Biosorption of Copper from Dye Industry Effluent using Aspergillus Niger

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Abstract *:* The present work is concerned to remove Cu using the biosorption potential of the copper resistant fungal biomass *Aspergillus niger* isolated from Dye insustry effluent. The dry fungal biomass was used to optimize various parameters such as contact time, initial metal ion concentration, pH, biomass loading etc. The percentage removal of copper using various chemical pre-treatments was studied. A maximum of 91% Copper removal was observed in 5 mg/L initial Copper metal ion concentration using dry *Aspergillus niger* biomass. A maximum Copper removal of 91% was obtained using sterilized dry chemically modified fungal biomass followed by 89% removal using sterilized wet chemically modified fungal biomass and followed by 85% removal using HNO_3 doped chemically modified fungal biomass at 37ºC, pH 2.0 and 150 rpm. The maximum percentage removal of Copper using growing *Aspergillus niger* was found out to be 91 %. The characterization studies were carried out using SEM and EDAX analysis. The Copper metal was found to desorb effectively using 0.1M HCl and was found to be 89 % and the reuse of the Sterilized dry fungal biomass showed 90.72 % Cu removal. Further removal of Cu from Dye insustry effluent was carried out using dry fungal and Sterilized dry biomass and an efficiency of 91.6 % and 94.2 % was obtained.

Keywords : Aspergillus niger, Biosorption, characterization, SEM and EDAX .

1. INTRODUCTION

In most areas, the careless disposal of industrial effluents and other wastes may contribute greatly to the poor quality of the water Industrial wastewaters generally contain high levels of heavy metals and create serious water pollution problems. Heavy metals are non-biodegradable and may be accumulated in living organisms through food chains. Some of the trace elements are essential to living organisms in minute concentrations as they play a significant role in many metabolic processes. However, they adversely affect human health when intake of these metals exceeds their permissible limit. A study on the impact of industrial effluent on water quality was carried out widely due to its most dangerous face on animals, humans and plants. Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters. Heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones, and also block functional groups of vital enzymes. The main threats to human health from heavy metals are associated with exposure to copper, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as WHO. Heavy metals have been used by humans for thousands of years. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years.

Heavy metals present in some industrial wastewaters, such as pulp and paper, petrochemicals, refineries, fertilizers, steel, dye industry and automobile industries have toxic effects on the receiving environment and also on the performance of biological treatment processes. Therefore, removal and recovery of heavy metals from industrial wastewater gained significant attention in recent years. Copper, zinc, nickel, lead, mercury, chromium and cadmium, are the most frequently found heavy metals in industrial wastewaters .

II. MATERIALS AND METHOD

A. Collection of Fungal Culture

Fungal culture (Aspergillus niger MTCC No.478) was collected from Microbial Type Culture Collection (MTTC), Chandigarh. This mother culture of fungus was then used for further studies as a biosorbent. The fungal culture was maintained without contamination.

B. Preparation of Media

Micro-organisms are usually grown or cultured in liquid medium (broth) or on solid medium (agar plates or slants).

1. Composition of Potato Dextrose Agar

Potato Dextrose Broth	2.4 g
Agar Agar	2.0 g
pH	5.6 ± 0.2
Distilled Water	100 ml

2. Medium Preparation

The desired amount of each component was taken in a conical flask and the volume was made up to 100 ml. The flask was shaken well in order to dissolve the components well. Then the mixture was heated in an oven to dissolve the components completely. The conical flask was plugged tightly with a cotton plug and covered. Then the medium was autoclaved at 121°C for 15 minutes to sterilize and to avoid any contamination. Petri plates were also autoclaved. After autoclaving the medium was cooled to about 40-45°C. Cooling the medium to lower temperature may solidify it. So when the medium was cooled to bearable warmth, 10 ml of the medium was poured into each petriplate and was left undisturbed and allowed to solidify for about 30 minutes. The solidified potato dextrose agar was then ready for streaking the fungal sample .

3. *Potato Dextrose Broth Preparation*

24 g of potato dextrose broth was weighed and added to 1000 ml distilled water. The potato dextrose broth medium was then poured into a conical flask and plugged with cotton plug. It was then autoclaved at 121°C for 15 minutes to avoid any contamination. The medium was then kept ready for inoculation.

