

REMOVAL OF HEAVY METAL POLLUTANTS BY BIOSORPTION USING LOW COST BIOSORBENTS

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1. INTRODUCTION

The term heavy metal is somewhat imprecise and refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Passow et al (1961); Hutton and Symon (1986); Nriagu and Pacyna (1988) and Hawkes (1997) have defined heavy metals as general collective term, which applies to the group of metals and metalloids with density greater than 5 g cm^{-3} and these includes elements from Group III transition metals, the actinides series, the lanthanide series and three of the Group IV metalloids (arsenic, tellurium, selenium). Heavy metals are classified into three categories on the basis of their usage in the field of biosorption (Volesky, 1990; Bishop, 2002):

- Toxic metals (such as Hg, Cr, Pb, Zn, Cu, Cd, As, Co & Sn)
- Precious metals (such as Pt, Ag, Ni, Au & Ru)
- Radionuclides (such as U, Th, Ra & Am)

Heavy metals interaction with water exist in two forms

1. *Water-soluble*

Chloride, sulphate and nitrates salts of heavy metals are water soluble. These are most common salts of heavy metal ions used in industrial operations. As a dissolved salt, heavy metal ions are in cationic form such as Cd^{2+} , Hg^{2+} , Pb^{2+} , Ag^+ , Cr^{3+} . Heavy metals can also exist in soluble form as oxymetal anions like chromium, which can also exist as chromate CrO_4^{2-} or dichromate $\text{Cr}_2\text{O}_7^{2-}$. Another example is arsenic, including arsenate (AsO_4^{3-}), which has an oxidation state of +5, arsenite (AsO_3^{3-}), where As has oxidation state of +3, as well as selenium (SeO_2^{3-} , SeO_4^{2-}) (Stephengen and Lester, 1987).

2. *Water-insoluble*

Oxide, hydroxide, sulphide and carbonate salts of most heavy metals are not soluble or are sparingly soluble in water.

Table 1: Sources and toxic effects of heavy metals

Metals	Sources	Effects and significance
Arsenic	Mining by-product, pesticides, chemical waste	Toxic, possibly carcinogenic
Cadmium	Industrial discharge, mining waste, metal plating, water pipes	Nausea, griping pain, vomiting, diarrhoea, replaces zinc biochemically, causes high blood pressure, kidney damage, destruction of testicular tissue and RBC's, toxicity to aquatic biota
Chromium	Metal plating, cooling tower water additive (chromate) normally found as Cr(VI) in polluted water	Essential trace element; possibly carcinogenic as Cr(VI)
Copper	Metal plating, industrial and domestic waste, mining, mineral leaching	Essential trace element; not very toxic to animals, toxic to plants and algae at moderate concentrations
Lead	Mining, plumbing, coal, gasoline	Toxic (anemia, kidney diseases, nervous disorders), wildlife destroyed
Mercury	Industrial waste, mining, pesticide, coal	Damages brain and CNS
Nickel	Metal plating, coal, diesel, oil, steel and non-ferrous alloys	Lung cancer and respiratory problems
Iron	Steel and electroplating industry, mining	Conjunctivitis, choroiditis, retinitis and damage vital organs
Zinc	Galvanizing, alloys and paper, etc.	Cancer
Barium	Water borne	A muscle stimulant that affects heart

Source: Abbasi et al, 1998

2. MATERIALS AND METHODS

The experiments were carried out in batch mode to explore the biosorption properties of selected biosorbents. The various steps performed to achieve the objectives of the present study are given below:

1. Collection of raw material and preparation of biosorbents
2. Characterization of biosorbents
3. Preparation of glassware and synthetic metals solutions
4. Biosorption studies
5. Collection, characterization and bioremediation of industrial effluent
6. Application of mathematical equations and models used to generated data

2.1 Collection of raw material and preparation of biosorbents

Two biomaterials, namely: Rice husk, an agriculture waste and Saw dust, a timber industry waste were used for the making the biosorbents. Rice husk and saw dust were procured from local rice mill and saw mill, respectively located at Kurukshetra (Haryana). These two raw materials were converted into six different biosorbents as described below:

Preparation of boiled Rice husk (BRH) and boiled Sawdust (BSD)

The collected rice husk and sawdust were dried under sun and impurities were separated manually. The materials were grinded and sieved through the sieves of 300 micron size. Then they were boiled with distilled water for 5h to make them free from colored compounds and filtered. The residual materials so obtained were washed several times with distilled water till the filtrates were colourless. These materials were dried at 60°C in hot air oven for 24h, and stored in airtight plastic containers for further use.

