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Eco-friendly waste water treatment by cow dung powder (Adsorption studies of Cr(III), Cr(VI) and Cd(II) using tracer technique)

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ABSTRACT

This explicit investigation aims to explore a green and clean alternative for the waste water treatment employing a natural biosorbent: Dry cow dung powder (DCP). The potential of DCP to sequester toxic heavy metal ions such as Cr(III), Cr(VI) and Cd(II) has been successfully demonstrated, employing Tracer Technique. We have carried out Batch equilibration method and all the important parameters such as pH, dose of sorbent, metal ion concentration, contact time, agitation speed, temperature and interference of different salts have been studied and optimized. The kinetic studies were carried out employing various models but the best fitting was Lagergren pseudo-second order model with high Correlation coefficient R^2 values approximately of 0.997 for all three metal ions. The adsorption capacity and the pseudo-second order rate constant for Cr(III), Cr(VI) and Cd(II) was obtained by regression analysis. Thus DCP proves to be Eco-friendly resin for the heavy metal removal from aqueous medium and for waste water treatment.

Keywords: Waste water treatment; Heavy metal toxicity; Biosorbent; DCP; Eco-friendly removal; Humic acid

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1. Introduction

Water, the basic and indispensable unit of eco-system, is the greenest substance, essential for life and recyclable naturally; hence since ages it has been taken for granted by the human society. A rising quality of life with high rate of resource consumption have an unintended and negative impact on environment, generating waste hulk with far beyond handling capacities of mankind. The threat of water famine looms greatest as our rivers and other water resources are poisoned due to each successive epoch of urbanization and industrialization leading to the water pollution. To combat against water pollution and to find sustainable solution for the same, globally, we have embraced Green Chemistry approach which is one of the Waste Management and Treatment Strategies. Waste management is the collection, transport, processing, monitoring and recycling or disposal of the waste material. It is based on waste hierarchy of reduce, reuse and recycle coined with rethink [1,2].

Heavy metal toxicity in our aqueous milieu is one of the most menacing situations as heavy metals are non-biodegradable and through the process of bio-magnification, they further accumulate in food chain [3]. Some of the heavy metals, viz. Cadmium, Mercury, Chromium, Lead, Arsenic etc., are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to human as well as to the biota of environment. Generally, in-vivo

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pathway, these heavy toxic metals, attacks the active sites of the Metalloenzymes, inhibiting the essential functions.

Trivalent Chromium has been demonstrated to decrease the fidelity of DNA synthesis and produce genotoxic DNA adducts that inhibit DNA replication thus turns to be mutagenic [4]. Acute exposure of Cr(VI) produces nausea, liver and kidney damage, dermatitis and respiratory disorders. In human, exposure of Cd(II) leads to both chronic and acute disorder like testicular atrophy, hypertension, damage to kidney & bones, anemia, itai-itai etc [5].

The effluents produced from various manufacturing industries contain Chromium and Cadmium compounds in alarming proportion. The increasing awareness of environmental pollution has led to a quest for effective and innovative treatment methods. Various methods of treatments such as chemical precipitation, electrodialysis, membrane process, liquid extraction and ion exchange have been employed for the removal of this heavy metal [6]. These methods are all costlier as well as have many loop-holes such as incomplete metal removal, high requirement of energy and reagents, generation of toxic sludge or other wastes.

Among all these separation techniques, ***Adsorption*** is the most promising technique for the removal of heavy metal pollutants due to its theoretical and practical simplicity, rapidity & most crucial its feasibility. Literature survey for the adsorption of heavy metals on the natural adsorbent material reveals that the adsorbents in current utility is from Biotic and Abiotic as well as Living and Non-living matrix. But these naturally available materials require some degree of physical and chemical enhancement so as to optimize as an adsorbent, which add on to the economy of entire adsorption process. In the present studies DCP is employed without any pre or post treatment.

Being freely and easily available it has an edge over other processed natural adsorbent considering their cost, time and energy efficiency. Also, it neither imparts any foul odour or coloration to treated water, nor does it lead to increase in biomass which abstract post treatment. Disposal of DCP is also easy as it can be sun dried and can be utilized as a landfill. These advantages coined with free abundance reduce operational cost which makes DCP a green and Eco-friendly adsorbent.

2. Materials and methods

2.1. Adsorbent

DCP (100 mesh) was provided by Keshav Shrushti, Research centre on Cow product (Thane, India) and due precautions were taken to avoid any contaminations. It is naturally available bio-organic, complex, polymorphic fecal matter. It is enriched with minerals, carbohydrates, fats, proteins, bile pigments, aliphatic - aromatic species such as 'Humic acid' and many functional group such as carboxyl, phenols, quinols, amide etc., which enhances its adsorption properties. It also possess certain dead biomass such as Aerobic heterotrophic bacteria viz. as Acinetobacter sp., and Petroleum utilizing bacteria such as Pseudomonas sp. [7]. 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.

