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Removal of copper from aqueous environment using Soyhull based biosorbent and its adsorption kinetics

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Abstract

Heavy metal pollution is one of the raise concern for the ecosystem. This study focused on the removal of heavy metals by soyhull based biosorbent from aqueous solution. We highlighted the use of soyhull as a bio adsorbent on removal of copper. Batch experiments were performed to study the adsorption of copper on soyhull biosorbent that revealed maximum adsorption capacity. The impact of various factors (adsorbent dose, initial concentration, contact time, and temperature) on adsorption was characterised and optimal conditions were determined. The effect of adsorbent dosage on the bio sorption of Cu from aqueous solution is studied at ambient temperature by varying the adsorbent amount from 1 g/100 ml to 4 g/100 ml. Maximum removal percentage of copper is observed at sorbent amount of 3 g/100 ml at 37 °C with the initial concentration range of 5 mg/l to 50 mg/l. Maximum percentage removal of copper was attained at 45 minutes of shaking time. Co-cation studies are also performed to understand the binding capacity of biosorbent in the presence of other heavy metals like zinc and magnesium. The Langmuir and Freundlich isothermal studies were performed to find the best fit model of adsorption. Among which both the models showed good fit. Kinetic studies were also done to study the adsorption mechanism by Pseudo first order and Pseudo second order kinetics. The results of this study suggested that copper could be removed using this soy hull based low cost biosorbent in an efficient environmentally friendly way.

Keywords: Adsorption, Soyhull, Biosorbent, adsorption, Langmuir and Freundlich Isotherm, Kinetics.

INTRODUCTION

Heavy metal pollution is one of the major environmental issues and has huge impact on ground water quality. Heavy metals contamination leads to serious environment problems due to their toxic effect on humans and other living organisms. In contrast to organic pollutants, heavy metal pollutants are not degraded and causes accumulation of toxic products in water bodies (Elsayed *et.al.,* 2019). Heavy metals like copper is widely used in many industries including metal plating, paper board, printed circuit board, wood pulp, paints etc (Chen *et.al.*, 2010). The industrial effluents leads to the accumulation of heavy metals in water bodies in turn enter into the food chain, resulting in a high risk to human health (Sitting, 1981 and Gaur *et.al.*, 2018). According to the report from US EPA, The limit of different heavy metals for Chromium, Lead and Cadmium are 0.05, 0.006 and 0.01 mg/L respectively beyond which is considered to be toxic for human consumption (Khoso W.A et.al. 2021). Copper (II) is known to be most toxic to living organisms and also highly widespread heavy metal contaminants of the environment (Ozer et al., 2004). Copper is regarded as 'inert' as it dissolves in acid in the presence of an oxidizing agent; ionic copper bind with a wide range of organic substances and has the ability to disrupt normal physiological and environmental processes. Copper, one of the most widely used heavy metal, is found in electrical and electroplating industries, and in larger amounts is extremely toxic to living organisms. The presence of copper (II) ions, cause serious toxicological problems, it is usually known to deposit in brain, skin, liver, pancreas and myocardium (Abia, 2006). The standardization maximum permissible concentration (MPC) of copper, values have been set by the

USEPA as shown in Table 1(Krstic *et.al.*, 2008). But, aquatic flora and fauna have been found affected even at much lowers concentrations these heavy metals. Several study have been carried on various techniques for removal of heavy metals from the environment and to reduce contaminations. The available water resources are increasingly diminishing and we must preserve them through treating wastes before discharging (Ghafari *et.al.*, 2008 and Kandah. *et.al.*, 2003).

The chemical precipitation, membrane separation, electrolytic separation, ion exchange and adsorption are traditionally used to remove these toxic metals from aqueous medium. The traditional wastewater techniques has disadvantages such as complicated treatment process, high cost, and energy use therefore Adsorption is an easy to operate and cost-effective process for the efficient removal of heavy metals from aqueous environment (Hameed *et.al.*, 2008 and Tansir Ahamad *et.al.*, 2017). Adsorption on activated carbon has shown to be very effective for removal of dyes and other pollutants from aqueous solutions but it is still considered expensive adsorbent and the higher the quality the greater the cost (El maguana Y. et.al., 2020) . Over the past two decades, numerous low-cost materials have been tested for their heavy metal sorption potential. In our research work, we chose soy hulls as the bio sorbent. As Soybean meal is a co-product obtained in the processing of soybean to produce dietary oil. After extracting most of the oil from whole soybeans the remaining product is utilized as soybean hull. In the extraction process of oil from soybeans around 75% of the whole mass is converted into meal, and about 18% into oil. The content of isoflavones is high in soybean meal which is rich in carbonyl functional groups and hetero oxygen atoms. The presence of these functional groups in soybean meal is useful in forming complexes with metal ions. Further soybean meal biomass used in this study was not modified with chemical or physical pre-treatment, which added to Soy hull abundance and its low cost makes it a good option for metal ion removal from aqueous solution (Witek *et.al.*, 2013). The objectives of this research work were to study the application of this novel adsorbent which are chemically free and environmental friendly for the removal of heavy metals from aqueous solution. The batch studies were carried out to determine the optimum conditions for standardizing parameters like adsorbent dose, contact time, temperature and pH (Benzaoui *et.al.*, 2017). This study also investigated the equilibrium of Cu (II) ion binding by soy hulls and the rate of the bio sorption was studied by using pseudo-first-order and pseudo- second-order models.