Preparation of formaldehyde treated Rice husk (FRH) and formaldehyde treated Sawdust (FSD)

To immobilize the color and water-soluble substances the ground rice husk and saw dust were treated with 1% formaldehyde in the ratio of 1:5 (rice husk/saw dust: formaldehyde, w/v) at room temperature (25±1°C) for 24h. The rice husk and saw dust were filtered, washed with distilled water to remove free formaldehyde and dried at 60°C in a hot air oven for 24h. The resulting materials were ground sieved through the sieves of 300 microns size. The materials were stored in airtight plastic containers for further use.

Preparation of Sulphuric acid treated Rice husk (RHC) and Sulphuric acid treated Sawdust (SDC)

Dried rice husk and saw dust were washed with deionized water until all leachable impurities were removed. The samples were then treated with concentrated H₂SO₄ (50%) in a

ratio of 2:1 (acid volume: weight of rice husk/saw dust) and allowed to get carbonized at 150°C in hot air oven for 24h and soaked with deionized water until solution pH was stable. Afterwards, the carbon so obtained was soaked in 2% NaHCO₃ (w/v) till any residual acid left was removed. Finally, the samples were dried in hot air oven at 110°C, cooled, ground and sieved in the size of 300 microns and stored in airtight containers for further use.

Characterization of biosorbents

Various equipments and instruments were used during characterization of biosorbents and batch experiments. Details are given below:

Equipments / Instruments used

FTIR analyzer

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional groups in the biosorbents. The spectrum of biosorbents are measured by an FTIR spectrometer FTIR-8400S, Shimadzu, Japan within the range of 400-4000 cm⁻¹ wave number.

SEM and EDAX analyzer

The surface morphology and metal ion distribution on biosorbents surface were visualized by scanning electron microscopy (SEM). The SEM images of suitable magnification and resolution obtained by model Quanta 200 FEG, FEI, Netherlands. Energy dispersive analysis X-ray (EDAX) measurements of the samples (with and without metal ions) for qualitative analyses of the elemental constitution of the various samples were also measured by using model Quanta 200 FEG, FEI, Netherlands.

Atomic Adsorption Spectrophotometer (AAS)

Atomic Adsorption Spectrophotometer was used for the analysis of metal ions. The metal ion concentrations in aqueous solution were analysed using a Shimadzu 6300 Atomic Absorption Spectrophotometer (AAS), from Japan at wavelengths respective to each metal ion.

pH Meter

pH meter used was Model pHep, from Hanna Instruments. pH meter was calibrated each time with standard buffer solution of 4.0, 7.0 and 9.2 as instructed in instrument manual.

Biosorbents features

Various features of prepared biosorbents were studied by adopting the standard procedure (APHA, 1976).

pH and conductivity

15 gm of the biosorbent was weighed and transferred to 500ml beaker. 300ml of freshly boiled and cooled water was added and heated to boiling. After digesting for 10 min, the solution was filtered and the first 50 ml of the hot filtrate was decanted. The remaining filtrate solution was cooled to room temperature and the pH and conductivity were determined.

Moisture

About 5 g of the biosorbent was weighed in a petridish. The dish was placed in an electric oven maintained at $110 \pm 5^\circ\text{C}$ for about 5h. The dish was covered, cooled in a desiccator. Heating, cooling and weighing was repeated at 30 min intervals until the difference between the two consecutive weighings was less than 5 mg.

$$\text{Moisture content (\%)} = 100 - (M-X) / M \quad (3.1)$$

Where, M = Mass of the material taken for test (g)

X = Mass of the material after drying (g)

Bulk density

Dried the biosorbent in hot oven at 105°C until constant weight was obtained. Transferred a little dried adsorbent to a measuring cylinder and noted the volume. Weight of this volume of biosorbent was recorded on the balance.

