Comparative study on raw and modified forms of sugarcane bagasse for biosorption of Cu^{+2} from wastewater

Ammara Waheed, Rabia Sabir, Awais Salahuddin

Abstract- Biomass based natural adsorbents have become center of interest for wastewater treatment to remove toxic heavy metals. Sugarcane bagasse has potential for the removal of heavy metals from water. In the current research work a comparison of raw sugarcane bagasse (RSB) and its two modified forms (Chemically treated sugarcane bagasse CTB, and bagasse fly ash BFA) has been presented. It was found that BFA gives highest metal uptake while, CTB gives highest acid resistance. The adsorption capacity of RSB, CTB and BFA was 1.98, 6 and 16.879 mg/g, respectively. Metal uptake increased by increasing pH in the range between 3 and 5. Optimum pH for removal of Cu was found to be 5.4, 5 and 5.5 for RSB, CTB and BFA, respectively. Equilibrium was achieved within initial 30 min. Kinetic studies revealed that biosorption of Cu+2 ions follows pseudo 2nd order kinetic model.

Index Terms- Bagasse fly ash, Biosorption, Chemically treated bagasse, Heavy metals, kinetic studies, Point of zero charge, Sugarcane bagasse

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1 Introduction

Constantly expanding industrial activity is majorly responsible for most of the pollution problems in environment as well as damage to ecosystem, which is mostly caused by the buildup of polluting substances; for example heavy metals (chromium, copper, lead, cadmium, zinc, nickel, etc.) that are very toxic and result in deterioration of human health. [1]

When aqueous media is contaminated by heavy metals it becomes one of the most crucial environment related problem because heavy metals are toxic and non-biodegradable in nature and can be concentrated in food chain.[2]

Despite the fact that numerous detrimental effects of heavy metals on health have been well recognized for quite some time now but still risk of being exposed to heavy metals lingers, and is even rising in some underdeveloped countries [3][4]. For instance, mercury is still being used in some areas of Latin America for gold mining.[5] Arsenic is commonly used for wood preservation purposes and tetraethyl lead (TEL) is an additive to petrol, although the use of these chemicals has declined drastically over the last 100 years in most of the developed countries but they are still being used in underdeveloped countries.[6] So, heavy metals become a part of effluent of many industries like metal plating, electroplating, mining operations, pesticide and fertilizer industry, smelting, atomic energy installation and aerospace, energy and fuel production, leather tanneries, paper and pulp industries, alloy industries and batteries industries.[7] [8][9][10][11][12]

Biosorption is a waste treatment technique that makes use of dead and inactive biomass for sequestration of highly toxic

heavy metals and this technique is gaining attention these days [21]. Biosorbents have high specific metal binding sites and this quality makes them efficient for the elimination of heavy metals from wastewater[22]. In recent years many agricultural wastes are being investigated to elude heavy metal ions from wastewater, some examples of such biosorbents include corn cobs [23] [24] [25], banana peels [26] [27], wheat bran [28][29], wheat straw [30], sugarcane bagasse [31], rice straw [32], rice bran [33] and soybean straw [34] , coffee husk [35] [36] etc. Though it has been discovered that capacity for metal binding of these agriculture based wastes is less when compared to commercially available activated carbon or ion exchange resins, but the bright side is that even small modifications such as base, acid or heat treatment have been known to improve the metal binding capacity of these biosorbents. This suggests that, agricultural wastes that are very economical can be employed for treatment of water, instead of expensive commercially available methods [37] [38] [39]

In the light of above discussion, sugarcane bagasse appears to be a significant candidate as a biosorbent. The existence of such compounds as lignin, cellulose, hemicellulose, and silica in this biomass along with available sites that are capable of taking up metal ions, accompanied by its abundant availability in most agricultural countries, proposes the usage of sugarcane bagasse as an economical and naturally available biosorbent for metal ions removal or recovery. That is the reason why we chose this particular biosorbent for our research work.

Over the past few years a lot of work has been done on sugarcane bagasse and raw sugarcane bagasse and its different modified forms have been used as biosorbent for removal of heavy metals from wastewater. These modified forms of sugarcane bagasse provide advantages in terms of process modification and process simplification. The modified forms of sugarcane bagasse include chemically modified sugarcane

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bagasse, fly ash from bagasse combustion and activated carbon obtained from sugarcane bagasse.