RESULTS

Effect of adsorbent concentration in Copper removal and recovery

The effect of adsorbent concentration on the cupper removal was studied at room temperature by varying the sorbent amount from 1g to 4 g for 100 ml. With increase in the concentration of soy hull adsorbent up to 3g/100 ml leads to increase of Cu adsorption and further increase in concentration of adsorbent decreases the Cu removal. It can be interpreted as the better access of the biosorbent surface for the adsorption process. A significant increase in the uptake of Cu was observed when the dose of adsorbent was increased from 1 to 4 g. Any further increase in the adsorbent did not cause any significant change in the adsorption. This may be due to overlapping of adsorption site as a result of overcrowding of adsorbent particles. The maximum removal of Cu was observed at the adsorbent dose of 3 g/100 ml.

On comparing different soyhull beads adsorbent dosages from 1g/100ml to 4g/100ml with sodium alginate of same initial doses, it was clear that soyhulls (Fig.2a-d) showed better adsorption than sodium alginate. The maximum removal of copper was found on 3g/100ml dose. On maintaining other parameters constant, Optimum adsorbent dosage was found to be 3g at maximum initial concentration of 50ppm, temperature 37 degrees Celsius with contact time of 40 minutes. The Maximum removal efficiency or the uptake efficiency of soy hulls is 70%. (Fig.2(e))

Effect of adsorbent contact time in removal of Copper

The dependency of the time for the adsorption process was studied at 37 °C by varying the duration of contact time from 5 to 60 min with fixed concentration of adsorbent and Cu in aqueous solution as 3 g/100 ml and 50ppm respectively. The rate of Cu removal was higher at the beginning. This was probably due to the access of large surface of the adsorbent at the beginning of adsorption process. At the later the time, the number of available sites on the bio sorbent gets reduced and hence the rate of adsorption was decreased. The maximum percentage removal of Cu was attained at 45 minutes of contact time (Fig.3). Adsorption of Cu metal ion increases with the increase in contact time, but it remained constant after equilibrium was attained. The maximum percentage removal (80%) of Cu was attained at 45 minutes of contact time.

Effect of Co- Cation in Copper removal from aqueous environment

Copper removal was tested in the presence of Magnesium and Zinc at different concentrations ranging from 10 to 50 ppm. The maximum reduction was found in the binary system $CuSO_4.5H_2O$ and $ZnSO_4$ as the reactivity of Zn is less than magnesium (Table 2). From the results it was clear that minimal (10ppm) equal concentrations of both zinc and magnesium did not show effects on copper removal. Zinc has less interference (Mg>Zn>Cu) and there was 50% efficient removal of copper in the presence of maximum amounts of both zinc and magnesium (Fig.4).

Characterisation of relationship between the adsorbate and surface of the adsorbent

Langmuir isotherm model

The Langmuir isotherm assumes that the uptake of copper ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions (T. A. Osmari *et.al.*, 2013). As such the surface will eventually reach a saturation point where the maximum adsorption will be achieved.

The linear form of Langmuir isotherm model is given by the following equation

$$C_e/q_e=C_e/q_m+ (1/K_Lq_m)\ldots\ldots\ldots 1$$

A linear Langmuir adsorption isotherm is given as equation 2.Multiply equation 1 by $1/C_e$ $1/q_e=1/q_m+ (1/K_Lq_m)*(1/C_e)\ldots\ldots 2$

The values of q_m and K_L of linear expression of Langmuir adsorption isotherm were calculated from the intercept and slope of the linear plot of $1/q_e$ versus $1/C_e$ (Fig.5a). The isotherm was found to be linear over the entire concentration range studies with a good linear correlation coefficient (R^2 = 0.9957) showing that Langmuir equation represents the best fit of experimental data.