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Weight of Biosorbent (g)}}{\text{Volume of Biosorbent (cm}^3\text{)}} \quad (3.2)$$

Particle density

Dried the biosorbent in oven at 105°C until a constant weight was obtained. Transferred a little dried adsorbent to measuring cylinder and noted the volume after compression. Weight of this volume of biosorbent was recorded with the help of a balance.

$$\text{Particle density (g/cm}^3\text{)} = \frac{\text{Weight of Biosorbent (g)}}{\text{Volume of Biosorbent (cm}^3\text{)}} \quad (3.3)$$

Porosity

Porosity was determined by formula given below:

$$\text{Porosity (\%)} = 1 - \frac{\text{Bulk density}}{\text{Particle density}} \times 100 \quad (3.4)$$

Solubility in water

A known amount of biosorbent was mixed with 100 ml of distilled water and shaken for 30 min. Then the biosorbent was filtered, dried and weighed. The difference in initial and final weight of biosorbent gave the solubility in water.

$$\text{Percentage solubility in water (\%)} = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Initial wt.}} \times 100 \quad (3.5)$$

Preparation of glassware and synthetic metals solution

All aqueous solutions used in metal biosorption studies were prepared using deionized water. The glassware used in the experiments was borosil glass. All glassware used in the experiments was cleaned using the following procedures: washed with detergent, than rinsed with tap water, rinsed with 10% nitric acid, rinsed again with tap water and finally rinsed with distilled water. After cleaning, the glassware was dried and used in the biosorption experiments. All metal solutions containing Cr(VI), Ni(II) and Cu(II) were prepared use the following chemicals: $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Ni}(\text{NO}_3)_2$ and CuSO_4 respectively. These salts were procured from Merck Scientific Ltd., New Delhi. The details of preparation of metals solution are given below.

Preparation of chromium (Cr) stock solution

2.82 gm of Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), was dissolved in double distilled water and final volume of solution was made 1.0 litre. This solution contained hexavalent chromium ion concentration of 1000 mg L^{-1} . It was further diluted with distilled water to make solution of different concentrations of Cr(VI) as desired in experiments.

Preparation of nickel (Ni) stock solution

4.95 gm of Nickel nitrate [$\text{Ni}(\text{NO}_3)_2$], was dissolved in double distilled water and final volume of solution was made 1.0 litre. This solution contained divalent nickel ion concentration of 1000 mg L^{-1} . It was further diluted with distilled water to make solution of different concentrations of Ni(II) as desired in experiments.

Preparation of copper (Cu) stock solution

3.92 gm of Copper sulphate (CuSO_4), was dissolved in distilled water and final volume of solution was made 1.0 litre. This solution contained divalent copper ion concentration of 1000 mg L^{-1} . It was further diluted with distilled water to make solution of different concentrations of Cu(II) as desired in experiments.

Biosorption studies

Batch mode experiments were carried out to explore the metal removal efficiency of from synthetic solution of prepared biosorbents.

2.4.1 Batch process

In this process a known volume of solution or natural sample is allowed to interact with a known quantity of biosorbent. The mixture is agitated to provide the mass transfer and after the attainment of equilibrium the biosorbent and biosorbate are separated by filtration or centrifugation.

Optimization studies

Biosorption process was optimized for important parameters like pH, adsorbent dose, initial metal concentration, contact time and temperature by varying the parameter under consideration while keeping other parameters constant and accordingly optimum value of each parameter for maximum removal of metal ion was determined. The batch experiments were carried out in the 250 ml conical flasks at 25°C temperature. All optimization experiments were performed with 100 or 50 ml synthetic metal ion solution. The orbital shaker was used for the batch studies at 180 rpm. After desired contact period conical flasks were removed and were allowed to stand for 2 min so as to settle down the adsorbents. The biosorbent and biosorbate were separated by centrifugation and residual metal ion concentration in the solution was estimated using Atomic Adsorption Spectrophotometer.