2.2. Characterization of DCP

Cow dung powder was dried properly before its utilization, so as to prevent its oxidation by acid due to presence of mixture of alcohols if any. The absence of alcohol is also supported by FTIR analysis of DCP, which is devoid of any characteristic band of alcohol. The integrity of DCP before and after the adsorption was studied by measuring the mesh size and was found to be same indicating during adsorption process there were no physical attrition of resin. The HA has been successfully extracted by authors from DCP and this piece of work has been published in the International Journal [8]. All the characterization techniques have been carried out at Indian Institute of Technology, IIT, Powai, Mumbai. The physical properties of DCP are listed in Table 1. The DCP has been characterized using XRF technology Table 2 for its quantitative as well as qualitative elemental composition.

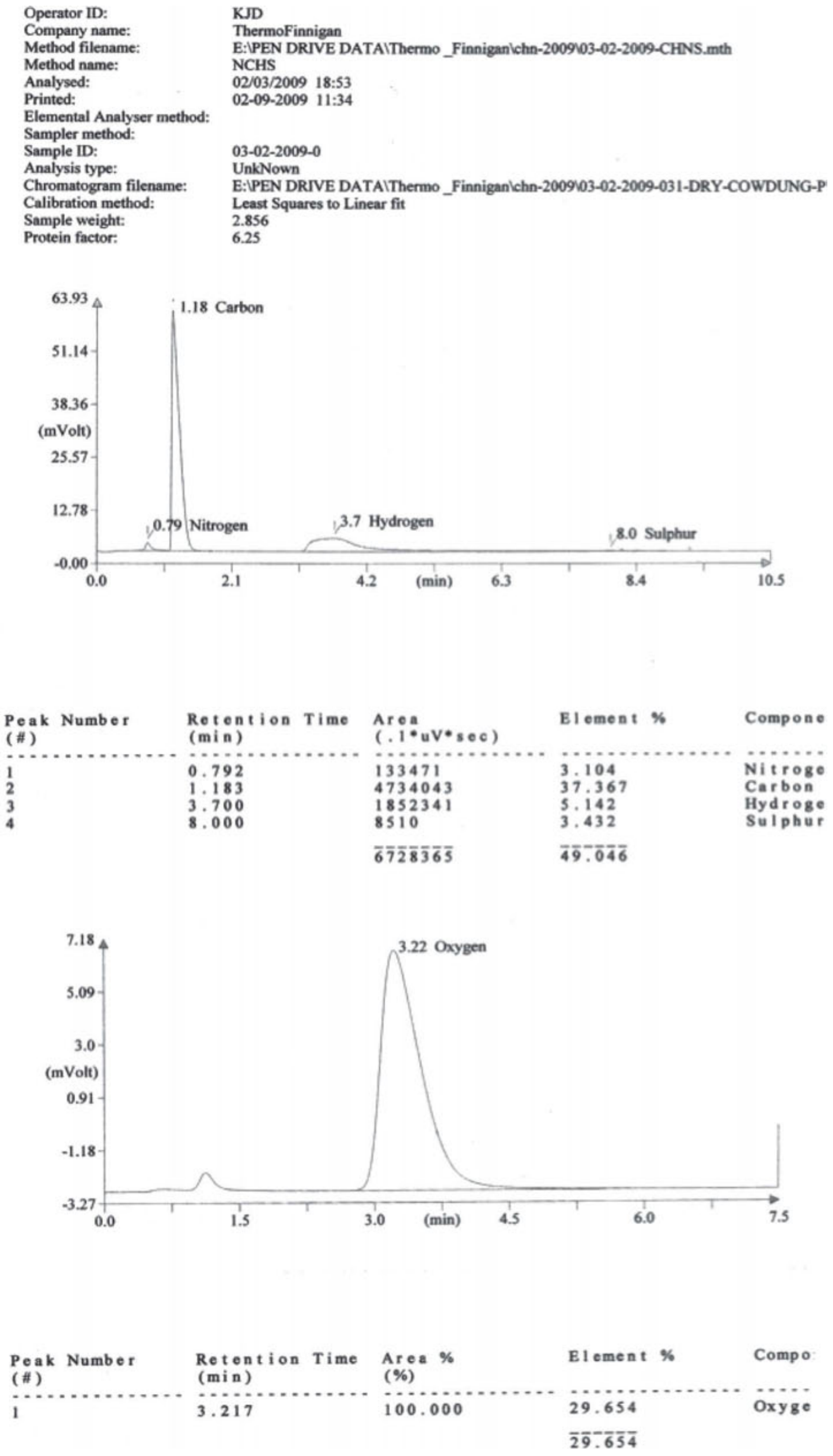
For the complete elemental composition, complimentary to XRF technique, C, H, N, S, (O), has also been obtained Fig. 1. FTIR analysis proves functionality of DCP as an adsorbent due to the presence of various adsorptive functional groups shown in Fig. 2 and the detailed information is given in Table 3. Also Fig. 3[a to i] shows SEM pattern of DCP which clearly reveals the surface texture and porosity of the DCP. Many pores and small openings have been found on the surfaces which are responsible for the easier diffusion during adsorption proccess.