C. Sub-Culturing of the Biosorbent

The freshly inoculated medium is then incubated at temperature 37°C appropriate for growing the organism. After a period of 7 days, it becomes necessary due to nutrient depletion and medium drying, to transfer the fungal culture to fresh media.

Slants were prepared using potato dextrose agar medium with the same composition as mentioned in the media preparation and poured into test tubes and the medium was allowed to solidify. The fungal culture was then streaked on the slants under aseptic conditions to avoid contamination. The slants were then kept for incubation at 37°C for 3-4 days.

D. Mass Culturing of the Biosorbent

Potato dextrose broth was prepared as per the composition and procedure mentioned in media preparation. Then under sterile condition a loop full of fungal culture was taken and diluted in 1 ml of the distilled water. Then the diluted fungal culture was inoculated into the broth and incubated at 37°C for 4 to 5 days. Proper sterilization

procedure was followed to avoid contamination. After the incubation period mat of fungal biomass was obtained which was further used as a biosorbent.

E. Filtration of the Biosorbent

Filtration is a mechanical or physical operation which is used for the separation of solids from fluids (liquids or gases) by interposing a medium through which only the fluid can pass. Filtration of the biomass is done to separate the fungal biomass from the medium so that it can be utilized as a biosorbent. The fungal biomass was obtained by mass culturing in potato dextrose broth. The fungal mat was then filtered using a filter.

F. Drying of the Biosorbent

Drying is to remove the moisture content in the fungal biomass. The fungal biomass obtained from mass culture was then placed in a petriplate and dried in the oven at 80°C for 5 hours to dry it. Dry biomass was then obtained. The dry biomass was then scrapped from the petriplate, weighed and stored in a container. This biomass was further used as a biosorbent material.

G. Chemical Modification of the Biosorbent

The biosorbent was subjected to pre-treatments using various chemicals. The pre-treated biomass was used in wet and dry forms. The biosorbent was pre-treated using 1N HNO3,1N NaOH, NaOH Doping, HNO3 Doping and Sterilization.

H. Chemical Pre-Treatment

The fungal biomass was boiled at 80°C in 1N HNO3 and 1N NaOH for half an hour. This pre-treated biomass was then used for Copper removal in both wet and dry forms.

I. Sterilization

The fungal biomass was sterilized in an autoclave at 121°C for 15 minutes. This sterilized biomass was then used for Copper removal in both wet and dry forms.

J. Aqueous Copper Solution Preparation

K. Stock solution

The stock solution of aqueous copper of concentration 1000 mg/L was prepared by dissolving 3.9 g of Copper sulfate salt of AR grade in 1000 ml distilled water. The test solution containing copper was prepared by diluting 1 ml of stock solution of metal to the desired concentrations. The Copper concentration was varied in the range of 5 to 25 mg/L.

1. Working solution

Copper working solution was prepared at different concentrations to carry out batch experiments.

5 mg/L: 0.5 ml of stock solution was taken and was made upto100 ml using distilled water.
10 mg/L: 1 ml of stock solution was taken and was made upto100 ml using distilled water.
15 mg/L: 1.5 ml of stock solution was taken and was made upto100 ml using distilled water.
20 mg/L: 2 ml of stock solution was taken and was made upto100 ml using distilled water.
25 mg/L: 2.5 ml of stock solution was taken and was made upto100 ml using distilled water.

2. Biosorption using aqueous copper Solution

Batch experiments were carried out using non-living mycelial suspensions. Batch experiments were carried out in Erlenmeyer flasks by adding 1g of the biosorbent in 100ml of aqueous copper solution at desired concentrations. The flasks were agitated on a reciprocating shaker at constant temperature and at constant pH. The samples were taken at regular intervals of 15 min until the equilibrium was reached. When equilibrium was reached, the biosorbent was separated and the supernatant liquid was analyzed Atomic Absorption Spectroscopy (AAS) and the amount of metal ion adsorbed onto per unit weight of biomass .

1. Effect of Contact Time

The effect of contact time were carried out in a batch reactor for different contact times (0, 15, 30, 45, 60, 120, 180, 240, 270, 300 min) at an initial concentration of 5mg/L of CuSO4 at pH 2.0. The adsorbent dosage was 1 g in 100 ml solution in 100 ml conical flask at room temperature (370C) . The samples were then agitated in a rotary shaker at 150 rpm and at regular intervals the samples were withdrawn, filtered and analyzed using Atomic Absorption Spectroscopy (AAS). Each determination was repeated three times in order to get accurate results.