Determination of Separation factor (R_L)

The Langmuir type adsorption isotherm shape can be classified by a dimension less constant separation factor (RL), given by Eq. (3) (Adegoke et.al., 2017)

$$R_L = 1 /1+K_LC_0 \text{........................} 3$$

The calculated RL values in different initial copper concentrations are shown in Table 3 (Meroufel et.al., 2013). It was observed that the value of RL in the range 0–1 confirms the favourable uptake of the adsorption process. (Chowdhury et.al., 2011). To understand the adsorption isotherm, the Langmuir equation is perhaps the most widely used model due to its simplicity and strong theoretical reasoning behind. Three essential premises of the Langmuir isotherm are monolayer coverage, adsorption site equivalence and independence (Bayrak, 2006).

Freundlich isotherm model

While Langmuir isotherm assumes that adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption over a heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by Eq. (4)

$$q_e= K_F\, C_e^{1/n} \text{…………......…………...} 4$$

Eq.(4) can be rearranged to obtain a linear form by taking logarithms

$$\log q_e = \ln K_F + 1/n \log C_e \text{…………..} 5$$

Freundlich isotherm is widely applied in heterogeneous systems especially for highly interactive species. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Fig.5b). Whereas, a value below unity implies chemisorption process where 1/n above one is an indicative of cooperative adsorption (physi-sorption).

The slope and the intercept correspond to (1/n) and K_F, respectively from fig.5c. It was revealed that the plot of ln q_e and ln C_e yields a straight line (Table 4). The favourable adsorption of this model can be characterized such that if a value for n is above unity, adsorption is favourable and a physical process. In the present study the value of n (n= 1.138) is greater than 1, indicating that the adsorption process is favourable (Rao et.al., 2018). The value of correlation coefficient R^2 = 0.9792. The best fit Langmuir isotherm with 13mg/g maximum uptake of copper ions (q_m)and R^2=0.9957 and the Freundlich adsorption isotherm resulted favorable adsorption as 1/n =0.878

Copper adsorption kinetics

Pseudo First order rate equation model

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation[6] (Simonin, 2016).

$$\ln (qe - qt) = lnqe - k1t \text{………………} 6$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t in min respectively. k1 (min−1) is the pseudo-first-order rate constant for the kinetic model which can be obtained from the slope of plot ln (q_e-q_t) versus time t shown in Fig.6a.

Determination of qt values in different concentrations of copper from experimental results.

To determine the value of reaction constant k1 in pseudo-first-order rate equation using experimental values given in Table 5 Thereby calculating the qt values of different concentration from experimental results.

$$q_t=(C_0-C_t)*V/m$$

Pseudo Second order rate equation model

The pseudo-second order kinetic rate equation was expressed as the driving force, (qe−qt), is proportional to the available fraction of active sites [equation 7]. Then, it yields

$$t/qt=1/h+1/qe *t \text{………………………} 7$$

Where $h=K2q_e^2$

The pseudo-second order linear plots of t/qt against contact time (t) at different initial Cu ions concentration Kinetic studies for the removal of copper ions were obtained and fitted to different kinetics models. Kinetics data were best fitted by the pseudo first-order model (Fig.6a) in comparison with the second order model shown in Fig.6b (Kowanga et.al., 2016) , R2 values were significantly high in pseudo first-order and the result indicated that this adsorbent is excellent in the removal of copper from aqueous solution at variable concentrations. The model fitted shown in Fig.6a proved that the adsorption process is inclined to physisorption which reveals the weaker interaction between the adsorbent and the copper ion. Hence kinetic models are fitted to know the binding mechanism of the copper with the soy hull bead surface.