2.3. Adsorbate

All the chemicals used were of Analytical Grade. The stock solution of Cd(II) was prepared using $Cd(NO_3)_2$

Table 1
Physical characteristics of DCP

No.	Characteristic	Values
1	Mesh size	100
2	Ash content	25%
3	Moisture	10–11%



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Method filename:               E:\PEN DRIVE DATA\Thermo _Finnigan\chn-2009\03-02-2009-CHNS.mth
Method name:                   NCHS
Analysed:                      02/03/2009  18:53
Printed:                       02-09-2009  11:34
Elemental Analyser method:
Sampler method:
Sample ID:                     03-02-2009-0
Analysis type:                 UnkNown
Chromatogram filename:         E:\PEN DRIVE DATA\Thermo _Finnigan\chn-2009\03-02-2009-031-DRY-COWDUNG-P
Calibration method:            Least Squares to Linear fit
Sample weight:                 2.856
Protein factor:                6.25
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Peak Number        Retention Time     Area               Element %          Compone
(#)                (min)              (.1*uV*sec)
---------------    ---------------    ---------------    ---------------    -------
1                  0.792              133471             3.104              Nitroge
2                  1.183              4734043            37.367             Carbon
3                  3.700              1852341            5.142              Hydroge
4                  8.000              8510               3.432              Sulphur
                                      -------            ------
                                      6728365            49.046
```

```
Peak Number        Retention Time     Area %             Element %          Compo
(#)                (min)              (%)
---------------    ---------------    ---------------    ---------------    -----
1                  3.217              100.000            29.654             Oxyge
                                                         ------
                                                         29.654
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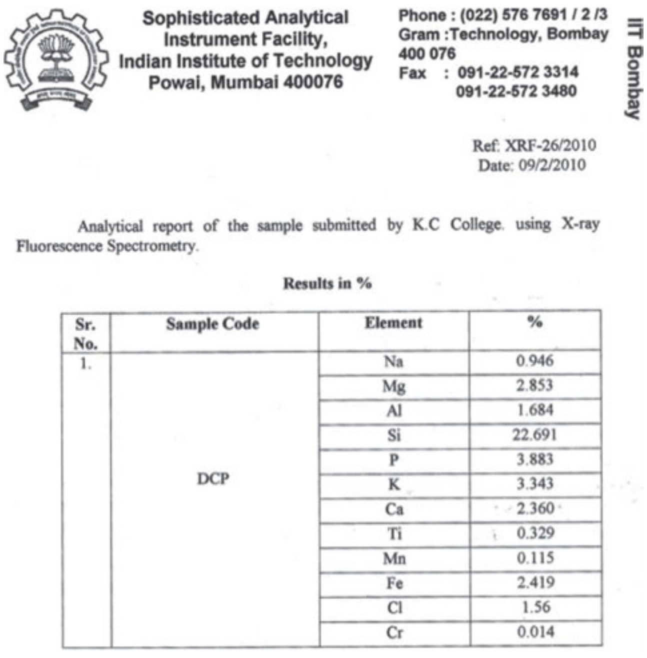
Fig. 1. C,H,N,S,(O) analysis of DCP.

Table 2
XRF data of DCP



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Ref: XRF-26/2010
Date: 09/2/2010

Analytical report of the sample submitted by K.C College. using X-ray Fluorescence Spectrometry.

Results in %

Sr. No.	Sample Code	Element	%
1.	DCP	Na	0.946
		Mg	2.853
		Al	1.684
		Si	22.691
		P	3.883
		K	3.343
		Ca	2.360
		Ti	0.329
		Mn	0.115
		Fe	2.419
		Cl	1.56
		Cr	0.014

and of Cr(III) & Cr(VI) was prepared using Cr_2O_3 & CrO_3 respectivily. Other solutions were prepared using distilled water and were standardized by standard analytical methods [9].

2.4. Tracer technique

It is the radioanalytical technique in which micro amount of radioactive isotope is added to a system in order to trace or monitor the chemical reaction of a certain element in the system [10]. In comparison to classical approach, tracer technique offers some unique advantage such as, high sensitivity, non-destructive pattern, freedom from reagent blank etc. The Radiotracer ^{51}Cr(III), ^{51}Cr(VI) (Gamma-ray emitter) & ^{115m}Cd(II), (Beta-emitter) were procured from BRIT (Board of Radiation & Isotope Technology, Mumbai, India).