To sum up all the above discussion we can say that since long biosorption has been investigated to remove or recover heavy metals from wastewater and a lot of biosorbents have been tested for this purpose. Some of the biosorbents have even been modified by chemical treatment or heat treatment to see if they become more efficient after modification. But usually most of the studies involve investigation of a biosorbent either in its raw form or any modified form. There is a shortage of data when it

2   Materials and methods

2.1 Preparation of biosorbent

Sugarcane bagasse was collected from a local sugar mill (Shakarganj sugar mill, Jhang, Pakistan).

Raw sugarcane bagasse

Raw bagasse was rinsed with distilled water many times to eliminate any dirt particles or an additional impurity then it was dehydrated in air, finally particle size was reduced and stored for further experimentation.

Optimum conditions for preparation of sugarcane bagasse for Cu (II) removal [40]:

Drying temp.: 120 °C

Drying time: 1 hr.

Particle size: 80-100 mesh.

Chemically modified sugarcane bagasse

Bagasse was treated with a chemical for its activation. The chemical activation of bagasse was performed by the use of concentrated sulphuric acid (0.1M) [21] and then it was retained in an oven for 24 h, oven temperature was kept in the range of 150°C. After that it was washed again with distilled water to confiscate any free acid content, it was placed into oven to eliminate moisture content and then passed through 80-100-mesh size and finally stored for further use. [41]

Bagasse fly ash

Raw bagasse sample was burned in laboratory and bagasse fly ash thus prepared was rinsed completely with distilled water to eliminate any debris and other external substance and then dried in sun for time duration of 6 to 7 hr.

2.2 Preparation of synthetic wastewater

Standard solution of Copper having 1000 ppm concentration was made using weighed amount of $Cu(NO_3)_2.3H_2O$. This standard solution was diluted when necessary using distilled water to make solutions of required concentration for biosorption experiments.

2.3 Determination of precipitation point of Cu+2

100 mL of Cu solution with 100 ppm concentration was prepared and point of precipitation was determined by adding 0.1 M NaOH drop wise and pH was noted at which considerable precipitates started to form.

2.4 Point of zero charge determination

Raw sugarcane bagasse (RSB)

is required to compare raw and modified forms of a biosorbent as to which must be chosen depending on process requirement. The results of this study will provide us with information that will help in making a decision that which form should be chosen for a particular operation depending upon whether our requirement is a higher metal uptake or more stability of the biosorbent under the conditions of biosorption i.e. acidic aqueous solution. Also this study will help in determining the effect of time on biosorption and the kinetics of process.

The pHPZC was determined, also called the point of zero charge; it is a pH value that corresponds to situation when charge on the surface of any adsorbent is zero. To find out this value 0.5 g of sugarcane bagasse was added in 50 mL of an aqueous solution of potassium chloride (KCl) 0.5 mol L-1 having pH values of solution in the range of 1 to 9, adjusted with a sodium hydroxide solution (NaOH: 0.1 mol L-1) and hydrochloric acid (HCl: 0.1 mol L-1). It was stirred in a water bath for three hours after that the final pH of each solution was obtained, finally a graph between initial and final pH was plotted. [42]

Chemically treated bagasse (CTB)

For pHPZC determination of CTB, experiments were performed by using 0.01 M KNO3 solution. The process was performed in 250 mL conical flasks (10 conical flasks) covered with cork, each contained 90 mL of 0.01 M KNO3 solution. The pH (pHi) of the solution, that was present in the conical flasks, was maintained in the range of 1 to 11 at intervals of 1 pH value by adding 0.2 M KOH or 0.2 N HNO3. Afterwards, solution volume was increased so that it became 100 mL by addition of KNO3 solution at the uniform concentration. Then the pHi of the solutions was accurately measured and set to one of the pH settings. At this phase, 1g of biosorbent were introduced in to each flask, and then flasks were enclosed promptly with corks. Subsequently, each flask was shaken manually and then placed to achieve equilibrium for 48 h with periodic manual shaking. And graph was plotted between initial and final pH. [43]

Bagasse fly ash (BFA)

