

Sustainable remediation of Hg(II) from wastewater by combo humiresin-dry cow dung powder

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

This research addresses an innovative application of dry cow dung powder (DCP), sustainable green biowaste, for the efficient remediation of toxic Hg(II) ions from aqueous medium. Batch equilibration experiments have been conducted employing radiotracer technique and the impact of various process parameters have been studied. The result indicated that 100 mg of DCP could effectively remove 80-82% of Hg(II) (1 mg/mL) within 10 min at pH 3. The thermodynamic parameters ΔG° , ΔH° and ΔS° have been evaluated, and the values obtained were -4.242 kJ/mol, -10.421 kJ/mol and 35.672 J/mol K, respectively. These values suggest spontaneous and exothermic process with high affinity of Hg(II) for DCP. The pseudo-second order kinetic model proved to be the best fitting with adsorption capacity of 16.0 mg/g and it also indicate the chemisorptive mechanism of DCP. The mechanism involved in Hg(II) adsorption has been also supported by FTIR, EDAX and desorption studies. DCP has a great potential in the field of wastewater treatment, which is embossed by successfully fitting in to 3A's selection criteria of affordability, adaptability and acceptability. Thus, DCP proves to be one of the best contenders of green chemistry and the concept of zero waste.

KEYWORDS

biosorption; combo-humiresin; dry cow dung powder; green chemistry; remediation; zero waste

1. INTRODUCTION

Universal plethora of an industrial urbanization is the paradigm cause of Anthropocene, the eon of pollution. Hydrosphere, the greenest and renewable center of our ecosystem is most affected and hence has been highly attended by our environmentalists. According to green chemists, real solution for water pollution is not in the technological advances but to maximize the applicability and efficiency of naturally available resources. Present scenario strongly advocates utilization of the biological technologies that are eco-friendly alternatives over current synthetic complements, which pollute ecosystem during the course of manufacturing and handling process (Volesky, 2003).

Wastewater management and treatment technology has major concern towards mercury poisoning, the most notorious neurotoxin in the

environment (Vallero, 2005). For the removal of mercury ions from wastewater effluent processes like sulphide precipitation, electrodialysis and ion-exchangers are employed (Das et.al, 2007). However, these methods have disadvantages like incomplete metal removal, high requirement of energy and reagents, generation of toxic sludge or other waste materials, which in turn require treatment for their cautious disposal and thereby questioning applicability. These challenging situations commanded fundamental shift towards bioremediation process, in particular biosorption. Biosorption process is most preferred due to metabolism-independent, passive and physico-chemical binding of metal ions involving biomass (Fomina and Gadd, 2014). Biosorbents have proven to be economical, less hazardous and functionally better than traditional or conventional options.

Literature survey, especially for Hg(II) removal, indicated that natural sorbents from biotic

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and abiotic origin such as *Cajanus cajan* husk (Devani et al., 2016), bagasse palm and yam peels (Tejada et al., 2016), fungal Biomass (Bedioui et al., 2015), orange peel (Chinyelu et al., 2015) peanut hull powder (Ding et al., 2014), pistachio hull waste (Rajamohan, 2014), sugarcane bagasse (Khoramzadeh et al., 2013), kenaf fibers (Garcia et al., 2012), rambai tree leaves (Sen et al., 2011), *Rhizopus oligosporus* (Ozsoy, 2010), Romanian peat moss (Bulgairu et al., 2009), *Carica papaya* (Basha et al., 2008), etc. are employed. Most biosorbents require some degree of physical and chemical modifications for optimum results and disposal of spent resin requires sophisticated approach, limiting its usage.

Our research is based on the hierarchy elucidated by Waste Management and Treatment Strategies of reduce, reuse and recycle coined with re-think. We have developed a simple, efficient and eco-friendly method for the utilization of DCP, exclusively obtained from research lab- Gaushala, without any pre- or post-modifications, confirming benign composition for remediation of wastewater. It neither imparts foul odour or coloration to effluent, nor does it lead to increase in biomass, which abstract post treatment. DCP after sun drying as powder, can be used as landfill, after learning the chemical makeup of landfill site, as desorption studies proved DCP has fairly resistant towards leaching (Barot and Bagla, 2012a).

2. MATERIALS AND METHODS

2.1. Adsorbent and adsorbate

We have collected DCP, 100 mesh sizes from the Keshav Shrushti Gaushala (Thane, India), a research centre on cow and cow product and it is a registered charitable trust under the guidance and instructions of the Vishwa Hindu Parishad. The fresh cow dung is collected by efficient workers and due safety measures are taken to avoid any contamination during collecting, sun drying and powdering. The cow dung was dried properly before its utilization, so as to prevent its oxidation by acid due to presence of mixture of alcohols in effluent. The integrity of DCP before and after the sorption was studied by measuring the mesh size and was found to be almost same; indicating during sorption process there was no physical attrition of DCP.