Discussion

The present study aimed at removal of copper ions from aqueous environment using soyhulls as biosorbent based on adsorption process. Experiments were carried out in batch conditions at varying levels of adsorbent dose from 1g/100 ml to 4g/100 ml, contact time interval of 5 minutes to 60 minutes and at initial concentrations of 5, 15, 25, 40 and 50 ppm. The adsorption of Cu increased with the increase in the amount of soy hull adsorbent up to 4 g/100 ml and after which it decreased. Any further increase in the adsorbent dose did not cause any significant change in the adsorption. This might be due to overlapping of adsorption site as a result of overcrowding of adsorbent particles (Khoso W.A *et.al.* 2021). On maintaining other parameters constant, optimum adsorbent dosage was found to be 3g at maximum initial concentration of 50 ppm, temperature 37 ℃ with contact time of 40 minutes. The Maximum removal efficiency or the uptake efficiency of soy hulls is 70% on using 3g/100ml. Adsorption of Cu metal ion increased with the increase in contact time, but it remained constant after equilibrium was attained. The maximum percentage removal (80%) of Cu was attained at 45 minutes of contact time. From Co-cation studies it was clear that the removal of copper ion from mixed ion contaminant system like industrial waste water would depend on the reactivity of the metal ion contaminants. As there was 50% efficient removal in the presence of maximum amounts of both zinc and magnesium. Maximum removal of copper was found in the presence of zinc as the reactivity of magnesium is high. The best fitted model was the Langmuir isotherm with 13mg/g maximum uptake of copper ions (q_m) and R^2=0.9957 and the Freundlich adsorption isotherm also resulted favorable adsorption as 1/n =0.878. Kinetic studies proved that R2 values were significantly high in pseudo first-order and the result indicated that this adsorbent is excellent in the removal of copper from aqueous solution at variable concentrations. In Pseudo second order kinetics the adsorption process was inclined to physisorption. On an overall basis, this study shows that adsorption process using soyhulls could be efficient in removal of copper from aqueous environment. Compared to other conventional techniques, this method is much promising in terms of cost, time and efficiency.

MATERIALS AND METHODS

Chemicals

A stock solution of Cu (II) was prepared by dissolving copper sulphate, extrapure from SD fine. Sodium alginate, Calcium carbonate and sodium hydroxide user were all of analytical grade. Copper testing kit (Aquasol) was used to check the amount of copper present in the solution.

Adsorbent preparation

Soya bean hulls were collected from cattle feed shop. It was sundried for about 2–5 days before being grounded into fine particles and sieved to obtain 1 mm fine dust particles. Soy hull particles were then mixed with 1.5 % sodium alginate slurry in the ratio 6:1 and added drop wise to 0.1M calcium chloride solution. Sodium alginate control beads were prepared similarly without soy. Beads formed instantaneously and were allowed to cure in the solution at 4°C for 24 h. They were washed thoroughly and allowed to dry to a constant weight at 37°C. The beads were stored in airtight containers away from moisture until further use which is shown in Fig.1

Adsorption studies

In this research 1,000 mg/L stock solution of Cu (II) was prepared by dissolving $Cu(SO_4)$ in deionised water and adding water to 1,000 mL. The biosorption of Cu (II) on the Soy hull beads were investigated in batch biosorption experiments [7] .The effect of adsorbent dose, contact time, initial metal ion concentration and co cation studies on the biosorption rate and capacity were studied. The optimum factors for efficient adsorption was determined by the addition 3g of biosorbent in solution at different time interval of 5 to 60 minutes containing 100mL of solution also studied with different initial concentrations of 5 to 50 mg/ L. In each set of experiment, the effect of one factor was evaluated by varying one factor at a time while keeping all other factors constant. The biosorption efficiency (R%) was also calculated. The equilibrium and kinetic studies were carried out at initial concentrations of 50 to 300 mg/ L. All the experiments were performed in duplicates and only the mean values are reported.

DECLARATION

Ethics approval and consent to participate

This study does not require any ethical approval and involve any participants for consent.

Consent for publication

I confirm that the manuscript has been read and approved for submission by all the named authors in this publication.

Availability of data and materials

Not applicable

Competing interests

Not available

Funding

No significant financial support acquired for this study.

Authors' contributions

CVK and RV conceived the project and RV performed all lab experiments and data analysis. CVK, RV and AP has involved in writing the manuscripts. All authors read and approved the final manuscript.

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Table 1-MPC Standards for Copper

Chemical element	**MPC in water (mg/l)**	**MPC^a in Waste waters (mg/l)**	**MPC^b in Waste waters (mg/l)**
Copper	0.1	1.0	0.1

[a] Waste water discharged in public sewage system
[b] Wastewater that can be discharged into public wastewater that can be discharged into the recipient (surface and groundwater)

Table 2 - Effect of Co Cations on removal of copper

Runs	Combination of copper, zinc and magnesium	Amount of copper in the solution after 60 minutes of adsorption	% Removal of copper after 60 minutes
1	C50Z10M10	15.5±0.707	69
2	C50Z30M30	19.5±0.707	61
3	C50Z10M50	33±2.828	34
4	C50Z50M10	14.5±0.707	71
5	C50Z30M30	20	60
6	C50Z30M58	30.5±0.707	39
7	C50Z30M1.7	15	70
8	C50Z1.7M30	26±1.414	48
9	C50Z30M30	19±1.414	62
10	C50Z30M30	20	60
11	C50Z50M50	23.5±2.121	53
12	C50Z30M30	20	60
13	C50Z58M30	19±1.414	62
14	C50Z50M0	16.5±2.12	67
15	C50Z0M50	30.25±0.35	40