2. Effect of Initial Metal Ion Concentration

The effect of initial copper ion concentrations were carried out for the initial copper concentration (5, 10, 15, 20, 25 mg/L) in a batch reactor at pH 2.0 at room temperature (370C) . 1g of biomass was added in 100 ml solution in 100 ml conical flask and agitated in a rotary shaker at 150 rpm . The samples were withdrawn at regular intervals until equilibrium was reached and analyzed for remaining copper concentration as mentioned earlier .

3. *Effect of pH*

The equilibrium batch experiments were carried out to study the effect of pH studies, 50ml of copper solution with 5 mg/L concentration was adjusted to various pH (1, 2, 3, 4, 5, 6, 7, 8 and 9) and 1g of biomass at room temperature was added to 100ml of aqueous solution and agitated in a rotary shaker at 150 rpm.The samples were withdrawn at regular intervals until equilibrium was reached and supernatant was analyzed for remaining copper concentration as mentioned earlier .

4. Effect of Biosorbent Dosage

For the effect of biomass loading studies 100 ml of 5 mg/L concentration of copper solution was loaded with different biosorbent dosages (0.5,1.0, 1.5, 2.0, 2.5 and 3g) by keeping pH and temperature as 2.0 and 370C respectively .

L. Effect of Pre-Treatment

The fungal biomass was subjected to modification by various pre-treatments as mentioned earlier. The effect of this pre-treated fungal biomass on percentage removal in 5 mg/L of the initial copper metal ion concentration was studied at pH 2.0 and 37°C.

M. Characterization of the Biosorbent- SEM Analysis

Scanning Electron Microscope was done for the characterization of the biosorbent. A Scanning Electron Microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. For SEM, a specimen is normally required to be completely dry, since the specimen chamber is at high vacuum . The sample for SEM analysis was prepared by drying and powdering the fungal mat obtained from mass culturing. 0.5 g of the dried fungal biomass was given for SEM analysis. 0.5g of fungal sample was added to 50 ml of the copper solution for biosorption. The biosorbed fungal sample was then collected, dried and given for SEM analysis. The surface of the fungal biomass was analyzed before and after Copper biosorption. The change in the surface morphology was studied.

N. Desorption Studies

Desorption studies were carried out so that the fungal biomass can be reused for biosorption purpose. Desorption was performed by desorption agents like 1N HCl, 1N NaOH and 0.1N EDTA. The desorption agents scrap away the Cu(So4)metal bound to the surface of fungus and hence makes the fungal biomass free from metal which can be further used for biosorption . The fungal biomass that has been used for biosorption is collected and weighed before desorption. The desorbing reagents were prepared and the adsorbed fungal biomass was added and kept in shaker overnight. Then the solution was centrifuged. The supernatant obtained was subjected to Atomic Adsorption Spectroscopy to estimate the amount of desorbed and the desorbed fungal biomass obtained as pellet was weighed.

III. RESULTS

A. Collection of fungus culture from MTCC (Chandigarh):

1. Mother-culture of Aspergillus niger

Figure1: The Mother-cultured *Aspergillus niger*.

2. Sub culture of Aspergillus niger

Figure 2: The sub cultured *Aspergillus niger* from its mother culture.

3. Mass culture of Aspergillus niger

Figure 3: The mass cultured *Aspergillus niger*.

B. Biosorption using Aqueous Solution

1. Effect of Contact Time

Table 1: Effect of Contact Time

Time (mins)	**Initial Conc. of Cu(II)**									
	5 mg/L		**10 mg/L**		**15mg/L**		**20 mg/L**		**25mg/L**	
	Conc. Of Cu (mg/L)	Copper Removal (%)	Conc. of Cu (mg/L)	Copper Removal (%)	Conc. Of Cu (mg/L)	Copper Removal (%)	Conc. of Cu (mg/L)	Copper Removal (%)	Conc. of Cu (mg/L)	Copper Removal (%)
0	0	0	0	0	0	0	0	0	0	0
15	2.97	40.6	6.37	36.3	9.85	34.3	14.0	30.0	17.9	28.4
30	2.74	45.2	5.82	41.8	9.46	36.9	13.4	33.0	16.75	33.0
45	2.53	49.4	5.32	46.8	8.74	41.7	12.25	38.75	15.3	38.8
60	2.33	53.4	4.53	54.7	7.67	48.8	11.08	44.6	14.71	41.16
120	1.80	64.0	4.23	57.1	6.87	54.2	9.83	50.85	13.05	47.8
180	1.39	72.2	3.29	67.1	5.57	62.8	8.63	56.85	11.46	54.16