For BFA 100 mL conical flasks were used and 45 mL of KNO3 solution of 0.01 M KNO3 was admitted into each one of them. The pH values of the solution were carefully regulated from pH 2 to 12 by addition of either 0.1M HCl or 0.1M NaOH, depending upon the requirement. After that the total volume of the solution in all the flasks were carefully increased precisely to 50 mL by adding KNO3 solution of the equal concentration. 1 g of BFA was introduced into every flask, which was covered immediately. Subsequently, each flask was shaken manually and then placed to achieve equilibrium for 48 h with periodic manual shaking. After achievement of equilibrium pH values were again noted carefully and graph of initial vs. final pH was plotted. [44]

2.5 Batch Biosorption Studies

For biosorption experiments, 5mg of adsorbent was mixed with 100 ml of solution containing 100ppm of Cu+2 ions in conical flask at room temperature. Afterwards the flasks were shaken

at 100 rpm and a steady rpm was maintained in the mechanical shaker. The influence of initial pH and contact time was examined at optimum conditions from 10 to 120 min at different pH values. Samples were taken after breaks until the attainment of equilibrium. Solutions pH was fixed with 0.1M HCL and 0.1M NaOH.

Atomic absorption spectrophotometer was used to measure final concentration of solution from which the remaining amount of metal was determined.

Heavy metal ions uptake was determined by using following material balance equation:

$$q_e = \frac{(C_i - C_f)V}{W} \qquad (1)$$

Removal percentage of metal ions from metal solution was evaluated by using percent equation

$$Removal\ \% = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (2)$$

3 Results and Discussions

3.1 Influence of pH

One of the essential factors for sequestration of heavy metal ions by adsorption from aqueous solutions is initial solution pH because it influences charge on the adsorbent surface, the degree of ionization, and the species of adsorbates. [45] [46]

In the current research work, the influence of pH on removal of Cu+2 ions from aqueous solution of constant initial concentration was carried out at pH of 2.5, 3, 4, 5 and 5.5; these pH values were selected in between the pHpzc of the three forms of adsorbent and point of precipitation of Cu+2. Experiments were carried out separately for the three forms of bagasse adsorbent i.e. raw bagasse, chemically treated and bagasse fly ash. The initial metal ions concentration and biosorbent dose was kept constant.

Percentage removal of copper ions (Cu+2) was significantly higher at pH 5 than at lower pH values for all three forms of bagasse adsorbent as shown in Fig. 1. Similar results were found by Homagai et al. [41]

Higher adsorption at pH 5 may be attributed to the presence of larger number of vacant sites for biosorption of Cu+2 ions in the acidic medium. This improvement in % age removal of Cu+2 ions with increase in pH can also be justified by taking into account the fact that as total negative charge on surface of biosorbent increased it resulted in an elevation in electrostatic forces, hence at higher pH the adsorption of positively charged ions increased. Additionally, the number of negatively charged functional groups that were present on the surface of biosorbent for binding of Cu+2 ions increased at higher pH that resulted in decreased struggle between protons and metal ions. This pattern of metal ions adsorption on biosorbent can also be attributed to point of zero charge of biosorbent and point of precipitation of metal ions, both of which are pH values. Above point of zero charge biosorbent surface is negatively charged while below it biosorbent surface is negatively charged.

Therefore, for biosorption of cations, pH of solution should be above its pHpzc.

The precipitation point of an ion is a pH value at which ions start to precipitate out of the solution. Precipitation point for Cu+2 ions came out to be pH=6. While the point of zero charge for raw, chemically treated and bagasse fly ash was 5, 1.5 and 3 respectively, as shown in fig. 2 (a, b & c).

From these results it can be concluded that optimum pH for removal of Cu+2 ions for raw bagasse, chemically treated and bagasse fly ash was 5.4, 5 and 5.5 respectively.

