RESEARCH REVIEW JOURNALS
Volume-03
Issue-10
October -2018

ISSN: 2455-3085 (Online)
RESEARCH REVIEW International Journal of Multidisciplinary
www.rrjournals.com [UGC Listed Journal]

Abatement of Cu (II) by dead biomass of *Mucor rouxii*

Dr. Kishor Kumar Singh

Associate Professor, Department of Chemistry, Govt. Post Graduate College, Obra, Sonebhadra (U.P.), India

ARTICLE DETAILS

Article History
Published Online: 10 October 2018

Keywords
Adsorption, Cu (II), Mucor rouxii, Exothermic, Multiple regressions, Isotherm

ABSTRACT

Dead biomass of Mucor rouxii has been used for the removal of copper (II) from an aqueous solution. The effects of different parameters such as contact time, adsorbate concentration, pH of the medium and temperature were examined. Optimum removal at 20^{0}C was found to be 98.6 % at pH 6.6, with an initial Cu (II) concentration of 100 mg L^{-1}. Dynamics of the sorption process and mass transfer of Cu (II) to sorbent were investigated and the values of rate constant of adsorption, rate constant of intraparticle diffusion and the mass transfer coefficients were calculated. Different thermodynamic parameters viz., changes in standard free energy, enthalpy and entropy were evaluated and it was found that the reaction was spontaneous and exothermic in nature. The sorption data fitted the Langmuir isotherm. The data were subjected to multiple regression analysis and a model was developed to predict the removal of Cu (II) from an aqueous solution.

1. Introduction

Nowadays heavy metals are among the most important pollutants in water, and are becoming a severe public health problem. Sorption of heavy metals by bacterial fungal or algal biomass (live or dead cells) and agricultural waste biomass[1-12] has been recognized as a potential alternative to existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for the removal of heavy metals from industrial wastewater because all these processes have the limitations of technical and/or economical viability.

The literature reveals two distinct approaches to use of living organisms and biomass[13-14]. There are practical limitations to systems, which employ living microorganisms. The most significant limitation is that microbial growth is inhibited when the concentrations of metal ions are too high or when significant amount of metal ions are sorbed by microorganisms[13]. Dead cells or agricultural wastes accumulate heavy metal ions to a greater extent than living cells[13-15]. For metal removal applications, the use of dead biomass or agricultural waste may be preferable as large quantities are readily and cheaply available as a byproduct of various industries[16]. Therefore, Mucor rouxii was used for the removal of Cu (II) from waste water.

2. Materials and methods

2.1 Physico-chemical analysis of the biosorbent

The strains were maintained and propagated in yeast extract-peptone-glucose (YPG) medium[17]. Spores were harvested in sterile distilled water from 3 to 5-day-old cultures, stored at 4ºC and used within two weeks of harvest. The harvested spores were inoculated in two flasks to a final density of 5 x 10^5 spores/ml. The two flasks contained 500 ml liquid YPG medium with pH adjusted to 4.5. Cultures were grown aerobically for 13-18 hr at 28ºC on a reciprocating shaker bath at 180 rpm. After 48 hr, cells were collected by filtration onto Whatman No.1 filter paper in a Millipore funnel. The resulting mycelium was washed, freeze-dried (in a Labconco freeze-dryer), ground and sieved to less than 178 µm size. The surface area of Mucor rouxii biomass was determined by a three point N_2 gas adsorption method using a Quantasorb Surface Area Analyser (model Q5-7, Quantachrome Carporation, USA). The bulk density was determined by densitometer. Porosity was determined by Porositometer (model: M7V, NGRI Hyderabad, India). X-Ray diffraction of the adsorbent was obtained using X-ray Diffractometer (model: ID-3000W, Rich Siefert and Company, Ahrensberg, Germany). Percentage of volatile matter, ash and moisture were determined as given in the "Vogel's Text Book of Quantitative Chemical Analysis", 5th Edition, Bath Press Ltd, U.K.