240	0.94	81.2	2.41	75.9	4.38	70.8	7.21	60.95	9.96	60.16
270	0.74	85.2	1.95	80.5	3.92	73.8	5.96	70.20	8.15	67.4
300	0.55	89.0	1.51	84.9	3.24	78.4	5.28	73.6	7.52	69.92
330	0.45	91.0	1.30	87.0	3.15	79.0	4.83	75.85	7.25	71.0
360	0.45	91.0	1.30	87.0	3.15	79.0	4.83	75.85	7.25	71.0
390	0.45	91.0	1.30	87.0	3.15	79.0	4.83	75.85	7.25	71.0

[100 ml Aqueous Metal Solution, pH=2.0, Initial Metal Ion Concentration (C_0) = 5 mg/L,10 mg/L, 15 mg/L,20mg/L and 100 mg/L; Weight of Biosorbent = 1 g, Temperature = 37^0C]

Effect of Contact Time

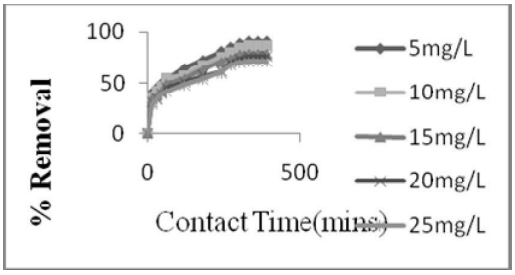

Figure 4: Effect of contact time on bisorption of Cu using A. Niger,

2.Effect of Initial Metal Ion Concentration

Table 2: Effect of Initial Metal Ion Concentration

Initial Metal Ion Concentration (mg/L)	Concentration of Copper (mg/L)	Copper Removal (%)
5	0.45	91
10	1.3	87
15	2.85	81
20	4.8	76
25	7.25	71

[100 ml Aqueous Metal Solution of Initial Concentration = 5 mg/L, 10 mg/L, 15 mg/L,20mg/L and 25 mg/L, pH=2.0, Weight of Biosorbent Dosage = 1 g, and Temperature = 37^0C].

Effect of Initial Metal Ion Concentration

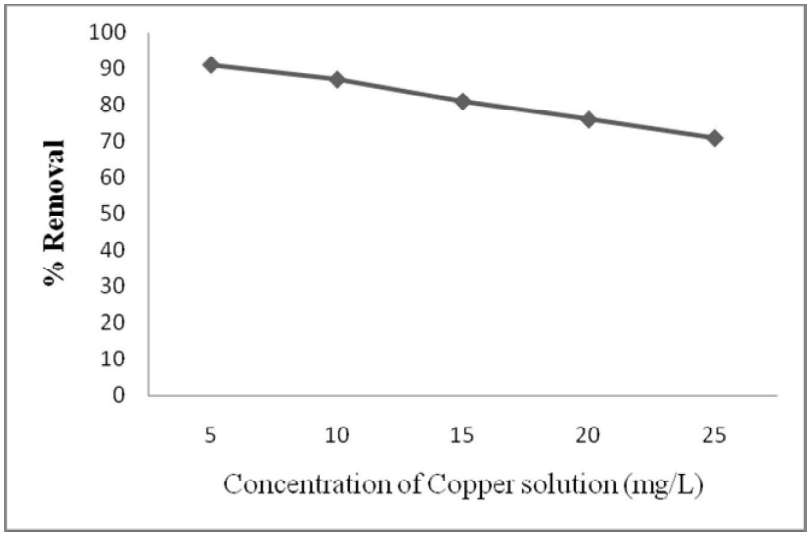

Figure 5: Effect of initial metal ion concentration on biosorption of Copper using *A.niger*;