Isotherm studies

The biosorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases and than the system reached at equilibrium. These were the presentation of the amount of solute biosorbed per unit of biosorbent, as a function of equilibrium concentration in bulk solution at constant temperature; the equilibrium of sorption is one of the important physico-chemical aspects for the evaluation of the sorption process as a unit operation. The aim of isothermal analysis of the biosorbent is to determine the maximum biosorption capacity. For this stock solution of the metal ion was diluted as required to obtain standard solutions of metal ion concentration (10-70 mg L⁻¹ or 100-250 mg L⁻¹ for Chromium, 5-500 mg L⁻¹ for Nickel and 5-500 mg L⁻¹ for Copper). Optimized dosages of biosorbent was added to 100 ml of metal ion solution of a desired concentration range at optimized pH which was adjusted using 0.1M NaOH/0.1M HCl, with respective metal ion in 500 ml flask and were agitated at 180 rpm for predetermined equilibrium time at 25⁰C temperature in a orbital shaker. At the end of agitation, suspensions were separated by centrifugation and supernatant was analyzed for their metal ion content. From metal ion concentration measured, before and after biosorption (C_i and C_e ,

respectively), weight of the biosorbents taken (W in gm) and volume of aqueous solution (V in litres), the amount of equilibrium adsorption of metals (q_e) was calculated using the equation 3.6.

$$q_e (\text{mg/g}) = \frac{(C_i - C_e)V}{W} \quad (3.6)$$

The removal percentage ($R\%$) is defined as the ratio of difference in metal concentration before and after biosorption. ($C_i - C_e$) to the initial concentration of metal in the aqueous solution (C_i) was calculated using the equation 3.7.

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3.7)$$

The batch biosorption study was replicated thrice for each of the adsorbent.

Kinetics studies

Kinetics mode studies enable to calculate mass transfer coefficients and kinetics rate modeling. It also provides equilibrium time for the different initial metal ion concentration. Different conical flasks with same (one) initial concentration maintained with optimized pH, dosages and temperature were agitated at 180 rpm taking time of start as t_0 . Samples were withdrawn at fixed time intervals up to 180 min from the flasks in triplicates and analyzed by AAS for residual metal ions concentration in the aqueous solution.

Multicomponent studies

In order to study the effect of the presence of some other metals, commonly present in the industrial effluents, on the removal of one metal by the biosorbents, experiments were conducted in batch mode. The following binary and tertiary metal systems were studied:

1. For Cr(VI)
 - Binary systems: Cr(VI)+Cu(II)
Cr(VI)+Ni(II)
Cr(VI)+Cd(II)
Cr(VI)+Zn(II)
 - Tertiary systems: Cr(VI)+Cu(II)+Ni(II)
Cr(VI)+Ni(II)+Cd(II)
Cr(VI)+Cu(II)+Cd(II)
Cr(VI)+Cu(II)+Zn(II)
Cr(VI)+Zn(II)+Cd(II)
2. For Ni(II)
 - Binary systems: Ni(II)+Cr(VI)
Ni(II)+Cd(II)

3. For Cu(II)
- Tertiary systems: Ni(II)+Cr(VI)+Cd(II)
- Binary systems: Cu(II)+Cr(VI)
Cu(II)+Ni(II)
Cu(II)+Cd(II)
Cu(II)+Zn(II)
- Tertiary systems: Cu(II)+Cr(VI)+Ni(II)
Cu(II)+Ni(II)+Cd(II)
Cu(II)+Cr(VI)+Cd(II)
Cu(II)+Cr(VI)+Zn(II)
Cu(II)+Zn(II)+Cd(II)
4. For Cd(II)
- Binary systems: Cd(II)+Cr(VI)
Cd(II)+Ni(II)
Cd(II)+Zn(II)
- Tertiary systems: Cd(II)+Cr(VI)+Ni(II)
Cd(II)+Cr(VI)+Zn(II)
5. For Zn(II)
- Binary systems: Zn(II)+Cr(VI)
Zn(II)+Cd(II)
Zn(II)+Cu(II)
- Tertiary systems: Zn(II)+Cu(II)+Cr(VI)
Zn(II)+Cu(II)+Cd(II)
Zn(II)+Cr(VI)+Cd(II)

Biosorption experiments were carried out by keeping concentration of first metal constant and varying concentration of other metals ions at optimized pH of former metal ion obtained in case of single metal system. Optimized values of other parameters such as biosorbents dose and contact time obtained by single metal experiment were used.