DCP is naturally available bioorganic, complex, polymorphic matrix enriched with minerals, carbohydrates, fats, proteins, bile pigments, aliphatic - aromatic species such as humic acid (HA), fulvic acid (FA) (Barot and Bagla, 2009) and many functional

group viz. carboxylic acid, esters, ketones, lactones, amine etc. (Barot and Bagla, 2012b) which enhances its adsorption properties. It also possess certain dead biomass such as bacteria, fungi, and actinomycetes; such as, fecal *Streptococcus*, *Streptococcus*, *Pseudomonas* sp., *Sarcina*, *Nocardia*, *Mucor* spp., *Phizopus stolonifer*, *Rhizopus* sp., *Aspergillus*, *E. coli* and *Penicillium* microbes (Geetha and Fulekar, 2008).

This inactive non-living biomass has an inherent property to bind and concentrate heavy metals from aqueous surrounding which facilitates faster as well as easier adsorption (Singh and Fulekar, 2010). All the chemicals used were of analytical grade. The stock solution of Hg(II) was prepared using HgCl₂ and other solutions were prepared using distilled water and were standardized by standard analytical methods (Vogel, 1975).

2.2. Characterization of DCP

All quantitative and qualitative characterization techniques have been carried out at Sophisticated Analytical Instruments Facility, SAIF at Indian Institute of Technology, Mumbai and Gemmological Institute of India, GII, Mumbai.

2.2.1. X-Ray fluorescence spectrometry (XRF)

DCP has been characterized using XRF for elemental composition. (X-Ray Fluorescence Spectrometer, PHILLIPS-PANALYTICAL, The Netherlands; Model- PW 2404) as described in Table 1.

2.2.2. CHNSO elemental analyzer (CHNS)

The CHNS analysis of DCP complements the XRF and gives information about stated elements (Thermo finnigan, Italy; Model- FLASH EA 1112 series). The values obtained for this analysis are, carbon-37.367%; hydrogen-5.142%; nitrogen-3.104%; sulphur-3.342% and oxygen-29.654%.

2.2.3. Fourier transform infrared spectroscopy (FTIR)

The spectra of DCP after and before sorption of Hg(II) has been obtained by FTIR, (Nicolet Instrument Co. USA, MAGNA 500, specification range 4000 cm⁻¹ - 50 cm⁻¹) which helped in determining the active sites of DCP.

2.2.4. Field emission Gun scanning electron microscopy (FEG-SEM)

The FEG-SEM (JSM 7600F; SEI Resolution – 1.0nm at 15 kv, 1.5 nm at 1 kv, in GB mode) analysis was carried out to learn the surface texture and porosity of DCP. It

provided visual confirmation of surface morphology of DCP.

Table 1. XRF data of DCP

Element	Percentage
Na	0.946
Mg	2.853
Al	1.684
Si	22.69
P	3.883
K	3.343
Ca	2.360
Ti	0.329
Mn	0.115
Fe	2.419
Cl	1.560
Cr	0.014

2.2.5. Energy Dispersive X-Ray Spectroscopy (EDAX)

The EDAX spectra of DCP before and after sorption of mercury ions were obtained from Gemmological Institute of India, GII, Mumbai. (HORIBA, Japan; Model – XGT 7200, Target- Rhodium)

2.3. Tracer technique

Radioactive tracer technique is an analytical technique (Lieser, 2001) for investigating recovery and loss of a microcomponent, in which a radioactively-labeled element or compound chemically identical with the micro- component is added to the sample before preconcentration, and its behaviour is followed by a sensitive, rapid and selective radioactivity measurements. Also radiotracers have unique advantage of freedom from reagent blank and non-destructive pattern that makes it suitable choice of analysis. Radiotracer $^{203}\text{Hg}(\text{II})$ (Gamma-emitter) was procured from Board of Radiation & Isotope Technology (BRIT) Mumbai, India.

2.4. Batch equilibration mode

At room temperature (RT) and pressure, a known amount of DCP was mixed with radiotracer $^{203}\text{Hg}(\text{II})$, 1 mg/mL carrier solution of HgCl_2 and pH range under study was adjusted using small quantity of dil. HCl or NaHCO_3 . The resultant solution was equilibrated for 10 min with mechanical stirrer and was centrifuged. After separating the supernatant, DCP was washed

with 5 mL of distilled water and the activity present in supernatant was measured using single channel NaI(Tl) well type gamma ray spectrometer (Type GRS 101P, model No. 013). The effect of different experimental parameters such as pH (from 1-10), metal ion concentration (0.5-20 mg/mL), contact time (0-30 min), amount of DCP (50-650 mg), temperature (283-363 K), have been studied to optimize the parameters for developing efficient adsorption process. The kinetic, thermodynamic and studies on interference of various organic and inorganic salts as well as different cations have been conducted to evaluate the mechanism, spontaneity and feasibility of the remediation process.

2.5. Statistical analysis

All experimental data were measured in triplicate and percentage adsorption value was calculated using formula as given below:

$$\% \text{ Adsorption} = [A(i) - A(f)] / A(i) \times 100 \quad (1)$$

where, A(i) is the activity taken and A(f) is the total activity in supernatant.