3. Effect of pH

Table 3: Effect of pH

pH	Concentration of Copper (mg/L)	Copper Removal (%)
1	1.5	70
2	0.75	85
3	0.95	81
4	1.05	79
5	1.2	76
6	1.4	72
7	1.55	69
8	1.75	65
9	1.9	62

[pH = 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0.Volume of Solution = 100 ml; Initial Copper Concentration = 5 mg/L, Weight of Biosorbent Dosage = 1 g, Temperature = 37^0C]

Effect of pH

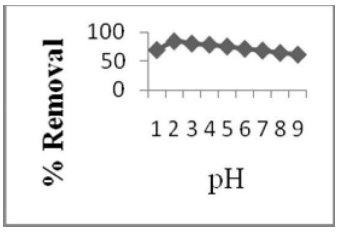

Figure 6: Effect of pH on adsorption of Copper using *A.niger;*

4. *Effect of Biosorbent Dosage*

Table 4: Effect of Biosorbent dosage

Biosorbent Dosage (g)	**Concentration of Copper (mg/L)**	**Copper Removal (%)**
1	1.4	72
2	1.25	75
3	1.05	79
4	0.75	85
5	0.45	91

[Weight of Biosorbent = 1.0, 2.0, 3.0, 4.0, and 5.0 g, Volume of Solution = 100 ml, Initial Copper Concentration = 5 mg/L, Weight of Biosorbent Dosage = 1 g, pH = 2.0,Temperature =37^0C]

Effect of Biosorbent dosage

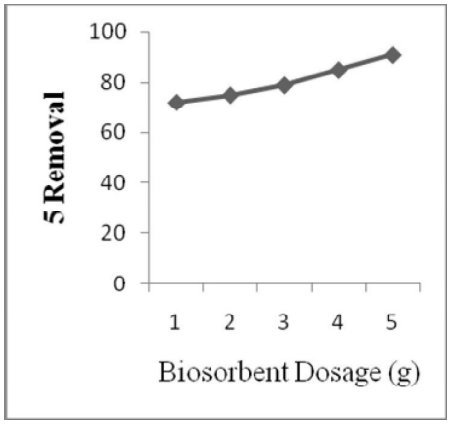

Figure 7: Effect of biomass loading on adsorption of copper using *A.niger;*

5. Effect of Pre-Treatment

Table 5: Effect of pre-treatment

Pre-Treatment	Concentration of Copper (mg/L)	Copper Removal (%)
HNO_3 Treated Dry	0.85	83
NaOH Treated Dry	1.05	79
Sterilized Dry	0.45	91
HNO_3Treated Wet	1.05	79
NaOH Treated Wet	1.2	76
Sterilized Wet	0.55	89
NAOH Doping	0.9	82
HNO3 Doping	0.75	85

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[Volume of Copper solution = 100 ml, Initial Copper Concentrations = 5 mg/L, pH = 2.0, Temperature = 37^0C].

Table 5: Effect of pre-treatment

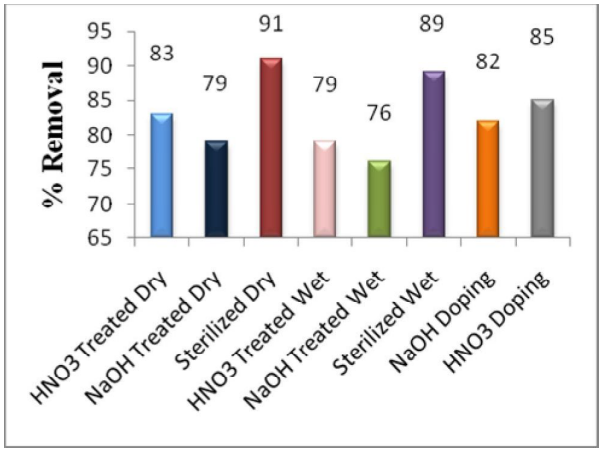

Figure 8: Effect of pre treatment of fungal biomass on adsorption of copper using variously pre-treated *A.niger*