Various physicochemical properties of Mucor rouxii thus obtained are given in **Table 1**.

Table 1

Physical and Chemical properties of biosorbent Mucor rouxii

Surface area (m^2g^{-1})	415.00
Bulk density (g cm^{-1})	0.2422
Particle size (µm)	<178
Porosity	0.32
Proximate Analysis (%)	
Volatile matter	42.15
Moisture	7.55
Fixed carbon	31.32
Ash (Oxides of Al, Mn, Si, Fe and others)	18.98

2.2 Batch Sorption Experiment[18]

Batch experiments were conducted by adding 1 g sorbent in 50 mL aqueous solution of copper nitrate of desired concentration (100,125 and 150 mg L^{-1}) at different temperatures (20, 30 and 40 ºC) and pH (3.2, 4.0, 5.0, 5.5, 6.0, 6.6, 7.0, 8.0 and 9.0) in different glass bottles in a shaking thermostat set at 20, 30 and 40 ºC at a constant speed of 125 rpm. The pH of the adsorbate solution was adjusted by adding 0.1M HCl or 0.1M NaOH. The progress of the adsorption process was observed at different time intervals till the attainment of saturation. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by centrifugation at 15000 rpm and the supernatant liquid was analyzed by AAS to determine the residual concentration of copper ion. Blanks solutions were run under similar conditions of concentration, pH and temperature without the adsorbent in all the cases to correct for any adsorption on the internal surface of the bottles.

3. Results and discussion

3.1 Effect of contact time and concentration[18]

A series of experiments were performed at different adsorbate concentration viz., 100, 125 and 150 mg L^{-1} and time interval. The Cu (II) removal was found to be 97.25, 92.65 and 86.55 % respectively, at 30 ºC and pH 6.6. The extent of adsorption increased rapidly in the initial stages and became slower at later stages until the attainment of equilibrium. Equilibrium time for the adsorption of Cu (II) on dead biomass of Mucor rouxii at various adsorbate concentrations was found to be 110 minutes, which indicated that equilibrium time was independent of the initial adsorbate concentration. The following correlation had been developed between percentage removal and initial adsorbate concentration (C_o) to predict the percentage removal of Cu (II) by dead biomass of Mucor rouxii at any initial concentration.

Percentage removal of Cu (II) $= 33.5\, C_o^{\,0.66}$

3.2 Adsorption dynamics

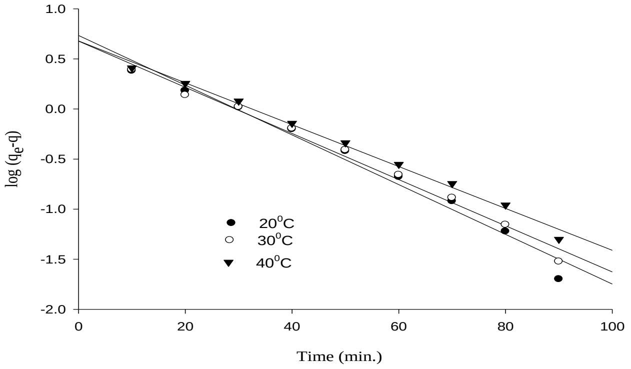
The rate constant k_{ad} (min^{-1}) for Cu (II) adsorption on Mucor rouxii was determined by using the Lagergren equation[19].

$$\log (q_e - q) = \log q_e - \frac{k_{ad}}{2.303} . t \qquad (1)$$

Where q (mgg^{-1}) and q_e (mgg^{-1}) are the amounts of adsorbate at time t (min.) and at equilibrium respectively. The linear plots of log (q_e-q) versus t (Fig. 1) suggest the first order kinetics of the uptake of Cu (II). The values of k_{ad} (5.682×10^{-2}, 5.158×10^{-2} and 4.676×10^{-2} min^{-1}) at different temperatures were calculated from the slopes of these plots[20].