The initial concentration of solution (C_i), the sorbed concentration (C_{sorb} , mol/g) onto the sorbent and residual concentration of metal ions in the solution at equilibrium (C_e , mol/dm³) were computed using the equation:

$$C_{\text{sorb}} = C_i \times [A(i) - A(f)] / A(i) \times V/W \quad (2)$$

$$= C(i) \times F \times V/W \quad (3)$$

$$C_e = C_i (1-F) \quad (4)$$

where, F is the fraction percent sorbed at equilibrium, V is the volume of aliquot and W is the weight of resin

3. RESULTS AND DISCUSSION

The FTIR spectrum of DCP Figure 1 was devoid of any characteristic band of alcohol, which prevents the oxidation of DCP due to probable presence of alcohol in effluent during the course of sorption. Figure 2 reveals the systematic changes in the spectral features of DCP after sorption of mercury ions. On comparing the spectral data as given in Table 2, remarkable shifts in the characteristic bands of DCP have been found, explaining the different sites or functional groups of DCP responsible for binding of metal ions.

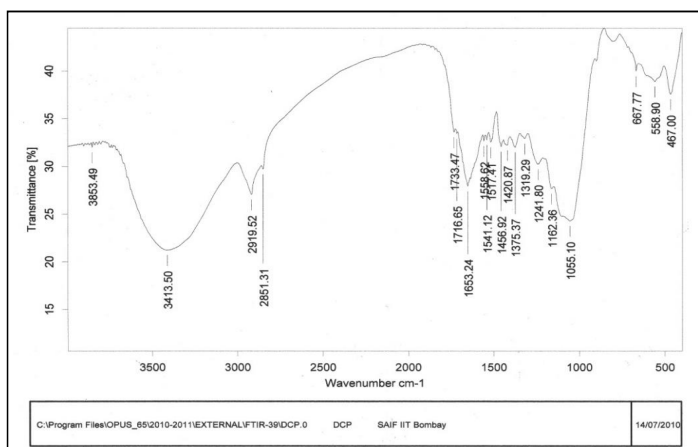


Figure 1. FTIR spectra of DCP before biosorption of Hg(II)

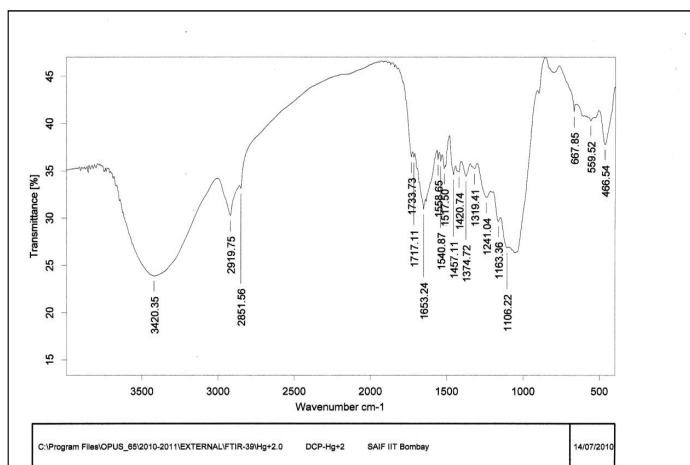


Figure 2. FTIR spectra of DCP after biosorption of Hg(II)

The SEM patterns (Figure 3) shows that DCP has fibrous structure with some holes and small

openings on the surface. Also, the surface of DCP is heterogeneous, rough, porous and with dentations. It shows the presence of debris of some prokaryotic cells. Thus metal ions can be sorbed on the surface as well as can go into the expanded pores; in that case, the metal ions should be difficult to desorb which is also supported by desorption study of spent DCP.

The EDAX spectrum of DCP before biosorption indicates the presence of naive metal ions such as Si, K, Ca, Ti, Mn, Fe and Zn as can be seen from the Figure 4. The spectrum after biosorption as shown in Figure 5, indicates presence of concerned metal ion, Hg(II) in the matrix along with all other naturally present elements indicating that ion exchange is not the mechanism for the sorption by DCP. This spectroscopic study substantiates chemisorption to be one of the most prevailing mechanisms. Also, desorption studies assert the chemisorption mechanism, as chemical interaction of metal ions with biosorbent hinders the back extraction or stripping from spent DCP.

All the batch equilibration parameters were comprehensively studied in possible experimental range for the optimization of the process. The results revealed that having 10 min of contact time at pH 3, 100 mg of DCP, proved optimum for about 80-85% sorption of 1 mg/mL Hg(II) from 15 mL of solution.

3.1. Effect of pH

The pH is clearly an important parameter as it affects the solubility of metal ions, concentration of counter ions and degree of ionization of the adsorbate during reaction. Also, it controls the adsorption rate of other metal ion as hydronium and hydroxyl ions are adsorbed strongly over others. It determines the hydrolysis of

Table 2. FTIR data of DCP after and before biosorption of Hg(II)

Functional groups	Compounds	Characteristic bands (cm ⁻¹)	DCP band before sorption (cm ⁻¹)	DCP band after Sorption (cm ⁻¹)
C-Br or inorganic impurities	Alkyl halide stretch clay, minerals	690-515(m)	558.90	559.52
N-H	Amines (1° – amines)	3400-3500(w)	3413.50	3420.35
C=C	Conjugated	1585-1625	1541.12	1540.64
C-O	Saturated secondary or cyclic tertiary amine	1125-1085 (s)	1055.10	1106.92
			1162.36	1163.36
C-H	CH ₂	1405-1465	1466.95	1457.97
	CH ₃	1355-1395	1375.37	1374.72

metal ions and average surface charge of adsorbent, which significantly affects the adsorption process (Chojnacka et al., 2005). DCP being heterogeneous biosorbent possess positively charged sites owing to proteins and negatively charged sites due to presence of some acidic groups. Hence, on varying the pH of a solution, the overall surface charge of DCP can be modified so as to get maximum sorption (Barot and Bagla, 2012c).