6. Characterization of Biosorbent using SEM Analysis

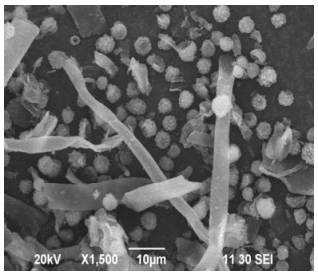

Figure 9: SEM image of *Aspergillus niger* Before Copper adsorption

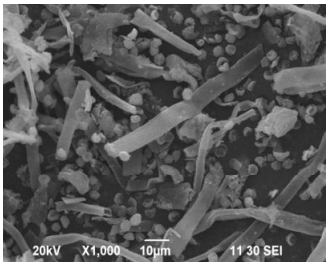

Figure 10: SEM image of Aspergillus niger after Copper adsorption

7. Characterization of Biosorbent using EDAX Analysis

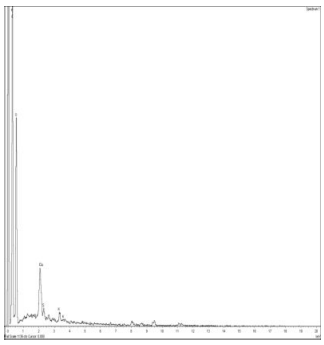

Figure 11: EDAX image of *Aspergillus niger* Before Copper adsorption

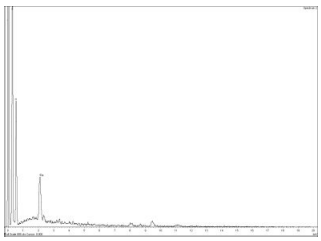

Figure 12: EDAX image of Aspergillus niger After Copper adsorption

8. Desorption Studies

Table 6: Effect of desorption

Reagents	**Weight of Biosorbent (g)**		**Concentration of Cu (mg/L)**	**Desorbed Copper (%)**
	Before Desorption	**After Desorption**		
1 N HCl	1.25	1.09	0.6	88
1 N NaOH	1.274	1.11	0.75	85
0.1 N EDTA	1.29	1.13	0.65	87

[Initial Cu Concentration = 5 mg/L, pH 2.0, Volume of solution = 100 ml, Weight of Biosorbent Dosage = 1 g]

Table 7: Effect of Recycled fungal biomass on biosorption

Reagents	**Concentration of Cu (mg/L)**	**Copper Removal (%)**

1 N HCl	0.55	89
1 N NaOH	0.60	88
0.1 N EDTA	0.65	87

[Initial Cu Concentration = 5 mg/L, pH 2.0, Volume of solution = 100 ml,Weight of Biosorbent Dosage = 1 g]

C. Biosorption of Dye industry effluent

A. Batch Experiment

Table 8: Percentage Removal of Copper from using dye industry effluent *Aspergillus niger*

Copper Solution	Biosorbent Used	Copper Removal (%)
Using Aqueous Solution	**Dry Fungal biomass**	92.48
	Sterilized Dry Fungal Biomass	96.99
Using Dye industry effluent	**Dry Fungal biomass**	91.6
	Sterilized Dry Fungal Biomass	94.2

[100 ml aqueous metal solution, pH=2.0, Initial metal ion concentration (C_0) =5 mg/L,Weight of biosorbent dosage = 1 g, and Temperature = 37^0C.]

Biosorption of Copper from using dye industry effluent using *Aspergillus niger*

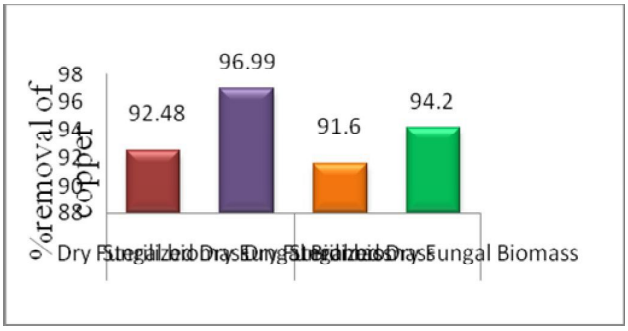

Figure 13: Biosorption efficiency of Aspergillus niger from Dye industry effluent.

D. Desorption Studies

Table 9: Effect of Desorption using Dye industry effluent

Reagents	Weight of Biosorbent		Concentration of Copper (mg/L)	Desorbed Copper (%)
	Before Desorption	After Desorption		
1 N HCl	1.4	1.13	0.11	89

[Initial Copper Concentration = 55 mg/L , pH 2.0, Volume of solution = 100 ml, Weight of Biosorbent dosage 1 g]

Table 10: Effect of Recycled Fungal Biomass on Biosorption

Reagents	Concentration of Copper (mg/L)	Copper Removal (%)
1 N HCl	0.5	90

[Initial Copper Concentration = 5 mg/L , pH 2.0, Volume of solution = 100 ml, Weight of Biosorbent dosage = 1 g, Temperature =37◦C.]

