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Biosorption of Cadmium from Aqueous Solutions by Banana Peel Powder

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Water pollution is worst in developing countries, where human health is gravely damaged by accelerating eutrophication, heavy metals, persistent organic pollutants and sewage pollution. Among the various contaminants in waters, the presence of heavy metals is proven to be extremely harmful due to their high toxicity and non-biodegradability. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. In this point of view, to remove cadmium by eco-friendly manner banana peel powder based biosorbents has been taken for the present investigation, and used Atomic Adsorption Spectrophotometer for metal estimation. The SEM image determined that banana peel contain irregular porous surface area, and also the FTIR peaks showed that banana peel has O-H, C-H, C=C, C-F and C-Cl functional groups which has important rule in adsorption of metals. The effects of pH and metal ion concentration on adsorption efficiency were studied in the present batch study of metal biosorption. The highest adsorption % of Cd (II) adsorbed was evaluated 88.01% from 75 ppm and pH 6 solution. In the conclusion of the study the banana peel has high capacity of heavy metals adsorption from wastewater such as Cd (II).

Key words: Biosorption, Banana peel, Cadmium and Atomic Absorption Spectrophotometer.

Heavy metals are the elements having specific gravity of five time greater than the specific gravity of water (Hawkes, 1997). Heavy metals causes' health and environmental risk therefore received a great deal of attention among the researchers (Arif *et al*., 2015). Cadmium, the seventh most toxic metal as per ATSDR, (2007) and also motivates cancer, diarrhea, damage to bones, kidney, mucus membrane, causes vomiting and also effects hormone secretion. The main sources of Cd are industrial effluents, like electroplating, paint, pigment, basic steel work, textile industries, industries metals, finishing and electric accumulator's batteries (Kumar *et al*., 2012, Ansari *et al.,* 2011). Removal of heavy metals through advanced technologies like vacuum evaporation, crystallization, chemical precipitation, membrane filtration, ion exchange/solvent extraction etc. have been employed in developed countries (Rich and Cherry, 1987). Whereas in developing countries, these treatments cannot be used due to technical difficulty as well as expensive. Some of these techniques furthermore, generate toxic sludge, the disposal of which is a burden on the techno-economic feasibility of treatment procedures (Kratochvil and Velosky, 1998). Therefore simple economical metal removal methods to be established for developing countries. Different researchers have used different biomass such as citrus pectin (Ankit and Silke, 1998), Black gram husk (Saeed *et al.,* 2005), Banana peels for the adsorption of Cd(II) and Pb(II) (Anwar *et al*., 2010), etc. for the removal of heavy metals. Hence an attempt was made to develop banana peel based adsorbent for the removal Cd from contaminated water.

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Material and Methods

Adsorbent preparation

The (*Musa paradisiac*) banana peel were collected from the banana chips industry in local market, Coimbatore - Tamil Nadu, India for experimental studies. The peels were washed 3-4 times with tap water for removing dust particles from the peels and then kept to sun light for drying for 6-8 days and then in an oven dried at 70^o C for 2 hours. Then minced by mixer into small particles and sieved over sieves to get banana peel powder.

Adsorbent solution

The $CdCl_{2.}$ H_2O was used for preparation of different concentration of cadmium. Milli-Q water was used for preparation of solution and adsorption experiments.

Characterization of adsorbents

The different characterization of banana peel such as electrochemical properties, biochemical components and elemental composition were analyzed by the following standard methods: pH and EC was examined at method given by Jackson, (1973), and Cation Exchange Capacity as per the method Crook, (1964). Biochemical components like organic carbon by Walkley and Black, (1934) method, crude protein, crude fiber, protein, carbohydrate, cellulose, hemicellulose and pectin substances as per methods Sadasivam and Manickam, (2009), Moisture content and Ash content of the substrate also analyzed methods given by Gupta, (2007). And the elemental composition like Nitrogen was determined as per Micro-Kjeldahl Method (Sadasivam and Manickam, 2009). Total Phosphorus and Total Potassium was estimated as per methods given by Jackson, (1973). Calcium and Magnesium by Versenate (EDTA) (Gupta, 2007). Sodium by Flame photometer method (Gupta, 2007). Iron, Manganes and Zinc was determined as per Atomic Adsorption Spectrophotometer method (Tandon, 2013).