Table 3 - Langmuir isotherm parameters and Separation factor values for corresponding initial copper concentrations

C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	$1/c_e$	$1/q_e$	R_L
50	15	0.7	0.066667	1.428571	0.004343
100	45	1.833333	0.022222	0.545455	0.002176
150	70	2.666667	0.014286	0.375	0.001452
200	105	3.166667	0.009524	0.315789	0.001089
250	120	4.333333	0.008333	0.230769	0.000872
300	135	5.5	0.007407	0.181818	0.000726

Table 4 - Freundlich isotherm parameters

C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	Log C_e (mg/l)	Log q_e (mg/g)
50	15	0.7	1.176091	-0.1549
100	45	1.833333	1.653213	0.263241
150	70	2.666667	1.845098	0.425969
200	105	3.166667	2.021189	0.500602
250	120	4.333333	2.079181	0.636822
300	135	5.5	2.130334	0.740363

Table 5 - Determination of qe values at different concentrations of copper from experimental results

C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)
50	15	0.7
100	45	1.1
150	70	1.6
200	105	1.9
300	190	2.2

Table 6 - Langmuir and Freundlich adsorption isotherm constants

Langmuir			Freundlich		
q_m (mg/g)	K_L (L/mg)	R_2	n	K_F(mg/g) $(L.mg)^{-1/n}$	R_2
13	0.00377	0.995	1.138	-1.19	0.979

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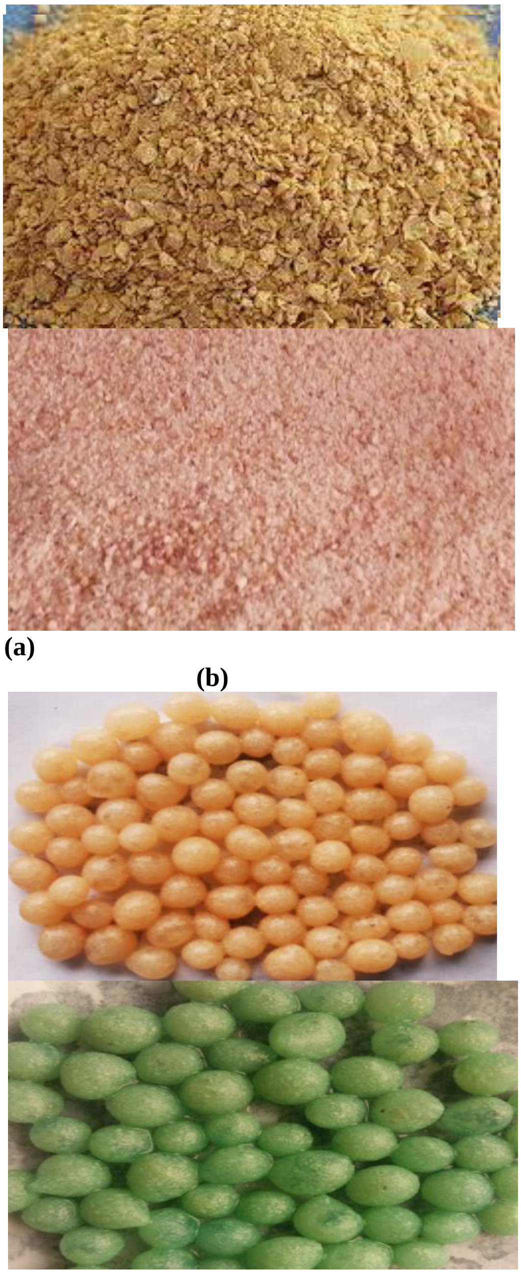

(a)

(b)

(c)

(d)

Fig.1 Adsorbent preparation (a) Soy hulls-Non uniform shape and size(b)Grinded and sieved soy hulls(particle size 1mm) (c)Beads prepared using 9% soy hulls + 1.5% Sodium alginate(6:1) Bead size 4.5 ±0.23 mm (d)Beads after adsorption process for about 45 minutes(In Optimum conditions)