Fig.1 RATE CONSTANT PLOT FOR ADSORPTION OF Cu (II) ON DEAD BIOMASS OF Mucor rouxii AT DIFFERENT TEMPERATURES

CONDITIONS: PARTICLE SIZE: < 178 µm; CONCENTRATION 100 mg L^{-1};
pH: 6.6; TEMPERATURE: 20, 30 and 40^0C.



The data was also tested for pore diffusion using the following equation[21].

$$q = k_{id}\, t^{½} \qquad (2)$$

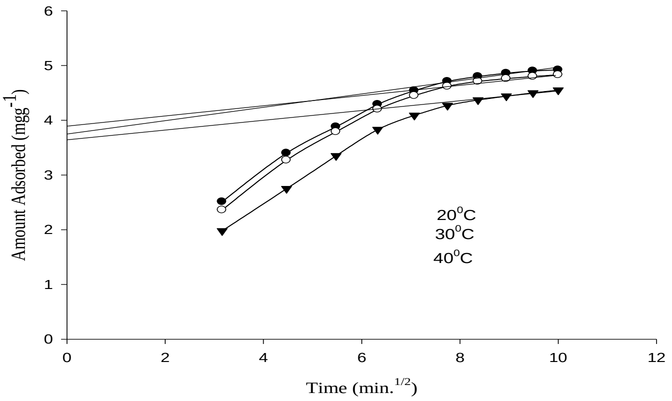
Where, q is the amount sorbed at time t and $t^{½}$ is the square root of the time. The values of k_{id} (3.595×10^{-2}, 3.275×10^{-2} and 2.865×10^{-2} $mgg^{-1}min^{-1/2}$) at temperatures 20, 30 and 40°C respectively, were calculated from the slopes of respective plot q versus $t^{½}$ (Fig. 2) at later stages. The dual nature of the curves was obtained due to the varying extent of sorption in the initial and final stages of the experiment[20]. This can be attributed to the fact that in the initial stages, sorption was due to boundary layer diffusion effect whereas, in the later stages (linear portion of the curve) was due to the intraparticle diffusion effects. However, these plots indicated that the intraparticle diffusion was not the only rate controlling step because it didn't pass through the origin. This was further supported by calculating the intraparticle diffusion co-efficient ($\overline{D}$, $cm^2\, sec^{-1}$) using the following equation[22].

$$\overline{D} = 0.03r^2 / t_{1/2} \qquad (3)$$

where r (cm) is the average radius of the sorbent particle and $t_{1/2}$ (min.) is the time for half of the sorption. According to the Michelsen et al. a $\overline{D}$ ($cm^2\, sec^{-1}$) value of the order of 10^{-11} is indicative of intraparticle diffusion as rate determining step[23]. In this investigation, the values of $\overline{D}$ (8.165×10^{-9}, 7.275×10^{-9} and 5.796×10^{-9} $cm^2 sec^{-1}$ at 20, 30 and 40 ºC respectively) obtained was in order of 10^{-9} $cm^2\, sec^{-1}$ which was more than two order of magnitude higher, indicated that the intraparticle diffusion was not the only rate controlling step. It was concluded that both boundary layer and intraparticle diffusion might be involved in this removal process[20].

Fig.2 INTRAPARTICLE DIFFUSION PLOT FOR ADSORPTION OF Cu (II) ON DEAD BIOMASS OF Mucor rouxii AT DIFFERENT TEMPERATURES

CONDITIONS: PARTICLE SIZE: <178 µm, CONCENTRATION: 100 mg L^{-1},
pH: 6.6, TEMPERATURE: 20, 30 and 40^0C.



3.3 Mass Transfer Study[20]

The uptake of pollutant species from liquid phase (sorbate) to solid surface (sorbent) is carried out by transfer of mass from the former to the latter. A number of steps can be considered participating in the process and out of various models tried for the present studies, overall sorption process is assumed to occur using a three-step model[24]:

Mass transfer of sorbate from the aqueous phase on to the solid surface.

Sorption of solute on to the surface sites, and

Internal diffusion of solute via either a pore diffusion model or homogeneous solid phase diffusion model.