2.5. Batch equilibration mode

A known amount of DCP was mixed with 10 ml of solution containing radiotracer and 1 mg/ml solution

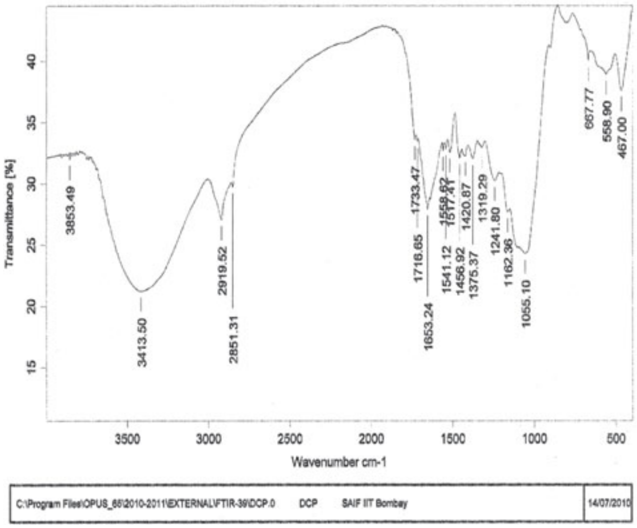

Fig. 2. FTIR spectra of DCP.

Table 3
FTIR data of DCP (FTIR instrument: Nicolet Instrument Corporation-USA, model-MAGNA 500 with specification range of 4000 cm^{-1} to 50 cm^{-1}, from IIT Mumbai.)

Functional group	Compounds	Characteristic absorption (cm^{-1})	DCP Signal (cm^{-1})
C=O	Carboxylic acid, (C=O strech)	1760–1670(s)	1716.65 1733.47
N-H	Amines (1^0 –amines)	3400–3500(w)	3413.50
C-O	Saturated secondary or cyclic tertiary amine	1125–1085 (s)	1055.10 1162.36
C-H	Alkane	2850–3000 (s)	2851.31 2919.52
C-Cl	Chlorine	600–800 (s)	667.77
C=OR	6 member cyclic ketone	1715 (s)	1716.65
C=C	Alkene	1620–1680(s)	1653.24
C=O & (RCOOR′	Esters & Lactones 6-membered lactone	1740 cm ± 10 cm^{-1}	1733.47
Si-CH_3	Silicon functions	1250 ± 10 (s)	1241.80
-Na	Metal group	460	467.00
-COOH	Carboxylic Acid O-H Stretch	3000–2500 (broad, v)	2851.31 2919.52

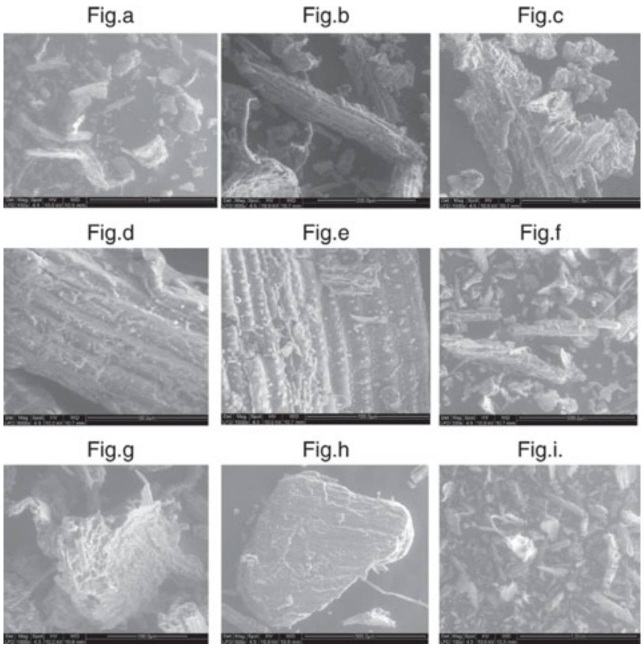

Fig. 3. Scanning Electron Micrograph (SEM) of DCP (a to i).

of carrier. The pH was adjusted using dil.H_2SO_4, HNO_3 and $NaHCO_3$ for Cr(VI), Cd(II) & Cr(III) respectively. The resultant aliquot was equilibrated for 10 min with mechanical stirrer and was then centrifuged. After separating supernatant, adsorbent 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) for gamma emitters and end window type Geiger-Muller Counter(PEA GCS 101P) in conjugation with a decade scalar, timer and a high voltage unit, for the beta emitter. 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), agitation speed (0–5000 rpm), amount of adsorbent (50–1000 mg), temperature (273–373 K), adsorption capacity and interference of different salts was studied so as to optimize the parameters for developing efficient adsorption process. We have also carried out kinetic studies so as to optimize the system for it to be feasible for real application.

2.6. Statistical analysis

All experimental data were wre measured in triplet and were calculated using percentage adsorption formula as given below:

$$\%\ \text{Adsorption} = \frac{A(i) - A(f)}{A(i)} \times 100$$

where, $A(i)$ is the Activity taken, $A(f)$ is the Total activity in supernatant.

3. Results and discussion

All the aforementioned parameters were comprehensively studied for the optimization of the system. The results revealed that having 10 min of contact time, at 4500 rpm of agitation speed, at the optimum pH, 100 mg of DCP can effectively remove Cr(III) and Cd(II) up to 75% and 85% respectively. Also, Cr(VI) was adsorbed up to 75% with 250 mg of DCP.