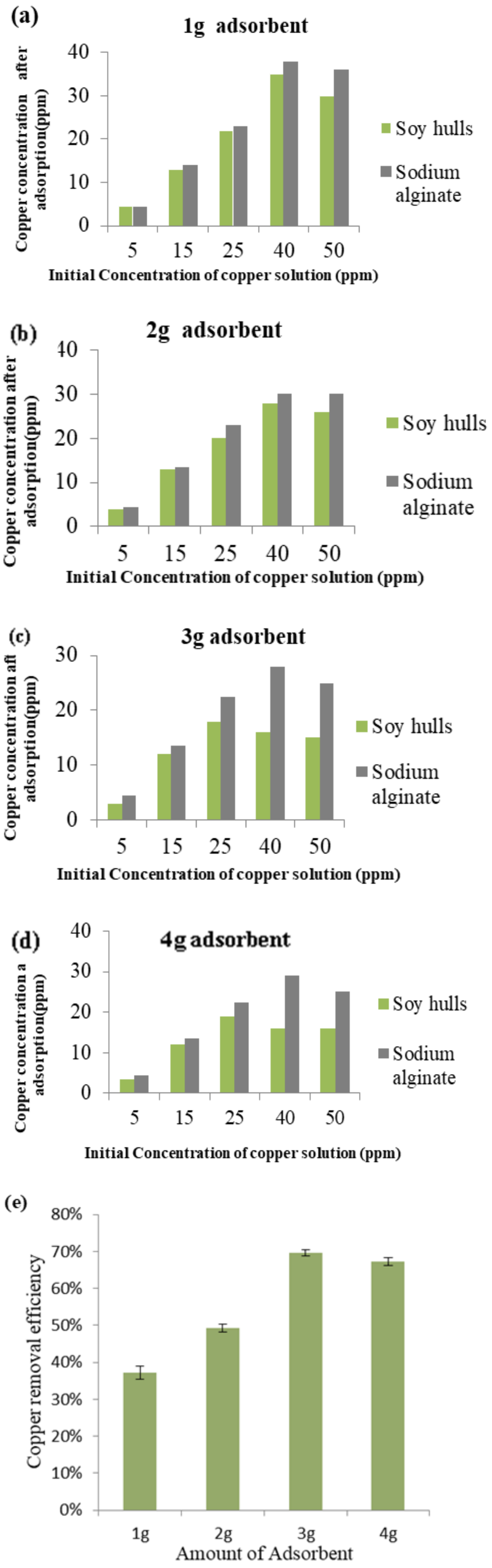

Fig.2 Effect of adsorbent dosage (a)1g of adsorbent (b)2g of adsorbent (c) 3g of adsorbent (d) 4g of adsorbent on metal ion adsorption onto soy hull beads at varying initial concentrations in comparison with sodium alginate control. (e) Maximum removal efficiency at different adsorbent dosage (Copper concentration 50 ppm, time 40 minutes)

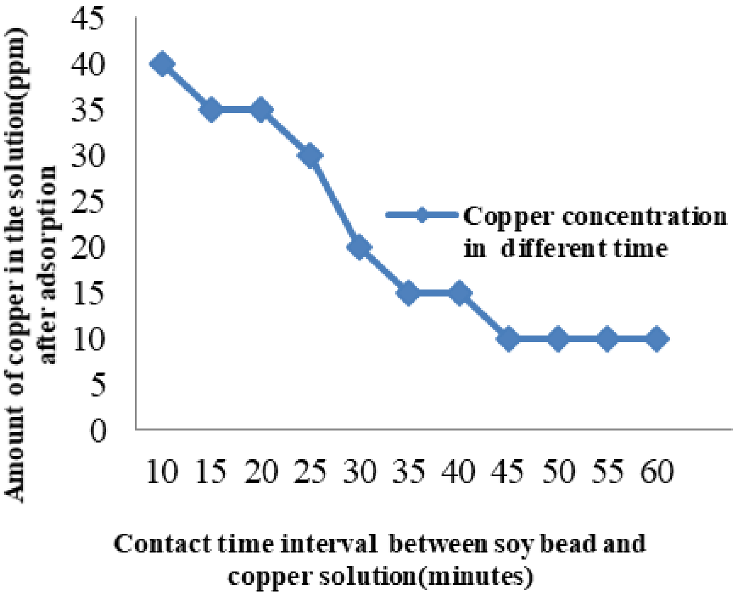

Fig.3 Effect of contact time on removal of copper at initial concentration of 50 ppm , room temperature,3g adsorbent dose, volume 100ml.