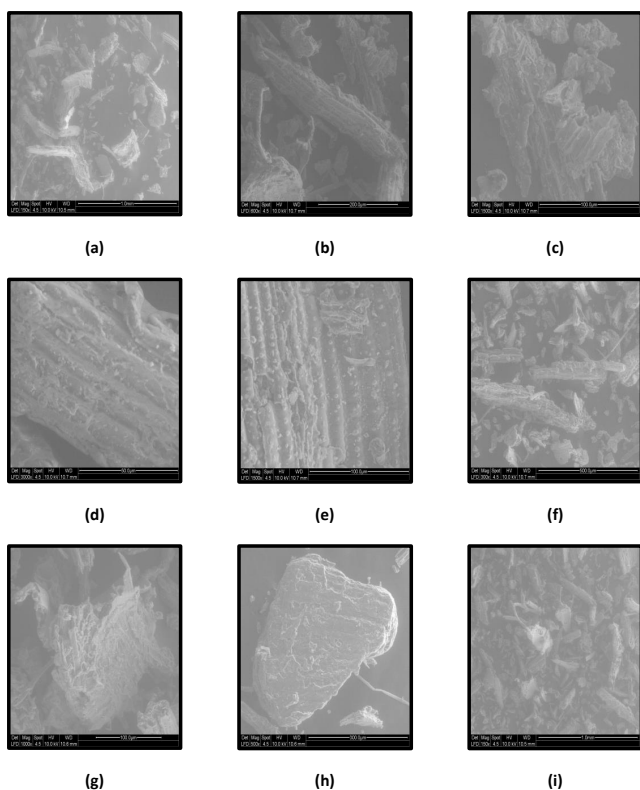


Figure 3. Scanning electron micrograph (SEM) of DCP (a to i) [Figure a, c, f, i - minute particles of fibers; Figure b - collagen strands; Figure d - cellulosic fibers with minute pores; Figure g, h- remains of protozoans]

On varying the pH from 1-10 as described in Figure 6, it can be concluded that optimum pH for maximum adsorption was 3. It is well established from the speciation studies that mercury exists as Hg^{2+} in solution at $pH < 3$ and forms $HgCl_2$, $HgCl^+$, $HgClOH$ and $Hg(OH)_2$ in the pH range of 3-7. The lower values of sorption in acidic pH, less than 3, is due to the high proton concentration and metal ions are present in solution as free cation, so protons can compete with metal cations for surface sites (Fiol et al., 2006). Also, at lower pH DCP surface gets protonated leading to electrostatic repulsion between Hg^{2+} and protonated functional group of sorbent.