IV. DISCUSSION

A. Mass culturing the organism

1 Culturing of Aspergillus niger

The culture Aspergillus niger was obtained from MTCC as shown in the figure 1. The fungus was grown in Potato Dextrose Agar. The obtained mother culture was subcultured using Potato Dextrose Broth as shown in the figure 2.

2 Mass culturing of Aspergillus niger

The fungal biomass was cultivated in large amount in potato dextrose broth. Mass Culturing of the biomass was carried out and was obtained as mat as shown in figure 3 which was further used as wet or dried to be used as dry biomass.

B. Biosorption using Aqueous Solution

1. Effect of Contact Time

The effect of contact time on Copper biosorption using dead Aspergillus niger was studied and the results are shown in Figure 4 and the values are tabulated in Table 1. It was found that the adsorption efficiency of Copper ion increases as the contact time is increased and equilibrium reached at 330 mins with a removal of 91%. Hence, in the present study, 330 mins was chosen as the equilibrium time. Initially the removal rate of the sorbate was rapid, but it gradually reached equilibrium and remained constant as time was increased above the equilibrium time. The rate in percent of metal removal was higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of the metals . The adsorption of the Copper was greater at earlier stages due to the availability of more number of active sorption sites. As time passes the metal uptake by the sorbent surface slows down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution .

2.Effect of Initial Metal Ion Concentration

The percentage removal of copper decreases with increase in initial copper concentration as shown in Figure 5 and the values are tabulated in Table 2. The percentage removal of copper decreased from 91% (at 5 mg/L) to 71% (at 25 mg/L). The decrease in the extent of removal percentage of copper with increase in the initial metal ion concentration may be due to the reduction in immediate adsorption due to the lack of available active sites . For higher concentration of copper the percentage removal decreases mainly due to the saturation of binding sites .

3.Effect of pH

The effect of pH on the percentage removal of copper at 5mg/L copper concentration was studied as a function of pH at constant fungal doses and the results are shown in Figure 6 and the values are tabulated in Table 3. It is clear from the figure that the percentage removal of copper is 85 % at pH 2.0. The percentage removal increases with increase in pH from 1.0 to 2.0 and thereafter decreases with further increase in pH. This behavior can be explained by considering the nature of the biosorbent at different pH in copper biosorption. The cell wall of Aspergillus species contains a large number of surface functional groups. The pH dependence of copper biosorption can largely be related to the type and ionic state of these functional groups and also on the metal chemistry in solution .Maximum sorption of copper occurs at pH 2.0 which suggests that the negatively charged copper species bind through electrostatic attraction to positively charged functional groups on the surface of fungal cell wall because at this pH more functional groups carrying positive charges would be exposed. But at pH above 3.0, it seems that fungal cell wall possess more functional groups carrying a net negative charge which tends to repulse the anions .

4. Effect of Biosorbent Dosage

The effect of biomass loading on percentage removal of copper was studied and is depicted in Figure 7 and the values are tabulated in Table 4. Metal uptake with variation in biosorbent dosages has been reported . It indicates that increase in the biomass loading from 1 g to 5 g increases the rate of sorption from 72% to 91%. The increase in Copper adsorption may possibly be due to the increased number of binding sites for copper ions at higher cell loading .

5. Effect of Pre-Treatment

The effect of various pre treated biomass on percentage removal was studied at 5 mg/L of the initial copper metal ion concentration. The corresponding values of percentage removal are depicted in Figure 8 and the values are tabulated in Table 5. A maximum Copper removal of 91% was obtained using Sterilized dry chemically modified fungal biomass followed by 89% removal using Sterilized wet chemically modified fungal biomass and followed by 85% removal using HNO3 doped chemically modified fungal biomass at 37ºC, pH 2.0 and 150 rpm. This indicates that when the cell wall of fungal biomass undergoes modifications and gets altered due to various pre-treatments and hence the extent of its copper adsorption varies .