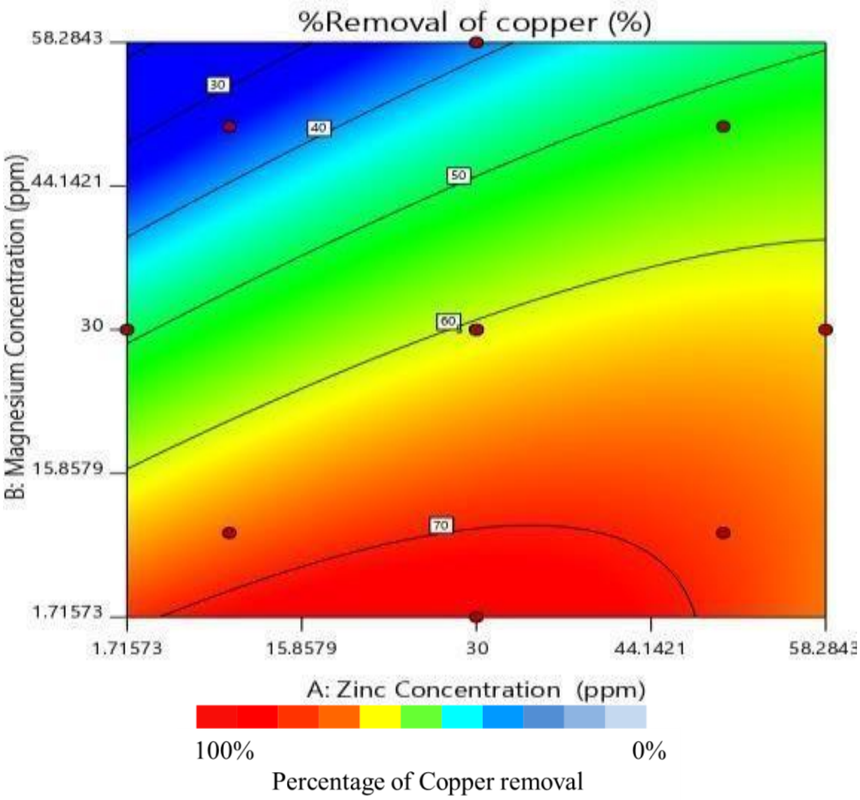

Fig.4 Two dimensional contour plot to show high removal of copper in the presence of other cations (Zn, Mg)