Desorption studies

Desorption studied are helpful to explore the possibility of recycling the biosorbents and recovery of the metal resource. After biosorption experiments with desired concentration of metal ion with known amount of biosorbent dosage, the metal laden biosorbent was separated by filtration. The biosorbents were given gentle wash with distilled water to remove any unbiosorbed metal ion. Different concentrations of KI and HCl ranging from 0.0125 to 0.150 M were tested to remove metals from adsorbents. In this experiments the contact time (60 min), temperature (25°C), desorbing agent volume (50 ml) and shaking speed (180 rpm) were kept

constant. The desorbed metal ion in the solution was separated by centrifugation and analyzed using AAS.

Collection, characterization and bioremediation of industrial effluent

The wastewater sample was collected from electroplating industry situated at Hisar, India. All precautions were taken during and after collection of samples. Various physico-chemical parameters (pH, color, BOD, COD, Heavy metal etc.) were analyzed according to APHA (1976) standard methods.

Application of mathematical equations and models used to generated data

The biosorption data obtained in the present study were analyzed using various equations and models.

Removal percentage of metal ions (R%)

$$R\% = \frac{C_i - C_e}{C_i} \times 100 \quad (3.8)$$

Where,

R% = Removal Percentage of metal ion from batch system

C_i = Initial concentration of metal ion (mg L⁻¹)

C_e = Equilibrium (Residual) concentration of metal ion (mg L⁻¹)

Uptake capacity or Solid phase equilibrium concentration (q_e)

$$q_e = \frac{(C_i - C_e)V}{M} \quad (3.9)$$

Where,

q_e = Solid phase equilibrium concentration of the metal ion or metal adsorbed (in mg) per gram of adsorbent mass (mg g⁻¹)

V = Volume of metal ion solution used (L)

M = Mass of adsorbent agitated with initial metal ion concentration (g)

C_i = Initial concentration of metal ion (mg L⁻¹)

C_e = Equilibrium (Residual) concentration of metal ion (mg L⁻¹) (Gadd and White, 1993)

Adsorption isotherms

Adsorption isotherm is an essential part of modeling adsorption equilibrium and thus, column or batch processing design, efficiency and economics (Dechow, 1989). The isotherm predicts the degree of the purification that might be achieved, the approximate amount of adsorbent required to reach that degree of purity and the sensitivity of the purification process to the concentration of the solute. Adsorbate molecules are simultaneously adsorbed and desorbed from the adsorbent surface and at the equilibrium, adsorption rate become equals to desorption

rate. The state of equilibrium changes with change in the parameters of the system so this equilibrium is of dynamic nature. Equilibrium behavior best describe adsorption isotherms which is a plot of amount of solute adsorbed per unit amount of adsorbent against the corresponding equilibrium concentration in the solution phase. Important conclusions can be drawn from these isotherms, which are important and useful in the designing of adsorption systems. There are numbers of isotherm equations have been proposed like Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Brunnauer-Emmett-Teller (BET), Redlich-Peterson etc. Among these the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm equations have been used in recent past several by researchers.

Langmuir isotherm model

Langmuir in 1918 gave first time the concept of monolayer adsorption formed on energetically homogeneous solid surfaces. In 1932; Langmuir awarded the Nobel Prize in chemistry for his discoveries and researches in the realm of surface chemistry. Langmuir isotherm was applied to estimate the adsorption capacity of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption. Langmuir isotherm was applied for adsorption equilibrium data.