As optimum pH for biosorption of Cu+2 metal ions onto three forms of sugarcane bagasse was around 5; this indicates that acidic medium is required for biosorption, hence for design purpose of a batch and industrial scale process we must be aware of the acid resistance of the three forms of sugarcane bagasse so as to know that how long our biosorbent will survive in acidic medium before being completely consumed. It was found that percent weight loss of raw, chemically treated bagasse and bagasse fly ash, in an acidic medium, was 9.35, 4.25 and 19.35 % respectively, which is an indirect representation of acid resistance. It is obvious that bagasse fly ash has minimum acid resistance while chemically treated bagasse has the highest acid resistance.
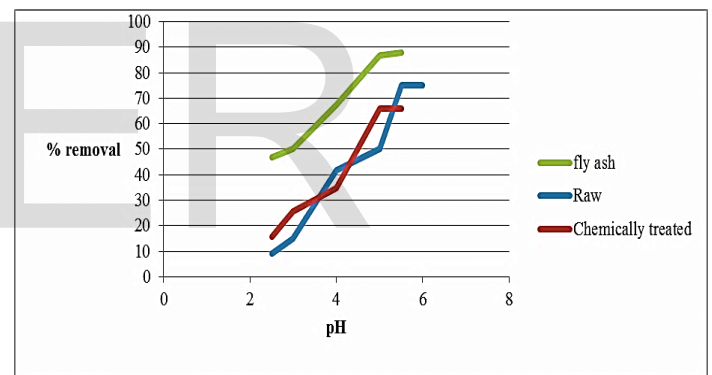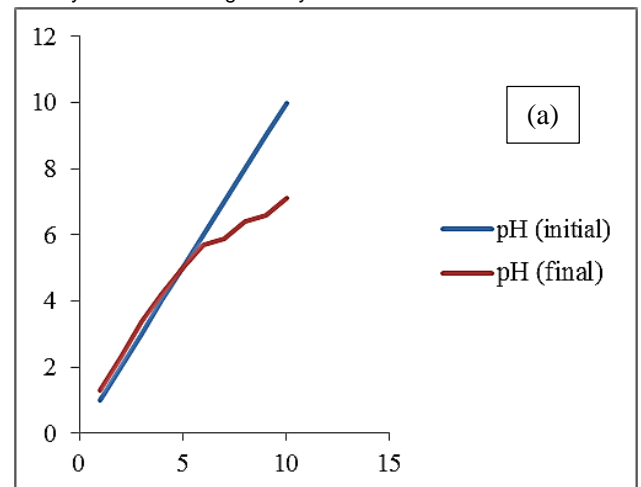

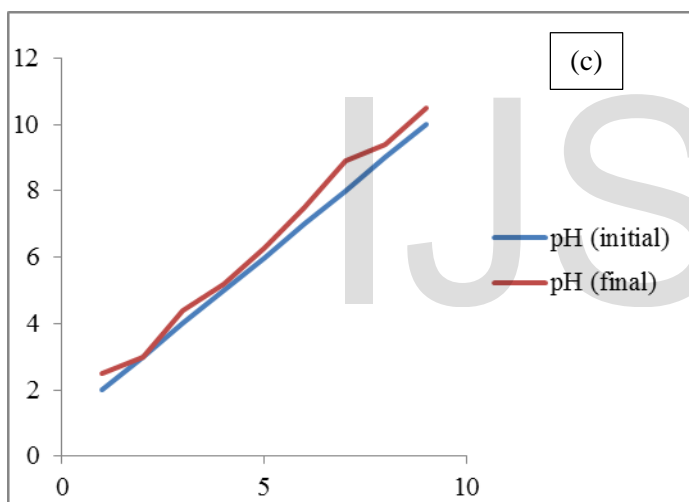Fig. 1 Influence of Initial pH on Biosorption of Cu+2 ions on raw, chemically treated and bagasse fly ash

number of vacant sites acquirable for biosorption was very large, therefore, as a first step these sites are occupied by metal ions. After some time has passed, the left-over vacant sites are hard to be occupied because of repulsive forces among the adsorbate molecules on the biosorbent surface and those present in the bulk liquid phase. Moreover, the metal ions are adsorbed into the meso-pores of biosorbent that become almost saturated with metal ions at early stage of biosorption. Therefore, the driving force available for mass transfer between the two phases i.e. bulk liquid phase and the solid adsorbent phase falls as time passes. In addition, the metal ions must travel even more far and deep into the pores of biosorbent hence, facing much larger resistance. That is why rate of adsorption decreases during the later phase of biosorption. The reason for decreasing rate of adsorption with respect to time could be that intraparticle diffusion dominates over adsorption. [47]

Fig. 3 Effect of contact time on sorption of Cu^{+2} ions on raw, chemically treated and bagasse fly ash

3.3 Kinetic modeling

For design of an efficient biosorption system, it is necessary to collect information on kinetics of metal adsorption, because of its critical role in the choice of optimized operating conditions of an industrial-scale operation.