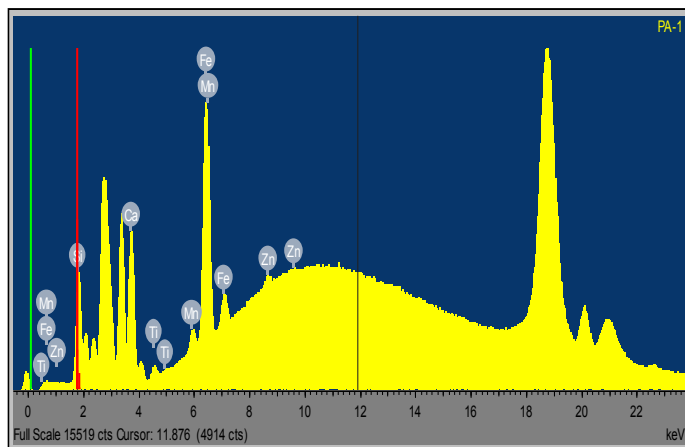


Figure 4. EDAX spectrum of DCP before biosorption

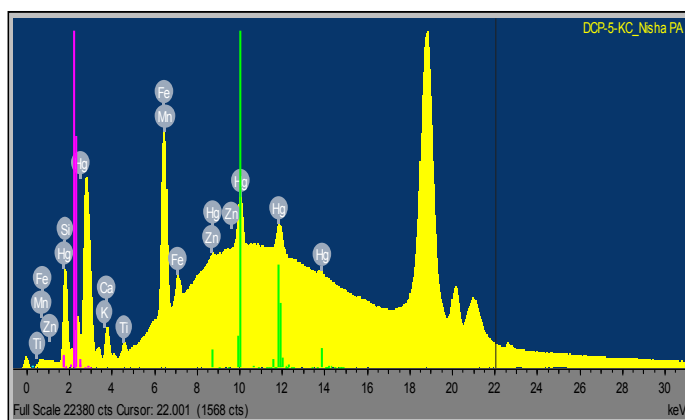


Figure 5. EDAX spectrum of DCP after biosorption

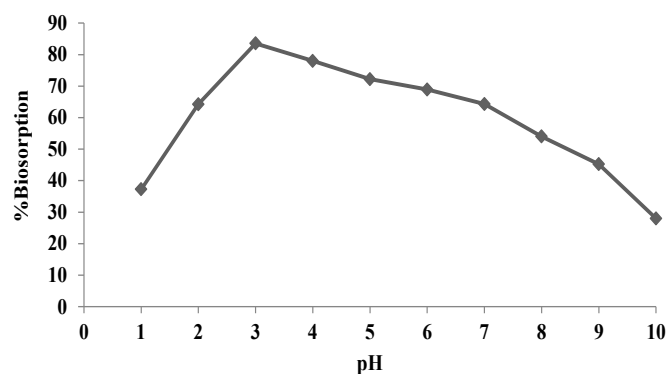


Figure 6. Effect of pH on adsorption of $Hg(II)$ on DCP. [contact time= 10 min; amount of resin= 100 mg; metal ion conc. =1 mg/mL at RT].

However, it was observed that biosorption increased with increasing pH and then reached almost a plateau value around pH 3. It is due to minimum surface protonation of DCP, leading to the enhancement of $Hg(II)$ ions sorption. The plateau at pH 3-6 implies that may be $Hg(OH)_2$ is retained in

the micropores of DCP by chemisorption, involving surface complexes (Meena et al., 2004). Also, the weakly acidic carboxyl group (R-COOH) is regarded as the main ligands involved in the Hg(II) uptake by DCP. Because the pK_a value of R-COOH is in the range of 3.5-5.5 more carboxyl groups will be deprotonated at pH over this range (DeRuiter, 2005), and thus resulting in more negative binding sites. This will result in an electrostatic force of attraction between negatively charged DCP and positively charged Hg(II) ions (Feng et al., 2011). At higher pH above 6, in the alkaline conditions, concentration of OH⁻ ions increases and precipitation of mercury ions becomes significant; lowering the sorption.

3.2. Effect of adsorbent amount

Sorption being surface phenomenon, the extent of sorption is directly proportional to the surface area available. Increasing the sorbent amount increases the available adsorption site, resulting in increased percentage sorption. Figure 7 suggests that after optimum dose, number of ions bound to DCP and the number of free ions remains constant even with further addition of the sorbent. It may be due to partial aggregation of active adsorbent sites (Waranusantigul et al., 2003). As shown in the results, the optimum amount of DCP for 80-81% removal of Hg(II) was 100mg and it is also noted that 95-96% sorption can be obtained with increasing amount of DCP to 500 mg.

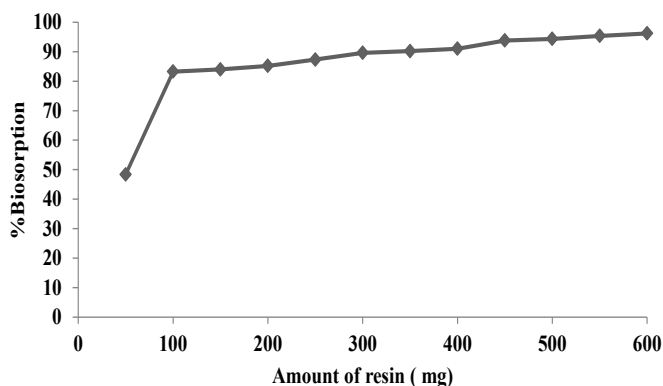


Figure 7: Effect of amount of resin on adsorption of Hg(II) on DCP. [pH = 3; contact time= 10 min; metal ion conc. =1 mg/mL at RT].

3.3. Effect of contact time

To optimize the contact time of the experiment, keeping all other optimum parameters constant contact time was varied from 0-30 min. Figure 8 reveals that as contact time was increased, percentage sorption was

increased and after some time, it gradually approached a constant value, denoting attainment of equilibrium. Further increase in contact time does not increase percentage sorption due to deposition of ions on the available sorption sites on DCP. Also, sorption rate got reduced in later stage because, initially a large number of vacant surface sites are available for sorption and after some time, the remaining vacant surface sites become difficult to occupy due to forces between the solute molecules of solid and bulk phase. The decrease in percentage removal with increasing time may also be due to intraparticle diffusion process dominating over sorption (Al-Homaidan et al., 2014). These results were typical for biosorption of metals involving no energy-mediated reactions, where metal removal from a solution is due to purely physico-chemical interactions between the biomass and metal ions in the solution (Aksu et al., 2002). It was evident from this experiment that 10 min of contact time proved sufficient for the system, which satisfy the criterion of minimum time, optimum result.

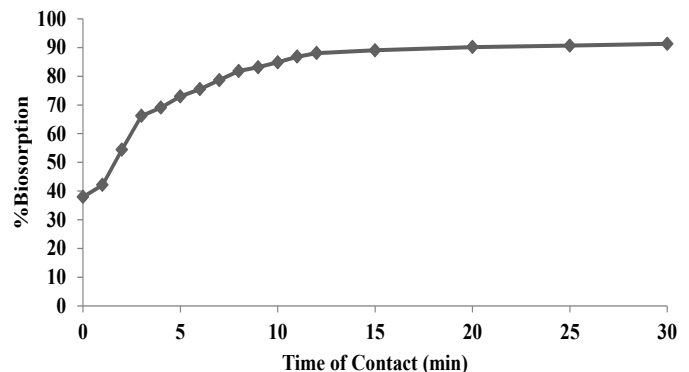


Figure 8. Effect of contact time on adsorption of Hg(II) on DCP. [pH = 3; amount of resin= 100 mg ; metal ion conc. =1 mg/mL at RT].