The Langmuir isotherm is based on the following assumptions (Langmuir 1918):

- Metal ions are chemically adsorbed at a fixed number of well-defined sites
- Each site can hold only one ion
- All sites are energetically equivalent
- There is no interaction between adsorbed ions

When the initial metal ion concentration increases, adsorption increases whilst the binding sites are not saturated. The unmodified Langmuir equation is given below:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (3.10)$$

Where,

q_e = The amount of adsorbate adsorbed per unit amount of adsorbent required for mono-layer adsorption (mg g^{-1})

Q_o = Maximum adsorption capacity (mg g^{-1})

b = The adsorption coefficient [a measure of the adsorption energy (L mg^{-1})]

C_e = The concentration of adsorbate at equilibrium (mg L^{-1})

The above equation can also be written in linearized form to allow the calculations of adsorption capacities and the Langmuir constants as given below:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3.11)$$

The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e .

Furthermore a dimensionless constant called separation factor (R_L) was also calculated to test the favorability of adsorption which is an essential feature of Langmuir isotherm (Hall et al, 1966). R_L is based on the equilibrium parameters and is defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (3.12)$$

Where, b is the Langmuir isotherm constant and C_0 is the initial metal ion concentration (mg L^{-1}).

Hall et al (1996) have shown through the use of mathematical calculations that the value of the parameter R_L indicates the type of isotherm involved as follows:

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Freundlich Isotherm model

The Freundlich isotherm is an empirical expression that accounts for surface heterogeneity by multilayer adsorption, exponential distribution of active sites of sorbent and their energies towards sorbate. It is widely used in environmental engineering practice to model adsorption of pollutants from aqueous medium empirically. It is most widely used non-linear sorption model.

Freundlich isotherm is derived from empirical consideration and expressed as (Freundlich and Helle, 1939).

$$q_e = K_f C_e^{1/n} \quad (3.13)$$

Where,

q_e = Amount of adsorbate adsorbed per unit amount of adsorbent (mg g^{-1})

C_e = Concentration of adsorbate at equilibrium (mg L^{-1})

K_f = Adsorption coefficient [Freundlich constant (mg g^{-1})], which is a measure of adsorption capacity or fundamental effectiveness of the adsorbent. It is directly related to the standard free energy change, Empirical constant 'n' is a measure of the adsorption intensity.

The linearized Freundlich model isotherm is represented by equation:

$$\text{Log}_{10}q_e = \text{Log}_{10}K_f + \frac{1}{n}\text{Log}_{10}C_e \quad (3.14)$$

Where,

K_f and n are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto adsorbent respectively.

The plots of $\text{Log}_{10} q_e$ Vs $\text{Log}_{10} C_e$ can be plotted to determine values of n and K_f from slope and intercept values of fitted linearised equation depicting the constants of Freundlich model. A high K_F and high 'n' value is an indication of high adsorption throughout the concentration range. A low K_F and high 'n' value indicates low adsorption throughout the studied concentration range. A low 'n' value indicates high adsorption at strong solute concentration.

The magnitude of the exponent n gives an indication of the favorability of the adsorption. It is generally stated that values of n between 1 and 10 correspond to beneficial adsorption (Treybal, 1980).

Dubinin-Radushkevich isotherm model

According to this model, characteristic sorption curve is related to the porous structure of the sorbent (Dubinin, 1960). Langmuir model represents the monolayer adsorption on to a homogeneous surface with a finite number of active sites whereas D-R model does not assume homogeneous surface. The D-R adsorption isotherm is represented as:

$$\text{Log}_{10} q_e = \text{Log}_{10} q_D - 2B_D R^2 T^2 \text{Log}_{10} (1+1/C_e) \quad (3.15)$$

Where,

q_e = Amount of adsorbate adsorbed per unit amount of adsorbent (mg g^{-1})

C_e = Concentration of adsorbate at equilibrium (mg L^{-1})

q_D = Theoretical saturation capacity (mg g^{-1})

B_D = A constant related to adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$)

R = Gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$)

T = Temperature (K)

The slope of the plot $\text{log}_{10} q_e$ versus $\text{log}_{10} (1+1/C_e)$ gives the q_D and B_D values. The constant B_D gives an idea about the mean free energy E_D (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the D-R isotherm constant B_D using following equation (Hall et al, 1966):

$$E_D = 1/\sqrt{2B_D} \quad (3.16)$$

The calculated E_D value indicated the type of adsorption. If the value of E_D was found less than 8 show that the adsorption process follows physical adsorption. If value found in range of 9-16 than adsorption process follows chemical adsorption (Hasany and Chaudhary, 1996).