Linear regression is the most commonly used method to find out the constants that are involved in the kinetic models and also in prediction of best-fit kinetic model.

Following equation represents the pseudo first-order kinetic model:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

(3)

Where, K_1 is the rate constant for pseudo first-order biosorption (g/mg.min).

The linear form of former equation, after integration and application of boundary conditions (At $t = 0$, $q_t = 0$; At $t = t$, $q_e = q_t$), becomes:

$$\log(q_e - q_t) = \log q_e - K_1 t$$

(4)

The graph of log (q_e – q_t) versus t will result in a linear relationship from this plot the values of K_1 and q_e can be determined as slope and as intercept, respectively.
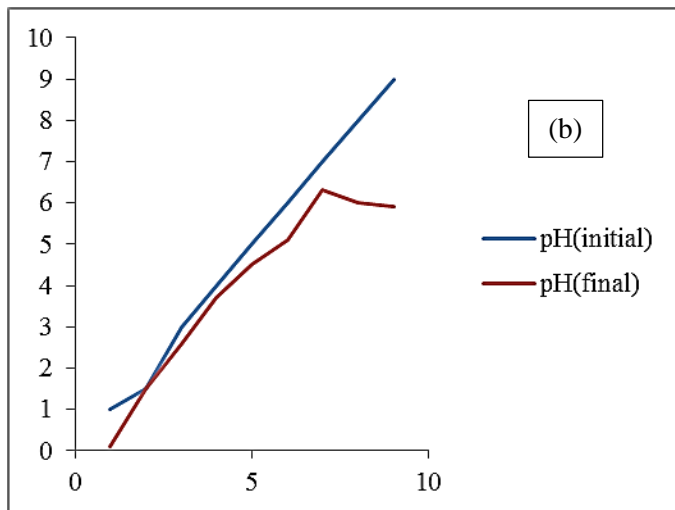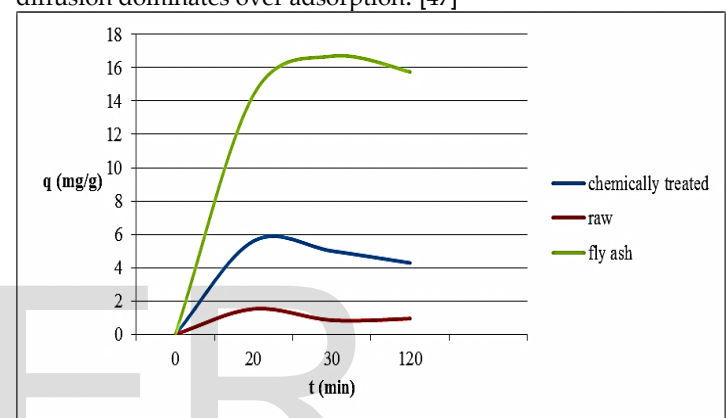

Fig. 2 Point of zero charge (a) for raw bagasse (b) chemically treated bagasse (c) bagasse fly ash

3.2 Effect of contact time

Time needed for metal ion biosorption is highly dependent on specific kind of biosorbent. To estimate the influence of contact time on biosorption, batch biosorption experiments were executed at time intervals ranging from 0 to 120 min under optimum conditions. Figure 4.5 shows that exclusion of Cu+2 ions increased during initial 20 min and then equilibrium was achieved within 30 minutes for the three forms of sugar cane bagasse, as no further increase in metal ion removal could be seen after 30 min of contact time. It is evident from fig. 3 that biosorption process comprised of two steps; first one was the fast step which lasted for shorter time and was proceeded by a second phase which was slower and lasted until the attainment of equilibrium. It has been observed that in the beginning the