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. As hydronium and hydroxyl ions are adsorbed strongly over others, it controls the adsorption rate of other metal ions [11]. The experiments of this stage were carried out as described above. DCP being heterogeneous adsorbent possess positively charged site owing to some proteins, enzymes and acidic groups. Hence on varying the pH of solution, its overall surface charge can be modified so as to get maximum adsorption. The behaviour of metal ions might be explained on the basis of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent.

On varying the pH from 1–10 as shown in Fig. 4, it can be seen that optimum pH for maximum adsorption of Cr(VI) is 1 and as pH increases there is significant decrease in adsorption percentage. The adsorption of Cr(VI) varies as a function of pH with H_2CrO_4, $(HCrO_4)^-$, $(Cr_2O_7)^{2-}$ and $(CrO_4)^{2-}$ ions appear as dominant species in acidic condition. In the alkaline atmosphere,

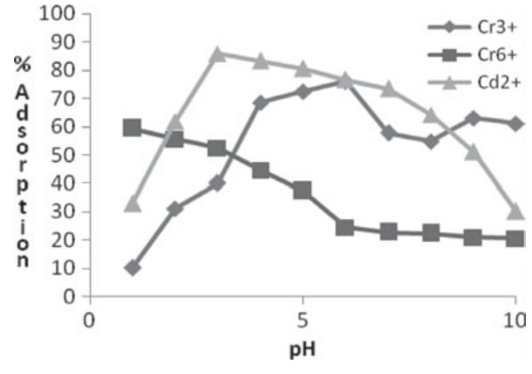

Fig. 4. Effect of pH on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP [Contact time = 10 min.; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Metal ion concentration = 1 mg/ml; agitation speed = 4000 rpm at room temperature].

concentration of OH$^-$ ions increases and overall charge on DCP becomes negative. Abundance of hydroxyl ion attribute great hindrance for the diffusion of chromium ion, resulting in weakening of electrostatic force of attraction between adsorbent and adsorbate which results in decreasing adsorption percentage. Hence acidic pH is favourable for the Cr(VI) adsorption process. We observed **pH 1** to be optimum for Cr(VI) system.

As can be seen from Fig. 4, the optimum pH for the Cr(III) is pH 6. At this pH, the dominant species are $Cr(OH)_2^+$ and $Cr(OH)^{2+}$ and these moieties have to face lesser repulsion of H$^+$ ion hence, we find maximum adsorption at this pH. Under the acidic condition in aqueous solution $Cr(OH)^{2+}$is the dominant dissolved species of trivalent chromium. At low pH, adsorption becomes unfavourable due to electrostatic repulsion between the positive charged surface, in excess of H$^+$ ions, and Cr(III) ions, hence decreasing the adsorption. As the pH increases beyond 6, the adsorption again decreases due to precipitation of Cr(III) as $Cr(OH)_3$. Hence optimum adsorption of Cr(III) is at **pH 6**.

For Cd(II), it was observed that within the pH range of 3–6, adsorption was maximum and highest at pH 3 and as pH increases there was a significant decrease in adsorption. At very low pH (less than 3) the concentration of H$^+$ ions is comparatively more than Cd(II) ions. The ionic radius of H$^+$ being smaller than that of Cd(II) (0.97 Å), H$^+$ ions gets easily absorbed, hence the adsorption is lesser at very low pH and it is maximum at pH 3 due to comparatively less concentration of H$^+$ ions [12]. Beyond pH 7, Cd exists as $[Cd(OH_3)]^{1-}$ & $[Cd(OH_4)]^{2-}$, causing repulsion towards negatively charged adsorbent site. Hence acidic pH is favourable for the Cd(II) adsorption process. We observed **pH 3** to be optimum for system.

3.2. Effect of amount of adsorbent

Adsorption being surface phenomenon, the extent of adsorption is directly proportional to the surface area available. Increasing the adsorbent amount, increase in adsorption percentage was observed. After certain dose of adsorbent, maximum adsorption sets in after which the percentage adsorption decreases to some extent which is evident from the data. This suggests that after optimum dose, number of ions bound to adsorbent and the number of free ions remains constant even with further addition of the adsorbent. It may be due to partial aggregation of active adsorbent sites [13]. Our results suggest that optimum amount of DCP for Cr(VI) is 250 mg and for Cr(III) and Cd(II) is 100 mg (Fig. 5).