3.4. Effect of metal ion concentration

Metal ion concentration was varied from 0.5-10 mg/mL and percentage sorption decreased with increase in Hg(II) concentration as observed in Figure 9. In case of low concentration, the ratio of number of moles of Hg(II) ions to the available surface area of DCP is lower and subsequently the fractional adsorption becomes independent of metal ion concentration (Ansari et al., 2016). However, at higher concentration the available site on the biosorbent becomes fewer, and hence decreases the sorption. It is due to increase in the number of ions competing for the available binding site in the biomass (Saiffudin and Raziah, 2007). Moreover, higher concentration provides higher driving force to

overcome all mass transfer resistance of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Hg(II) ions, which also results in decrease in sorption process.

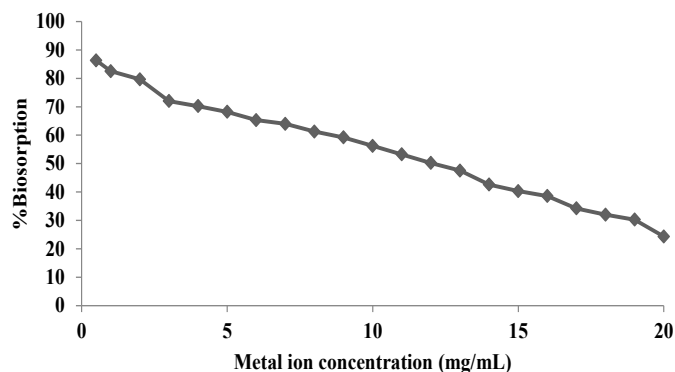


Figure 9. Effect of metal ion concentration on adsorption of Hg(II) on DCP. [pH = 3; contact time= 10 min; amount of resin= 100 mg at RT].

3.5. Effect of temperature

Temperature plays a vital role in the process of sorption, as these reactions are normally exothermic, affecting the enthalpy of entire system. Optimum thermal energy imparts the mobility to metal ion. At pH 3 and metal ion concentration of 1 mg/mL temperature was varied between 283 - 363 K (10 - 90 °C). The results revealed that the % sorption of Hg(II) increases at lower temperature and is found to be maximum at room temperature as shown in Figure 10. Further increase in temperature decrease the percentage of sorption. It may be due to desorption caused by an increase in the available thermal energy. Higher temperature induces mobility of adsorbate, eventually causing desorption, due to weakening of adsorptive forces between the active sites of adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase (El-Sayed et al., 2011).

3.6. Desorption study of spent DCP

Desorption studies are of utmost significance because it assists to understand the pathway and fate of sorbed ions after the disposal of the biosorbent into the environment. Also, it helps in understanding the mechanisms involved in the biosorption process as well to formulate the regeneration of adsorbent making it economically feasible and environmentally benign (Mishra, 2014). Our results revealed that the stripping of sorbed mercury ions from DCP could yield only 8–12 % in presence of stripping agents i.e. various

inorganic acids such as 0.1 M HCl, H₂SO₄ and HNO₃. Use of plain water as desorption agent also failed in the purpose. These results help to postulate that different chemisorptive mechanism such as chelation, complexation and chemisorption were fundamentally involved in Hg(II) sorption and not the physical adsorption.

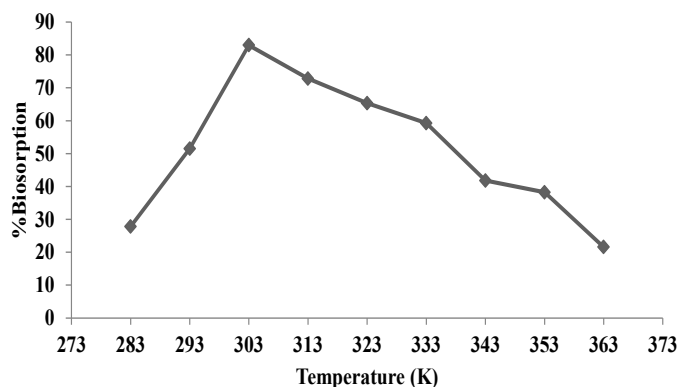


Figure 10. Effect of temperature on adsorption of Hg(II) on DCP. [pH = 3; contact time= 10 min.; amount of resin= 100 mg ; metal ion conc. = 1 mg/mL]

3.7. Interference of different salts and metals

To study the effect of interference of different salts on the percentage sorption, 23 different salts have been studied with varying proportion of 10 mg, 25 mg, 50 mg and 100 mg/L. All the optimized experimental parameters, obtained in prior experiments, were kept constant for this study. It was observed that some salts were proved to be non-interfering with concentration of 100 mg, whereas some were profoundly suppressing the sorption process even with concentration of 10 mg and some were enhancing the sorption as shown in Table 3.