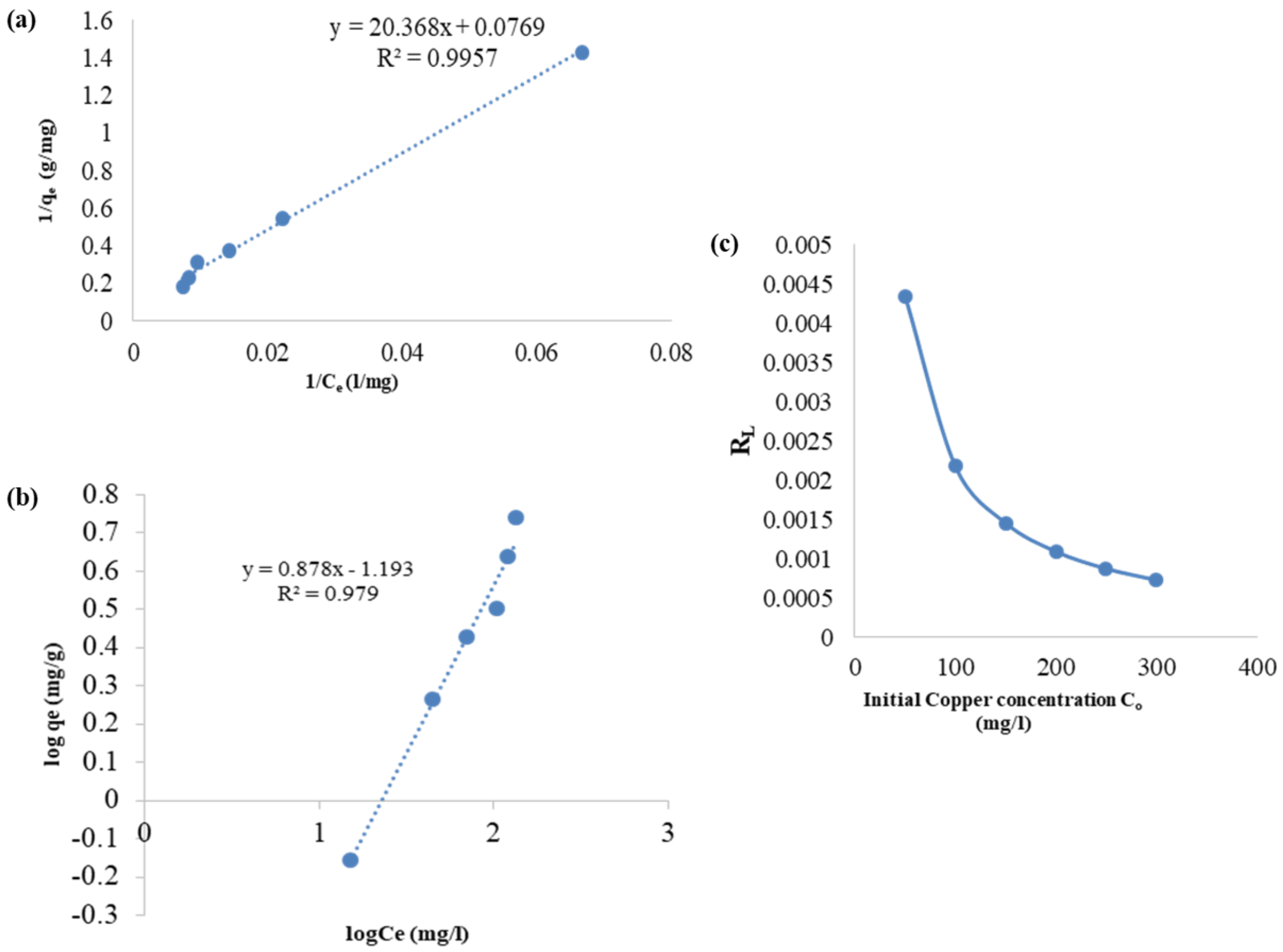

Fig.5 (a) Langmuir isotherm (Linear) model, From the values and graph, Intercept , $1/q_m=0.0769$, Slope (m) $=1/K_Lq_m=20.368$ Maximum adsorption capacity qm=13 mg/g. (b) Freundlich isotherm model, (c) Plot of separation factor versus initial Copper concentration, Slope 1/n =0.878 Therefore n = 1.138(Heterogeneity factor), $K_F=$ 0.064 (mg/g) $(L.mg)^{-1/n}$

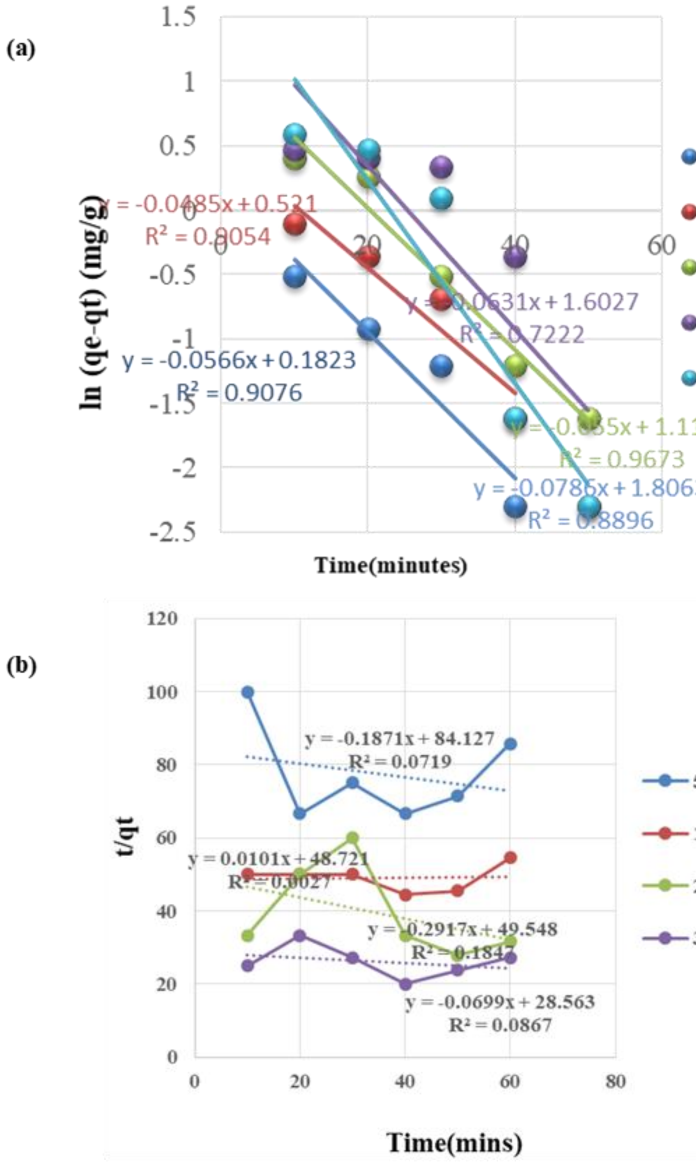

Fig 6 (a) Pseudo-first order kinetic model and (b) Pseudo Second Order model for Soyhull copper adsorption process.