Graph of log (qe – qt) against t is presented in Fig. 4 (a, b & c) for raw bagasse, chemically treated bagasse and bagasse fly ash, respectively. The values of pseudo 1st order equilibrium constant K1 and equilibrium uptake qe calculated by slope and intercept of plot are given in Table 1. The value of correlation coefficient R^2 for raw, chemically treated bagasse and bagasse fly ash is 0.09447, 0.05542 and 0.01294, respectively. The calculated (qe,cal) and experimental (qe,exp) values of equilibrium uptake are very different from each other which suggests that kinetics of biosorption does not follow pseudo 1st order model.
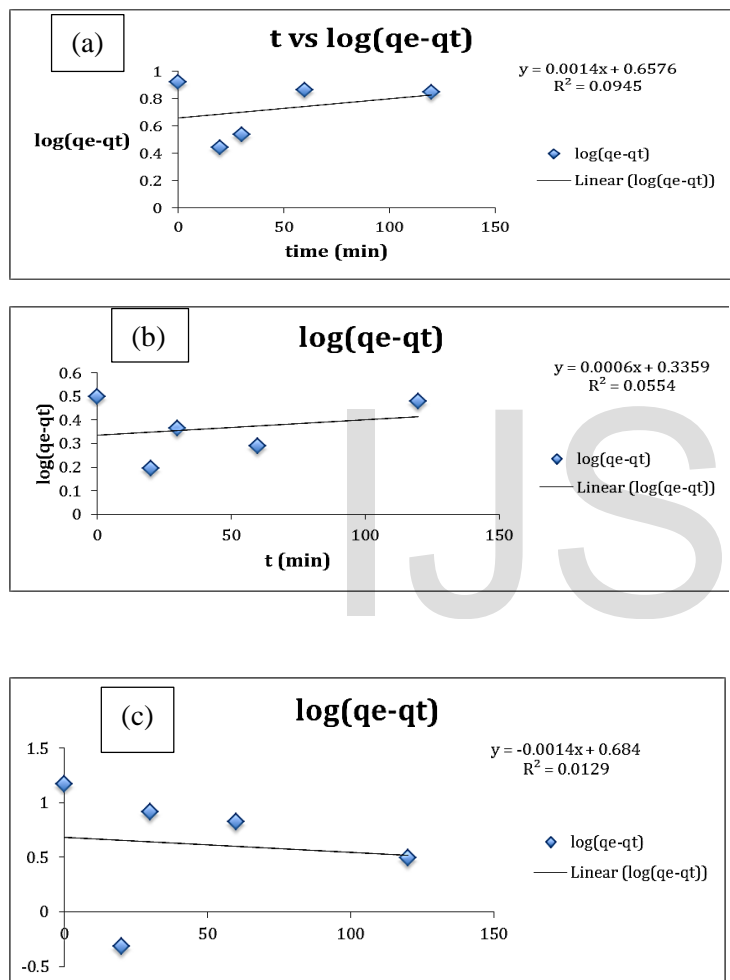

(a) t vs log(qe-qt)

$y = 0.0014x + 0.6576$
$R^2 = 0.0945$

log(qe-qt) — Linear (log(qe-qt))

(b) log(qe-qt)

$y = 0.0006x + 0.3359$
$R^2 = 0.0554$

log(qe-qt) — Linear (log(qe-qt))

(c) log(qe-qt)

$y = -0.0014x + 0.684$
$R^2 = 0.0129$

log(qe-qt) — Linear (log(qe-qt))

Fig. 4 Pseudo 1st order plot of Cu+2 ions sorption on (a) raw sugarcane bagasse (b) chemically treated bagasse (c) bagasse fly ash

Table 1
Pseudo 1st order regression model parameters

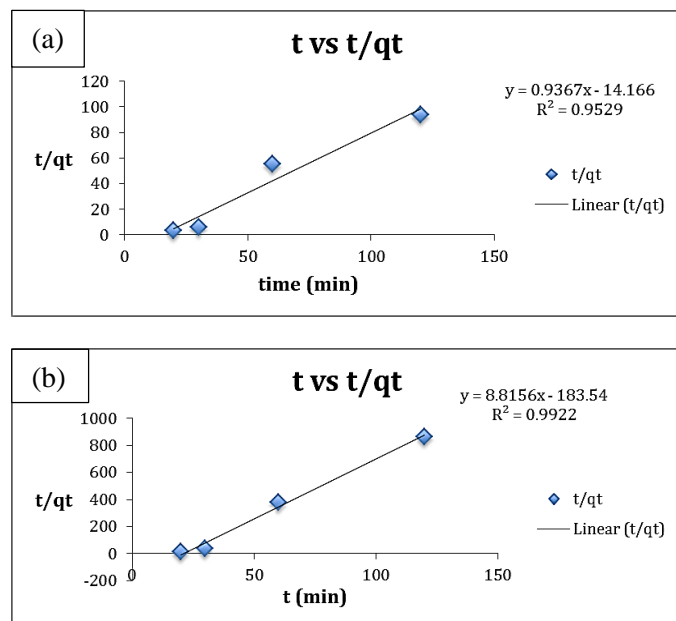| Bagasse form	$q_{e,exp}$ (mg/g)	K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2
Raw bagasse	1.98	0.394	6.32	0.09447
Chemically treated bagasse	6	0.015	1.17	0.05542
Bagasse fly ash	16.879	0.0084	10.87	0.01294