There are many factors governing the sorption process in mixed solute system, where metals are not only present as free ions but also some ligands are present forming a complex compound. The key factors such as relative size of solute, solute-solute interaction, their solubility, stability, ionic character, relative affinity, speciation and most important their concentration, plays a vital role in the sorption process. All these factors can either result in mutual inhibition of competing adsorbate, which decreases the efficiency of sorption or their mutual complex can enhance the percentage of sorption. The higher concentration of ligands reduces the percentage sorption due to readily forming stable metal-ligand complex or due to competition between metal ion and ligands for the sorption sites. Some ligands with optimum

concentration increase the sorption of concerned metal ions due to co-adsorptive effect on the adsorbent (Jackson et al, 1978).

Table 3. List of interfering salts on biosorption of Hg(II)

Amount of salt (mg/L)	Salts under study
100: Non-Interfering	Nitrate, Manganate, Hydroxide
50: Non-Interfering	Bicarbonate, Carbonate, Chlorate, Dichromate, Bromide, Iodate
25: Non-Interfering	Phosphate, Sulphate, Fluoride, Acetate, Chromate
10: Non-Interfering	Nitrite, Iodide, Citrate, Chloride, Sulphite
10 *: Interfering	Thiourea, Thiosulphate, Tartrate, Oxalate, Sulphate thiocyanate, EDTA

* treated with doubling the amount of DCP

This obvious behaviour can also be explained by HSAB theory (Hard & Soft Acid Base concept) given by Pearson (Pearson, 1968). Metal ions are classified as Hard or Soft, on the basis of "hardness scale". According to this theory, metal ions act as Lewis acid and ligands act as Lewis base. Hard acids tend to form a strong bond with hard base and soft acid with soft base. The FTIR studies of DCP confirm that it is enriched with both hard and soft base (functional groups or ligands) as seen from Figure 1, 2 and Table 2. Presence of oxygen containing functional groups such as carboxyl, phenols, aldehydes, lactones etc. creates hard base site and similarly, presence of nitrogen and sulphur containing functional groups such as amines, amide, CN⁻, RS⁻, SH⁻, etc. produces soft base sites (Naja et al., 2010) and this makes DCP a heterogenous biosorbent. Hg(II) being soft acid readily binds with soft base; ligands containing N and S and forms stable metal-ligand complex in aqueous medium (Volesky, 1990).

In realism wastewater effluents contain various chemical contaminants with bulk of interfering ligands or salts of organic-inorganic nature and a multi-metal system with various oxidation states. In regular practice of bioremediation, the interfering agents are chemically treated or masked with appropriate reagents to suppress the decrease in sorption. Even on addition of small quantities of foreign chemicals or masking agents in the system, it not only affects feasibility of reaction but also objects the clean phenomenon

of process (Michalak et al., 2013). Due to dynamic composition of industrial effluent or wastewater there arise an essential need of typical resins, which are more suitable for the removal of a wide range of pollutants simultaneously and not just being specific in selection. DCP being heterogeneous in nature, it efficiently sequesters metallic contaminants in presence of various salts and metal ions. This is supported by our successful sorption studies (Barot et al., 2014) of hard acid i.e. Chromium, Cr and Strontium, Sr as well as soft acid i.e. Mercury, Hg and Cadmium, Cd by DCP, as detailed in Table 4. As depicted from Table 4, the presence of foreign ions in system decreases the sorption of concerned metal ion, which confirms the heterogeneous nature of DCP. Also, the problem of various interferences is successfully solved with simply increasing the amount of DCP by two folds, without affecting the efficiency of the process and thus boosting zero waste theory of entire remediation process.

Table 4. Interference of different cations on biosorption of Hg(II)

No.	Interfering Cation	Remarks	% Hg(II) Biosorption
1*	Cr(III)	Cr(III)+ ⁵¹ Cr(III)	49.21
#		⁵¹ Cr(III)	48.24
2*	Cr(VI)	Cr(VI)+ ⁵¹ Cr	54.33
#		⁵¹ Cr	52.85
3*	Cd(II)	Cd(II)+ ^{115m} Cd(II)	45.64
#		^{115m} Cd(II)	41.58
4*	Sr(II)	Sr(II) + ⁹⁰ Sr(II)	46.52
#		⁹⁰ Sr(II)	44.73

* = with carrier; # = without carrier; interference was treated by doubling the dose of DCP

3.8. Thermodynamic studies

Thermodynamic considerations are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change, ΔG° is an indication of spontaneity of chemical reactions. The free energy of biosorption reaction, can be evaluated by considering the biosorption equilibrium constant K_a which is given by the following equation.

$$\Delta G^\circ = -RT \ln K_a \quad (5)$$

where ΔG° is the standard free energy change (J), R is the universal gas constant = 8.314 J/mol K, and T is absolute temperature (K). K_a values for thermodynamic

calculations are determined from the experimental values obtained as C_{ad} / C_{liq} .

The free energy change for the temperature range of 293-308 K has been calculated using Eqn. 5 and the values of ΔG° were observed negative for the entire range as shown in the Table 5.