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. Fig. 6 reveals that as contact time increased, percentage adsorption also increased, but after some time, it gradually approached a constant value, denoting attainment of equilibrium. Further increase in contact time did not increase percentage adsorption due to deposition of ions on the available adsorption sites on adsorbent material. Also, adsorption got reduced in later stage because, initially a large number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface site may be 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

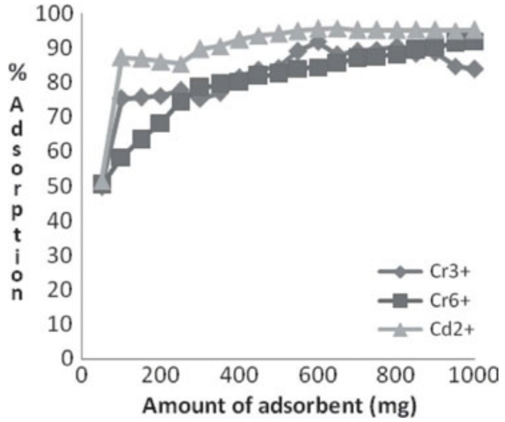

Fig. 5. Effect of adsorbent dose on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP [Contact time = 10 min.; pH = Cr(III) at 6, Cd(II) at 3 & Cr(VI) at 1; Metal ion concentration=1 mg/ml; agitation speed = 4000 rpm at room temperature].

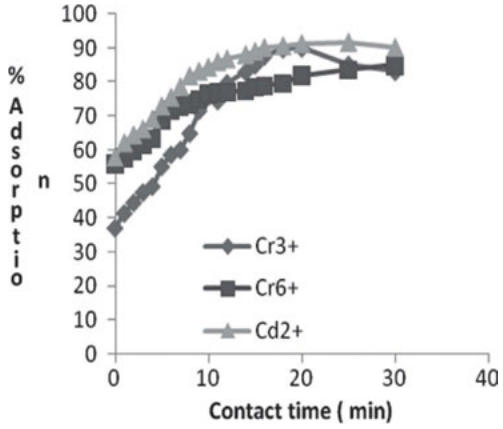

Fig. 6. Effect of contact time on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP [pH = Cr(III) at 6, Cd(II) at 3 & Cr(VI) at 1; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Metal ion concentration = 1 mg/ml; agitation speed = 4000 at room temperature].

over adsorption. These results are typical for biosorption of metals involving no energy-mediated reactions, where metal removal from a solution was due to purely physico-chemical interactions between the biomass and metal ions in the solution [14]. 10 min of contact time proved sufficient for the system, which satisfy the criterion of minimum time, optimum result.

3.4. Effect of metal ion concentration

Metal ion concentration was varied from 0.5–20 mg. As shown in Fig. 7, percentage adsorption decreased with increase in metal ion concentration in all three cases. In case of low concentration, the ratio of number of moles of metal ions to the available surface area of adsorbent was larger and subsequently the fractional adsorption becomes independent of metal ion concentration. However at higher concentration the available site on the resin became fewer, and hence the percentage adsorption decreased which depends upon initial concentration. This appears to be due to the increase in the number of ions competing for the available binding site in the biomass [15]. 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 metal ions, resulting in decrease in adsorption process.

This study reveals that 250 mg of DCP can adsorb 20 mg/ml of Cr(VI) and 100 mg can remove 18 mg/ml of Cr(III) upto 50%. The removal efficiency for Cd(II) has been found comparatively to be lesser. The uptake of 100 mg of DCP is only 35% for 6 mg/ml of Cd(II). On increasing the amount of DCP, the removal of these heavy metals can be increased even at higher metal ion concentration.

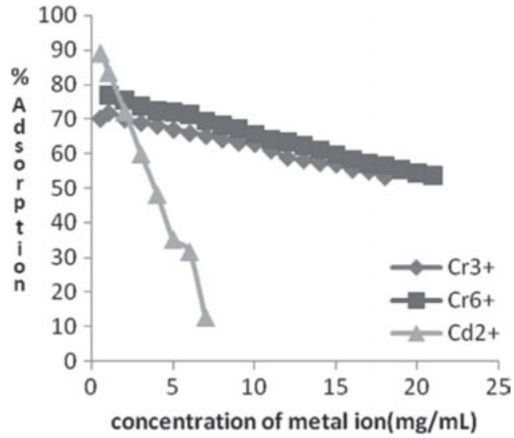

Fig. 7. Effect of metal ion concentration on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP. [pH = Cr(III) at 6, Cd(II) at 3 & Cr(VI) at 1; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Contact time = 10 min; agitation speed = 4000 at room temperature].

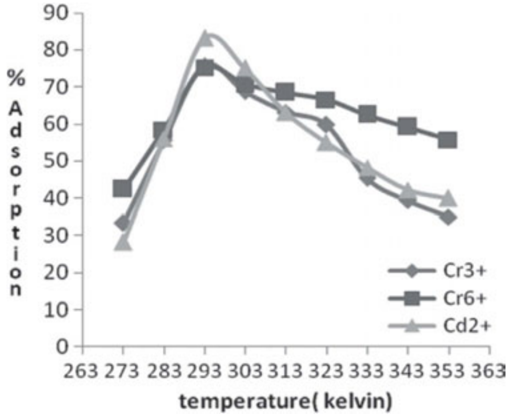

Fig. 8. Effect of temperature on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP. [pH = Cr(III) at 6 ,Cd(II) at 3 & Cr(VI) at 1; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Contact time = 10 min; Metal ion concentration = 1 mg/ml; agitation speed = 4000].