During the present investigation, step (2) has been assumed rapid enough with respect to the other steps and therefore it is not rate limiting in any kinetic study. Taking in to account these probable steps, Mckay et al. model has been used for the present investigation[24]:

$$\ln\left(\frac{C_A}{C_{A_0}}-\frac{1}{1+mK}\right)=\ln\left(\frac{mK}{1+mK}\right)-\left(\frac{1+mK}{mK}\right).\beta_1.S_s.t \qquad (4)$$

where, m is the mass of the biosorbent per unit volume, K is the constant obtained by multiplying Q^0 and b (Langmuir's constants), β_1 is the mass transfer coefficient, S_s is the outer specific surface of the biosorbent particles per unit volume of particle-free slurry. The values of m and S_s were calculated using the following relations:

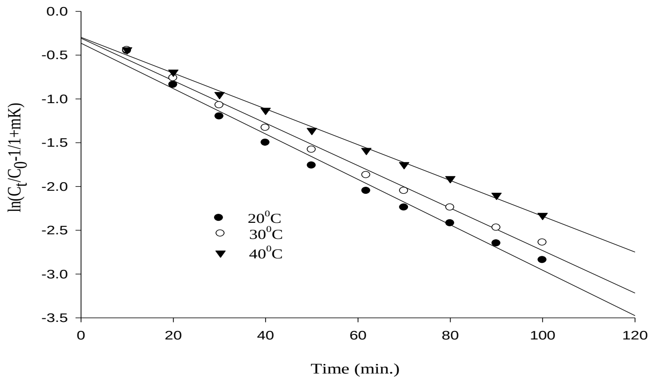
$$m=\frac{W}{V}, \qquad (5)$$

$$S_S=\frac{6m}{d_P\delta\rho(1-\varepsilon_P)}, \qquad (6)$$

where, W is the weight of the adsorbent, V the volume of particle-free slurry solution, and dp, δρ and εp are the diameter, density and porosity of the adsorbent particles, respectively. The values of β_1 (5.615×10^{-5}, 4.995×10^{-5} and 4.175×10^{-5} cm sec^{-1}) calculated from the slopes and intercepts of the plots (Fig. 3) of ln (C_t/C_0 – 1/1+ mK) versus t (min.) at different temperatures (20, 30 and 40 ºC). The values of β_1 obtained show that the rate of transfer of mass from bulk solution to the biosorbent surface was rapid enough so it cannot be rate controlling step[25]. It can also be mentioned that the deviation of some of the points from the linearity of the plots indicated the varying extent of mass transfer at the initial and final stages of the sorption[20].

Fig.3 MASS TRANSFER PLOT FOR THE ADSORPTION OF Cu (II) ON DEAD BIOMASS OF Mucor rouxii AT DIFFERENT TEMPERATURE

CONDITIONS: CONCENTRATION: 100 mg L^{-1}; PARTICLE SIZE: < 178 µm; pH: 6.6; TEMPERATURE: 20, 30 and 40^0C.



3.4 Thermodynamic evaluation of the process[20]

This was again confirmed by thermodynamic parameters such as free energy (ΔG^0, k cal mol^{-1}), enthalpy (ΔH^0, k cal mol^{-1}) and entropy (ΔS^0, cal mol^{-1} k^{-1}) changes during the process. These parameters (**Table 2**) were calculated at 20, 30 and 40^0C temperatures[26]. The negative and small values of free energy change (ΔG^0) were an indication of the spontaneous nature of the adsorption process. The negative values of standard enthalpy change (ΔH^0) for the intervals of temperatures was indicative of the exothermic nature of the adsorption process and the negative values of ΔS^0 for the corresponding temperature intervals suggested the probability of favourable adsorption[20].