6. Characterization of Biosorbent Using SEM Analysis

Scanning electron microscopy analysis has been used for the characterization of the adsorbent. The adsorbent Aspergillus niger biomass was characterized before and after it was subjected to Copper metal ion adsorption is shown in Figure 9 and figure 10 respectively. The Scanning electron microscopy scans the surface of the adsorbent and the change in morphology of the adsorbent surface was studied. The surface of the fungal biomass showed that the biomass appeared scattered before adsorption to Copper and the biomass appeared complexed with Copper after adsorption.

7. EDAX Analysis

EDAX (Energy Dispersive X-ray Spectroscopy) is an analytical technique which utilizes x-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental composition of the specimen. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons. The EDAX detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements. Modern SEM/EDS instruments are operated using very sophisticated software. These software programs allow unattended feature analysis and “mapping” of the composition of the elements on the surface of the specimen. .

8. Desorption Studies

The adsorbed biomass was found to be clustered with Copper metal ion. These heavy metals retard the further adsorption of Copper metals to A.niger . Hence inorder to recycle the fungal biomass the metal adsorbed to A.niger was subjected to desorption studies and the values of desorption based on the weight of biosorbent tabulated in Table 7. The Copper metal was found to desorb effectively using 0.1 N HCl and was found to be 88 %. Desorbed A.niger was again subjected to Copper adsorption and the metal removal was slightly higher than the first cycle and was found out to be 88%. The biomass was also weighed after adsorption of Copper metal and after Desorption. The weight of biomass showed significant difference. The weight of fungal biomass increased from 1 g to 1.25 g after adsorption and the weight of fungal biomass decreased to 1.09 g after desorption in 1N HCl indicating that the desorption was effective. Desorption is essential in order to reuse the fungal biomass. The biosorption using desorbed fungus was also found to be efficient and the values are tabulated in Table 6.

C. Biosorption using Dye industry Effluent

1. Batch Experiment

The AAS results showed that the electroplating effluent had 0.60 mg/L concentration of Cu (So4). So the dye industry effluent was made to 5 mg/L of Cu (So4) and the pH was adjusted to 2.0 and 37°C. The OD values obtained after 330 minutes showed that a maximum removal of 91.6 % was obtained using 1 g of the dry fungal biomass. The removal performed using Sterilized dry fungal biomass also showed a maximum Cu (So4) removal of 94.2%. The percentage adsorption using the dry and pre-treated fungal biomass is shown in Figure 13 and the values are shown in Table 8.

2. Desorption Studies

The biosorbed fungus was then weighed which showed increase in weight from 1 g to 1.4 g. then after desorption using 1N HCl the weight of fungal biomass decreased to 1.13 g indicating the efficiency of desorption process. The concentration values of the desorbed supernatant showed 90 % removal of Cu (So4) from the biosorbent. The values of desorption based on OD and weight and the recycle efficiency of the biosorbent are tabulated in Table 9 and Table 10 respectively.

V. CONCLUSION

The present work has been successfully carried out. The results show that the Copper can be effectively removed upto 91% from the aqueous solution using 1 g dry fungus from 5 mg/L concentration copper solution at pH 2.0, 37°C. The results also showed that when the biosorbent dosage was increased the removal was also found to increase linearly. Further when the fungus Aspergillus niger was pre-treated using various chemicals the efficiency of their copper metal removal increased. Maximum Copper removal of about 91% was obtained when the biosorbent sterilized dry was used followed by alkali treated dry biosorbent and biosorbent sterilized wet yield 89 % and 85 % removal efficiency respectively at 37ºC, pH 2.0 and 150 rpm. The percentage removal of Copper using growing fungus was found out to be 91%. The desorption studies showed that 89 % of the Copper was effectively desorbed from the biosorbent using 1 N HCl and the reuse of the biosorbent showed a maximum of 90.72 % Copper removal. Copper concentration 5 mg/L, pH 2.0, 1 g biomass was used for biosorption in Dye industry effluent. A maximum removal of about 91% was obtained using dry Aspergillus niger. Further pre-treated biomass was used for removal from Dye industry effluent. Maximum Copper removal of about 94.2 % was obtained when the biosorbent doped with nitric acid was used. The desorption studies showed that 89 % of Copper was desorbed from the fungal biomass using 1 N HCl and the reuse of the biosorbent showed a maximum of 90% Copper removal.

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