3.5. Effect of temperature

Temperature plays a vital role in the process of adsorption as these reactions are normally exothermic; hence the extent of adsorption generally increases with decrease in temperature. It also affects the enthalpy of entire system. Optimum thermal energy imparts the mobility to metal ion. For this parameter the temperature was varied between (10–90ºC). Fig. 8 shows that the adsorption of metal ions increases at lower temperature and was found maximum at room temperature. Further on increasing temperature, percentage adsorption was found to decrease. 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 [16]. Hence, room temperature favours the adsorption rate of all the three system.

3.6. Effect of agitation speed

Adsorption was carried out under all optimum parameters and result of this experiment proved that speed of agitation has important role. Fig. 9 shows that all agitation speeds were found to have a positive impact on the system. Increasing the speed at rate of 500 rpm, percentage adsorption showed markedly high values. This is because agitation facilitates proper contact between the metal ions in solution and the binding sites and thereby promotes effective transfer of adsorbate ions to the adsorbent sites [17]. The agitation speed of 4000 rpm was standardized for entire system.

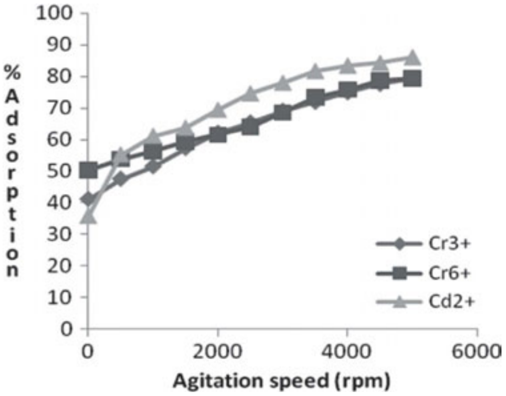

Fig. 9. Effect of agitation speed on adsorption of Cr(III), Cr(VI) and Cd(II) on DCP [pH = Cr(III) at 6 ,Cd(II) at 3 & Cr(VI) at 1; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Contact time = 10 min; Metal ion concentration = 1 mg/ml at room temperature].

3.7. Effect of Interference of various salts

Industrial effluent or any other polluted water body contains different organic and inorganic salts in different proportions. To investigate the effect of interference of different salts on the percentage adsorption of Cr(III), Cr(VI) and Cd(II) on DCP, we have studied different organic as well as inorganic salts with varying proportion of 10 mg, 25 mg, 50 mg and 100 mg. All the optimized experimental parameters, obtained above, were kept constant for this study. We observed that some salts were proved to be non-interfering with concentration of 100 mg, whereas some were profoundly suppressing the adsorption process even with concentration of 10 mg. The interfering salts were chemically treated with appropriate reagents so as to suppress their interference. We also found that some salts were enhancing the adsorption of metal ions.

There are many factors governing the adsorption process in mixed solute system, where metals are not only present as free ions but some ligands are also 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 adsorption process. All these factors can either results in mutual inhibition of competing adsorbate, which decease the efficiency of adsorption or their mutual complex can enhance the adsorption rate.

The variation in the concentration of one component influences the concentration of other component. In case of metal–metal interaction it has positive impact whereas the metal-ligand interaction exhibits a negative impact. The free ion concentration of a metal decreases with an increase in the ligand concentration [18]. Thus the various concentration of ligand, in present studies the concentration of various salts; profoundly interfere in the adsorption process. The higher concentration of ligand reduces the percentage adsorption due to readily forming stable metal-ligand complex or due to competition between metal ion and ligand for the sorption sites on the adsorbent. Some ligands with optimum concentration increase the adsorption of concerned metal ion due to co-adsorptive effect on the adsorbent. Table 4 shows the detailed information about the same.

This obvious behaviour can also be explained by HSAB theory (Hard & Soft Acid Base concept) given by Pearson [19]. Metal ions are classified as Hard or Soft, on the basis of their "hardness scale". According to this theory, metal ions act as Lewis acid and ligand act as Lewis base. Hard acids tend to form a strong bond with hard base and soft acid with soft base. Heavy metals are considered as soft ions and thus they form very strong bond with soft base such as CN^-, RS^-, $–SH^-$ etc., nitrogen or sulphur containing ligand, which decreases the adsorption of metal ions [20].

All the three heavy metal ions under the studies, shows the same adsorption pattern which can be learnt from Table 4. Salts such as tartarate, thiourea and thiosulphate proved to be interfering at 10 mg concentration, in all the three cases. In such situation amount of DCP can be increased to get the positive results.