3.5 Adsorption isotherm[20]

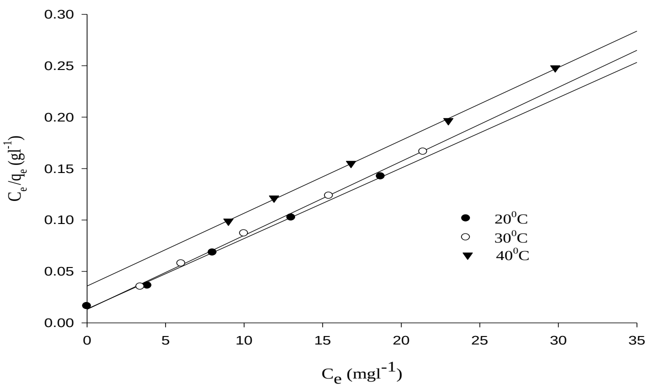
The experimental data was found to fit the Langmuir isotherm. The basic assumption of Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent. The saturated monolayer is represented by the following equation.

$$\frac{C_e}{q_e}=\frac{1}{Q^0 b}+\frac{C_e}{Q^0} \qquad (7)$$

Where, C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, q_e (mgg^{-1}) is the amount of adsorbate adsorbed at equilibrium; Q^0 (mgg^{-1}) and b (lmg^{-1}) is the Langmuir constants related to the capacity and energy of the adsorption respectively. The linearity of the plots C_e/q_e versus C_e (Fig. 4) showed the applicability of the Langmuir isotherm for the present system. Q^0 and b were determined from the slopes and intercepts of the respective plots. The decrease in their values (**Table 2**) with temperature increase also supported that removal of Cu (II) on Mucor rouxii was exothermic in nature[8,25]. High Q^0 values (Table 1) also showed that the adsorbent had a good capacity to remove Cu (II)[20].

Fig.4 LANGMUIR ISOTHERM PLOT FOR THE ADSORPTION OF Cu (II) ON Mucor rouxii AT DIFFERENT TEMPERATURES.

CONDITIONS: PARTICLE SIZE: <178 µm; TEMPERATURE: 20, 30, 40^{0}C; pH: 6.6; CONCENTRATION: 100, 110, 125, 140 and 150 mg L^{-1}.



The equilibrium parameter R_L which is defined as $R_L = 1/(1+bC_0)$ in the range $0 < R_L < 1$ reflects a favourable adsorption process[27] where b (l mg^{-1}) is the Langmuir's constant and C_0 (mg L^{-1}) is initial adsorbate concentration. In the present investigation the equilibrium parameter (Table 2) was found to be in the range $0 < R_L < 1$ indicating that the adsorption process was favourable and the Langmuir isotherm was applicable[27].

Table 2

Values of thermodynamic parameters, Langmuir constants and R_L values of Cu (II) adsorption on dead biomass of Mucor rouxii at different temperatures

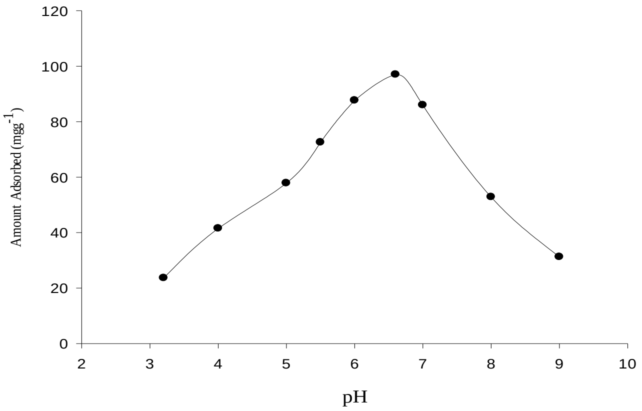
Temp. ^{0}C	$-\Delta G^0$ (k cal mol^{-1})	$-\Delta H^0$ (k cal mol^{-1})	$-\Delta S^0$ (cal mol^{-1} k^{-1})	Q^0 (mg g^{-1})	b (l mg^{-1})	R_L
20	1.475			142.95	0.965	0.0115
30	1.070	18.355	57.025	140.90	0.550	0.0185
40	0.495			136.95	0.215	0.0474