The second order kinetic model equation is:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2$$

(5)

Where, K2 is the rate constant of pseudo second-order biosorption (g/mg min).

It can be represented in linear form as:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(6)

A plot of t/qt vs. t will provide us with the values of K2 and qe. Graphs of t/qt against t are shown in fig. 5 (a, b & c) for raw, chemically treated bagasse and bagasse fly ash. Pseudo 2nd Order equilibrium uptake qe and rate constant K2 are presented in Table 2. It is evident that correlation coefficients were close to unity and experimental and calculated values were also in good agreement. Thus, it can be inferred that pseudo 2nd order kinetic model is more appropriate for representing the biosorption of Cu+2 metal ions on all three forms of sugarcane bagasse that are discussed here.
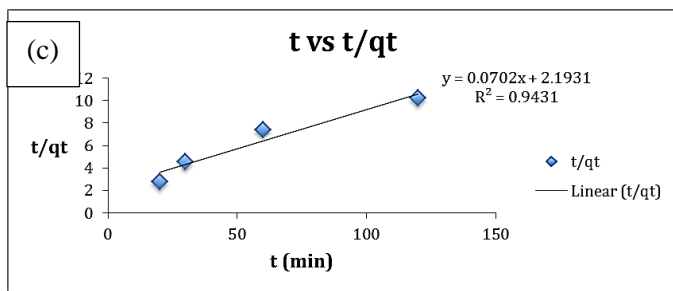

(a) t vs t/qt

$y = 0.9367x - 14.166$
$R^2 = 0.9529$

t/qt — Linear (t/qt)

(b) t vs t/qt

$y = 8.8156x - 183.54$
$R^2 = 0.9922$

t/qt — Linear (t/qt)

Fig. 5 Pseudo 2nd order plot of Cu^{+2} ions sorption on (a) raw sugarcane bagasse (b) chemically treated bagasse (c) bagasse fly ash

Table 2
Pseudo 2nd order regression model parameters

Bagasse form	$q_{e,exp}$ (mg/ g)	K_2 (1/min)	$q_{e,cal}$ (mg/g)	R^2
Raw bagasse	1.98	0.412	1.79	0.9521
Chemically treated bagasse	6	0.0559	5.995	0.99217
Bagasse fly ash	16.8 79	0.635	16.663	0.9431

4   Conclusion

This study reveals the potential of bagasse and two of the modified forms of sugarcane bagasse i.e. chemically treated and fly ash as biosorbents to adsorb Cu+2 ions present in simulated wastewater. Pseudo 2nd order model was found to be most suitable for Cu+2 ion adsorption on bagasse and its modified forms. Metal uptake increases by increasing pH in the range of 3 to 5. Optimum pH for removal of Cu+2 is 5.4, 5 and 5.5 for raw, chemically treated and bagasse fly ash, respectively. Acid resistance of different forms of sugarcane bagasse is in the order: Chemically treated bagasse > raw bagasse > bagasse fly ash with 4.25, 9.35 and 19.35 % weight loss. Maximum metal uptake was achieved within first 30 mins of biosorption for raw bagasse and its modified forms.

Bagasse fly ash has the lowest acid resistance but it reaches equilibrium slowly and its metal uptake per gram of sorbent is high. Although, chemically treated bagasse has highest acid resistance but its metal uptake is less as compared to bagasse fly ash.

Deciding whether we want higher metal uptake or higher acid resistance, we can select a suitable form of sugarcane bagasse for removal of Cu+2 ions from wastewater.

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