Future work need to focus on the above challenges for sustainable solution for treatment of metal ions in wastewater.

Conflict of interest

The authors declare no conflict of interest.

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