3.6 Effect of pH[20]

Experiments were performed at different pH values (3.2, 4.0, 5.0, 5.5, 6.0, 6.6, 7.0, 8.0 and 9.0). The percentage removal increased from 23.6 to 97.25 % with an increase of pH from 3.2 to 6.6 and thereafter removal decreased from 97.25 to 31.4 % with an increase of pH from 6.6 to 9.0, at 30^{0}C and Cu (II) concentration of 100 mg L^{-1}. The optimum pH for the removal of Cu (II) on Mucor rouxii was found 6.6 (Fig. 5). Furthermore, the adsorption process can be explained on the basis of the nature of adsorbent used which contained several metal oxides. These oxides when mixed up with adsorbate solution undergo surface hydroxylation and form hydroxyl compounds on the surface which gives positively or negatively charged surface as a result of subsequent acid base dissociation[28]. It can be seen that adsorption increased in the pH range 3.2-6.6 and beyond pH 6.6, it started to decrease. The increase in adsorption correlated with the presence of Cu (II) ions up to pH 6.6. Beyond pH 6.6, the formation of hydroxide of Cu (II) occurred which resulted in a decrease in adsorption. This fact was alsosupported by the distribution of copper species at different pH values [29].

Fig.5 EFFECT OF pH ON THE REMOVAL OF Cu(II) BY Mucor rouxii.

CONDITIONS: CONCENTRATION: 100 mg L^{-1}; PARTICLE SIZE: <178 µm; TEMPERATURE: 30^{0}C; pH: 3.2, 4.0, 5.0, 5.5, 6.0, 6.6, 7.0, 8.0 and 9.0.



MULTIPLE REGRESSION ANALYSIS[20]

The effect of initial adsorbate concentration, contact time, temperature and pH of the system on Cu (II) removal by Mucor rouxii had been examined. The cumulative effect of all these independent variables (copper removal) is given by the following relation:

$$Y= 6.5598 + 0.6386a_1 + 0.5172a_2 - 0.4674a_3 + 0.2838a_4 - 0.0952a_5 \qquad (14)$$

Where, Y is the predicted value of Cu (II) removal, a_1, concentration of adsorbate, a_2, contact time; a_3, temperature; a_4, pH; a_5, agitation rate of the system. The model values calculated with the help of equation (14) and the experimental values are given in **Table 3**. It may be seen that predicted values were pretty close to the experimental values. From these results it is concluded that all independent variables have cumulative effect on copper removal by Mucor rouxii.

TABLE 3

PERCENTAGE REMOVAL AT DIFFERENT CONDITIONS (EXPERIMENTAL AND PREDICTED VALUES AT EQUILIBRIUM TIME, pH 6.6 AND AGITATION RATE 125 RPM).

Initial Cu (II) concentration (mg L^{-1})	**PERCENTAGE REMOVAL**		**Temp. (^{0}C)**	**PERCENTAGE REMOVAL**	
	Exp. value	**Predicted value**		**Exp. value**	**Predicted value**
100	97.25	97.55	20	98.95	99.60
125	92.65	93.20	30	97.25	97.55
150	86.55	86.85	40	91.76	92.85

4. Conclusion

The dead biomass of Mucor rouxii was found to be an effective biosorbent for the removal of Cu(II). The study showed that the temperature and pH of the solution strongly influenced the adsorption process. Adsorption in the initial stages was very rapid due to the boundary layer diffusion whereas in the later stages became slower due to intraparticle diffusion. Thermodynamic studies confirmed that the process was spontaneous and exothermic. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption. Mass transfer studies confirmed that the rate of mass transfer from sorbate to adsorbent was rapid enough. The data thus obtained would be useful in designing and fabricating an efficient treatment plant for Cu (II) rich effluents.

REFERENCES

[1] YG Bermudez; ILR Rico; OG Bermudez; E Guibal. *Chem. Engg. J.*, **2011**, 166, 122 – 131.