3.8. Kinetic parameter

The Kinetic biosorption data were obtained by Batch experiments to explore the rate of biosorption by DCP at optimum parameters and varying the time of reaction from 1–30 min. The kinetic adsorption data can be processed to understand the dynamics of the biosorption reaction in terms of the order of the rate constant. We have studied different kinetic models such as First order, Second order, Pseudo-first order, Pseudo-second order and the intraparticle diffusion model. But among these models best fitting model was Lagregren Pseudo-second order model. The correlation coefficients of all the three elements have R^2 values close to 1 as shown in Table 5, indicating the applicability of pseudo second order model to the present system. 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. The kinetic data was treated with the Lagergren Pseudo second-order kinetic model [21]. It is generally expressed as follows:

$$dq_t/dt = k_2\left(q_e - q_t\right)^2 \tag{1}$$

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).

Table 4
Effect of various salts on the adsorption of Cr(III), Cr(VI) and Cd(II) on DCP

Amount of salt in mg	Cr(III)	Cr(VI)	Cd(II)
100 Non-Interfering	Nitrate Iodide Bromide Carbonate	Nitrate Iodide	Nitrate Iodide Chloride
50 Non-Interfering	Bicarbonate Chlorate Fluoride	Bicarbonate Carbonate Chlorate Fluoride Bromide	Bicarbonate Carbonate Chlorate
25 Non-Interfering	Phosphate Sulphate Sulphite Chloride Hydroxide Nitrite	Phosphate Sulphate Sulphite Chloride	Phosphate Sulphate Sulphite Fluoride Bromide Mangnate
10 Non-Interfering	Citrate Thiocynate Chromate	Hydroxide Citrate Thiocynate Chromate Mangnate	Hydroxide Citrate Thiocynate Chromate
10 Interfering *Treated	Mangnate*	Nitrite* Oxalate*	Nitrite*
10 Interfering ■ Could not be treated	Thiourea Thiosulphate Tartrate Oxalate	Thiourea Thiosulphate Tartrate	Thiourea Thiosulphate Tartrate Oxalate

*Treated with appropriate reagents, ■ Could not be treated.

Table 5
The Lagergren Pseudo-second order model parameter

Elements	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
Cr(III)	0.1060	19.31	0.976
Cr(VI)	0.0116	10.20	0.997
Cd(II)	0.0108	8.387	0.998

[Regression Analysis for the adsorption of Cr(III), Cr(VI) and Cd(II) on DCP, k_2 = the second-order rate constant of adsorption (g/mg min), q_e = adsorption capacity at equilibrium (mg g^{-1}), R^2 = regression coefficient.]

Integrating the Eq. (1) for the boundry conditions q=0 to q=q_t at t=0 to t=t is to obtain the following equation:

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

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. The equilibrium rate constant, k_2 and equilibrium capacity or adsorption capacity, q_e were determined from the slope and intercept of the line in Fig. 10.

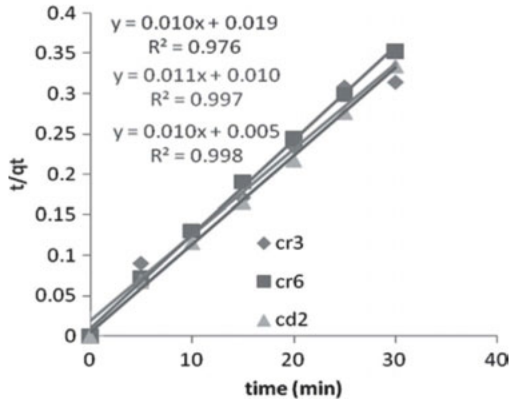

Fig. 10. The Lagergren pseudo-second order model for the adsorption of Cr(III), Cr(VI) and Cd(II) on DCP[pH = Cr(III) at 6,Cd(II) at 3 &Cr(VI) = 1; amount of resin = 100 mg for Cr(III) and Cd(II) & 250 mg for Cr(VI); Contact time = 10 min; Metal ion concentration = 1 mg/ml; agitation speed = 4000 at room temperature].

4. Conclusions

The real solution for waste water treatment is not in the technological advances but it aims to maximize the applicability and efficiency of naturally available resources.

Our results revealed that 100 mg of DCP with 10 min of contact time can effectively remove 75% Cr(III) at pH 6 and 85% Cd(II) at pH 3. For removal of 75% of Cr(VI), 250 mg of DCP was required at pH 1. The room temperature favours the adsorption process. The Lagergren pseudo-second order kinetic model was proved to be best fitting with high correlation coefficient R^2 values approximately of 0.997 for all three metal ions. The adsorption capacity of DCP for the removal of Cr(III), Cr(VI) and Cd(II) from aqueous medium obtained was 19.31, 10.20 and 8.39 mg g^{-1} respectively. Also, the mechanism of the metal ion adsorption on DCP is chemisorption type and is explained by pseudo-second order kinetics.

The present study concludes that we have developed a simple, efficient and eco-friendly method for the utilization of DCP as an effective green adsorbent material for the removal of carcinogenic and heavy metal water pollutant. Being naturally and easily available, DCP can be employed without any pre or post treatment. Hence it has an edge over processed natural and synthetic adsorbent considering their production cost, time and energy efficiency. Thus the utility of DCP will surely contribute to convert waste into wealth, refuse into resource and trash into cash, the ultimate aim of waste management strategy.

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