Tempkin isotherm model

Tempkin isotherm equation contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate repulsions and the adsorption is uniform distribution of maximum binding energy (Kavitha and Namasivayam, 2007). In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich model. It has commonly been written in the following equation 3.17 (Aharoni and Sparks, 1991):

$$q_e = RT/b_T \log(A_T C_e) \quad (3.17)$$

Where $B_T = (RT)/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The constant b_T is related to the heat of adsorption; A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy (Pearce et al, 2003). The adsorption data can be analyzed according to eq. 3.17. A plot of q_e versus $\log C_e$ enables the determination of the isotherm constants A_T and b_T .

Adsorption kinetics

It is the velocity of adjustment of distribution equilibrium between metal ions bound to the surface of biomass and remaining metal concentration in the surrounding liquid solution. Pseudo first order and second order rate equations were used to investigate the kinetics of metal sorption.

Pseudo-first order rate equation

$$\text{Log} \left(\frac{q_e - q_t}{q_e} \right) = \text{Log} \frac{q_e - k_1}{2.303} t \quad (3.18)$$

Where,

k_1 = Lagergren rate constant for adsorption (min^{-1})

q_e = Amount of metal adsorption at equilibrium (mg g^{-1})

q_t = Amount of metal adsorption at time t (min) (mg g^{-1})

In order to obtain the rate constant graph plotted between $\log (q_e - q_t)$ vs time t (min^{-1}) (Balasubramanian et al, 1998).

2.6.4.2. Pseudo-second order rate equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.19)$$

Where,

k_2 = Second order rate constant for adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$)

q_e = Amount of metal adsorption at equilibrium (mg g^{-1})

q_t = Amount of metal adsorption in time t (min^{-1}) (Ho et al, 2001)

In order to obtain the rate constant graph plotted between t/q_t vs t .

Line obtained after plotting $\log(q_e - q_t)$ vs t and t/q_t vs t shows degree of fitness of metal sorption to first and second order rate kinetic models respectively. Straight line indicated best fitness of experimental data to corresponding models. This is based on the assumption that the adsorption capacity for metal on the adsorbent is proportional to the number of active sites occupied on the sorbent and metal uptake is due to chemisorption (Ho, 2004).

3. CONCLUSION

The present study mainly focused on the develop of inexpensive and effective biosorbents for removing and recovering Cr(VI), Ni(II) and Cu(II).

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cr(VI) from aqueous solutions were 2.0, 4 g L^{-1} , 120 min and 25⁰C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cr(VI) removal was in the order

SDC>RHC>FSD>FRH>BSD>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Ni(II) from aqueous solutions were 6.0, 20 g L^{-1} , 120 min and 25⁰C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Ni(II) removal was in the order

RHC>SDC>FSD>BSD>FRH>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cu(II) from aqueous solutions were 5.0, 20 g L^{-1} , 120 min and 25⁰C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cu(II) removal was in the order

SDC>RHC>FSD>BSD>FRH>BRH

The maximum desorption of Cr(VI), Ni(II) and Cu(II) was recorded for BRH. The desorption of the studied metal ion from the exhausted biosorbents was in the order

Cu(II)> Cr(VI)>Ni(II)

The presence of other metals had antagonistic effect on the biosorption efficiency of the biosorbents. Further the metal removal efficiency of each biosorbent was lesser in actual effluent than aqueous solutions.

The biosorption pattern of all studied biosorbents studied followed the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm for biosorption of Cr(VI), Ni(II) and

Cu(II). Kinetics results showed that all studied biosorbents for Cr(VI), Ni(II) and Cu(II) followed pseudo-second order model with determination coefficient (R^2) > 0.98.

Finally it was concluded that RHC and SDC were best biosorbents for the biosorption of studied metal ions. So rice husk and saw dust biosorbents can be attractive options for the small scale industries located in countryside. Rice husk and sawdust are readily available in developing nations, so this data can be used by small scale industries having low concentrations of Cr(VI), Ni(II) and Cu(II) in wastewater using batch or stirred-tank flow reactors where standard material, such as activated carbon, is not available.

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