[2] X Li; Hao Yu; X Zhang; K Wu; Y Yuan; S Zhang. *J. Haz. Mater.*, **2017**, 330, 1-8.

[3] H Wang; X Wang; J Ma; P Xia; J Zhao. *J. Haz. Mater.*, **2017**, 329, 66-76.

[4] S Wang; T Vincent; C Faur; E Guibal. *Bioresource Technol.*, **2017**, 231, 26 -35.

[5] MMM Rahmati; P Rabbani; A Abdolali; AR Keshtkar. *J. Haz. Mater.*, **2011**, 185, 401- 407.

[6] X Xie; R Deng; Y Pang; Y Bai; Y Zhou. *Chem. Engg. J.*, **2017**, 314**,** 434-442.

[7] D Mohan; CU Jr Pittaman. *J. Hazard. Mater.*, **2006**, B137**,** 762-811.

[8] PYR Suzaki; MT Munaro; CC Triques; MRF Klen; LMM Jorge; R Bergamasco. *Chem. Engg. J.*, **2017**, 313**,** 364-373.

[9] N Feng; X Guo; S Liang; Y Zhu; J Liu. *J. Haz. Mater.*, **2011**, 185, 49-54.

[10] R Dobrowolski; M Czemierska; AJ Wilolazka. *Bioresource Technol.*, **2017**, **225**, 113-120.

[11] AJ Munoj; F Espinola; E Ruiz; *J. Haz. Mater.*, **2017**, 329, 166-177.

[12] Y Niu;K Li; D Ying; Y Yang; J Jia. *Bioresource Technol.*, **2017**, **229**, 63-68.

[13] SG Tuncel; S Tugrul; T Topal. *Water Res.*, **2007**, 41, 365 – 372.

[14] SH Hasan; KK Singh; O Prakash; M Talat; YS Ho. *J. Hazard. Mater.*, **2008**, 152, 356- 365.

[15] HT Nguyen; KH Kim. *Atmos. Environ.*, **2008**, 42, 5015 – 5031.

[16] H Yin; B He; X Lu; H Peng; J Ye; F Yang. *Water Res.*, **2008**, 42, 3981 – 3989.

[17] S. Bartnicki-García and W.J. Nickerson, Nutrition; *J. Bacteriol.*, **1962**a, 84, 841-858.
[18] Kishor Kumar Singh; Int. *J.Inno.Sc.Engg. Technol.*, **2017**, 4(6), 259-264.

[19] S Lagergren. *Handlingar*, **1898**, 24, 1- 39.

[20] Kishor Kumar Singh; J. Chem. Pharm. Res., **2015**, 7(11), 680-686.

[21] WJ Weber; JC Morris. *J. San. Eng. Div. Proc. Anal. Soc. Civil Engr.*, **1963**, 89, SA2, 31- 38.

[22] AK Bhattacharya; C Venkobachar. *J. Environ. Eng.*, **1984,** 110, 110 – 120.

[23] LD Michelsen; PG Gideon; EG Pace; LH Kutsal, . *USDI, Office of Water Res. and Tech. Bull.*

No. 74, **1975**.

[24] G Mckay; MS Otterburn; AG Sweeny. *Water Res.*, **15**, 327- 339 **(1981)**.

[25] DB Singh; DC Rupainwar; G Prasad; KC Jayaprakas. *J. Hazard. Mater.*, **1998**, 60, 29-40.

[26] DB Singh ; DC Rupainwar ; G Prasad; VN Singh. *Water Air Soil Poll.*, **1988,** 42, 373- 380.

[27] GN Manju; MC Gigi; TS Anirudhan. *Indian J. Chem. Tech.*, **1999,** 6, 134-141.

[28] KK Pandey; G Prasad; VN Singh. *J. Chem. Technol. Biotechnol.*, **1984**, 34A, 367-374.

[29] GE Jean; GM Bancroft. *Geochimica et Cosmochimica Acta*, **1986**, 50, 1455- 1463.