Table 5. The Gibb’s free energy change for adsorption of Hg(II) on DCP

T° (K)	ΔG° (kJ/ mol)
293	-0.145
298	-1.820
303	-3.648
308	-4.242
313	-2.566

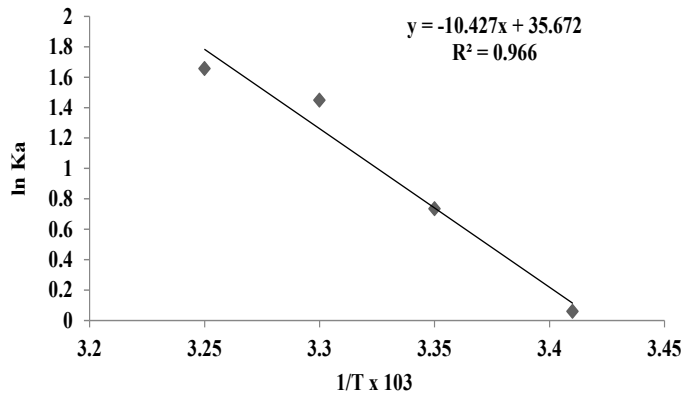


Figure 11. Plot of $\ln K_a$ Vs $1/T \times 10^3$. [pH = 3; contact time= 10 min; amount of resin= 100 mg; metal ion conc. = 1 mg/mL at RT].

For spontaneous reaction at a given temperature, the value of ΔG° is always a negative quantity. The negative value also confirms the feasibility of the process and the spontaneous nature of biosorption process of Hg(II) on DCP. A plot of $\ln K_a$, versus temperature $1/T \times 10^3$, was found to be linear Figure 11. The values of ΔH° and ΔS° were determined from the slope and intercept of the plot. The enthalpy change ΔH° and the entropy change ΔS° , for the biosorption process were deduced from the graph to be -10.42 kJ/mol and 35.67 J/mol K, respectively. The negative value of enthalpy suggests the exothermic reaction. The positive value of entropy change suggests the increase in the randomness at the solid/liquid

interface (Ho and Ofomaja, 2006), reflecting affinity of DCP for the Hg(II) ions.

3.9. Chemical kinetics

The kinetic biosorption data were obtained through batch experiments by varying the time of reaction from 1- 30 min to explore the rate of biosorption by DCP at optimum parameters. The pseudo-second order kinetic model (Ho and McKay, 1999) was applied and which can be generally expressed as follows:

$$dq_t / dt = k_2(q_e - q_t)^2 \tag{6}$$

where q_e and q_t is adsorption capacity at equilibrium and at time t, respectively (mg/g) and k_2 is the second-order rate constant of adsorption (g/mg.min).

Integrating the Eq. (6) for the boundary conditions $q=0$ to $q=q_t$ at $t=0$ to $t=t$ is to obtain the following equation:

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e) t \tag{7}$$

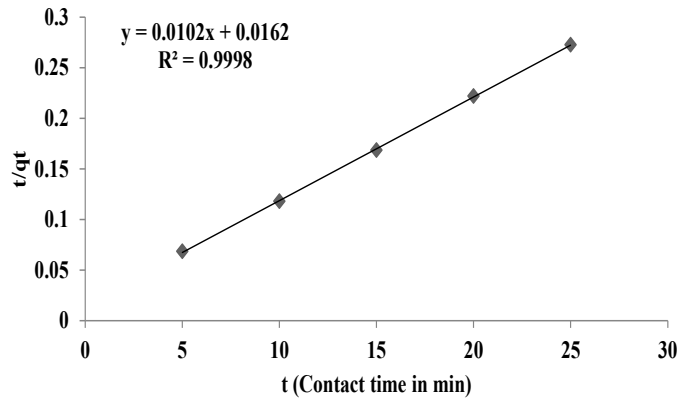


Figure 12. The pseudo-second order kinetic model. [pH = 3; contact time= 10 min; amount of resin= 100 mg; metal ion conc. = 1 mg/mL at RT].

The plot of t/q_t versus t should show a linear relationship if the second-order kinetics is applicable and same is evident from the graph as described in Figure 12. The correlation coefficient (R^2) values were close to 1, indicating the applicability of pseudo-second order model to the present system. The equilibrium rate constant, k_2 and equilibrium capacity or adsorption capacity, q_e were determined from the slope and intercept of the line and their values were 0.0100 g/mg.min and 16.00 mg/g respectively. The applicability of this model suggested that biosorption of elements under study, on DCP was based on chemical reaction, between metals and active sites of the biosorbent.

4. CONCLUSIONS

The results clearly explain that at pH 3 with 100 mg of DCP within 10 min of contact time, 80-82% of uptake of Hg(II) was achieved. The biosorption process followed pseudo-second order-kinetic model. The negative values of Gibb's free energy indicated the feasibility and spontaneous nature of the process. The positive value of entropy suggests the affinity of DCP towards the Hg(II) and negative value of enthalpy ascertain the exothermic nature of the biosorption process. The kinetic study, EDAX, FTIR and desorption studies confirms that chemisorption is the major mechanisms involved in sorption process. The interference study indicated the efficiency and applicability of DCP to be used directly in the mixed solute system of various water effluents. Thus this study proves DCP is a sustainable, eco-friendly and feasible adsorbent for Hg(II)-bearing wastewater remediation.

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