Scanning electron microscope (SEM) with energy dispersive X-ray (EDX)

Scanning electron microscope (M/s. FEI – Quanta 250, Czech Republic) was used to record the surface texture and morphological characteristic of banana peel samples (Ucar *et al.,* 2014). The banana peel samples were grounded to nanosize and spreaded on double sided conductive carbon tap fixed on the stub. After attaining high vacuum the filament was turned on and adjusted to various required parameters like electron beam, intensity, spot size, voltage, emission current then the SEM images were captured and pore space was measured to study the adsorption properties of banana peel. The SEM was also equipped with EDX analyzer which determine the elemental parameters of banana peel surface.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded with 0.5 mg of banana peel sample embedded in potassium bromide (0.1 wt % KBr) and then pressed into pellets separately and observed in a FTIR (Model 8400S of Shimadzu, Japan) using Attenuated Total Reflectance (ATR) technique having wavelength source (400-4000 cm^{-1}) (Trakal *et al.,* 2014).

Particle size analyzer (PSA)

Exactly 0.5mg of banana peel sample was dispersed in 50 ml of distilled water and sonicated using ultrasonic processor for 30min at 10 seconds in on-off mode. A drop of surfactant (Tween – 80) was added to the suspension and particle size was analyzed (Horiba Scientific Nanopartica SZ-100, Japan) (Beesley *et al.,* 2010).

Zeta potential

The surface charge of banana peel samples were examined by determination the zeta potential. About 0.5 mg of sample was dispersed into 20 ml of deionized water (DI) and the solution shaked by mechanical shaker at 180 rpm for 2 hours. After shaking the solution was placed in sonic bath to break the particles into colloids. Then the solution was filtered by filter paper Whatsman no. 42. The zeta potential of supernatant solution was determined using PSA (Horiba Scientific Nanopartica SZ-100, Japan). The suspension measured the size distribution of the particle, average diameter and zeta potential (Ucar *et al.,* 2014).

Batch adsorption

One gram of banana peel powder (0.5 mm size) was added to 100 ml of the metal ion solutions with different initial concentrations (25 ppm, 50 ppm, 75 ppm and 100 ppm). After mixing pH of each solution (4, 5, 6, 7 and 8) was adjusted by drop-wise addition of 0.1N NaOH and 0.1N HCl. The solutions were filtered through whatsmann No. 42 filter paper after the equilibration time and final metal ion concentration was measured by Atomic Adsorption Spectrophotometer. Removal efficiency % was calculated using the formula: Removal efficiency (%) = (Ci – Cf)/ Ci x 100 Where, Ci is the initial concentration of metal ion in solution before sorption (mg L-1) and Cf is the final metal ion concentration after the sorption analysis (mg L-1).

Results and Discussion

Electrochemical, biochemical and elemental characterization

The electrochemical and biochemical characteristics of banana peel and the elemental composition are given in table 1 and 2.

Table 1. Electrochemical and biochemical characterization of banana peel

Parameter	Result	Parameter	Result
pH	6.18	Protein (%)	5.02
EC (dSm^{-1})	1.55	Carbohydrate (%)	45.03
CEC (cmol + kg^{-1})	5.6	Cellulose (%)	12.08
Particle size (nm)	11286.5	Hemicellulose (%)	26.23
Zeta potential (mV)	-50.1	Pectin (%)	15.4
Organic carbon (%)	36.74	Moisture content (%)	8.51
Crude protein (%)	10.51	Dry matter (%)	91.49
Crude fiber (%)	15.93	Ash content (%)	10.65

The crude protein and crude fiber of banana peel were 10.51% and 15.93% respectively and according to Memon, *et al.,* (2008) estimation crude protein is 10.14% and crude fiber is 11.04% , but Anhwange and Joseph, (2009) reported higher percentage of crude fiber and then Monisha *et al.,* (2014) determined very less compare to our result.

Table 2. Elemental composition of banana peel

Parameter	Result (mg g^{-1})	Parameter	Result (mg g^{-1})
Total Nitrogen	16.8	Sodium	19.5
Total Phosphorus	6.61	Iron	0.29
Total Potassium	64.5	Manganese	63.54
Calcium	20.45	Zinc	0.16
Magnesium	6.56		

Protein was observed in banana peel 5.02% but Anhwange and Joseph, (2009) and Monisha *et al.,* (2014) reported 0.90% protein in banana peel which is very less compare to our result and Raymundo *et al.,* (2014) reported 5.62% which is near to our estimation. The carbohydrate was observed 45.03% in banana peel but it is lesser than the report of Anhwange and Joseph, (2009) who's reported 59%. Cellulose and hemicellulose was estimated 12.08% and 26.23% in banana peel and the results of Raymundo *et al.,* (2014) were also near to our estimation. He reported 11.45% cellulose and 25.52% hemicellulose of at banana peel. The moisture content and dry matter content of banana peel consider with the finding of Memon, *et al.,* (2008) who reported 9.94% as moisture content and 90.36 as dry matter, and Anhwange and Joseph, (2009) reported 6.70% moisture content lesser and Suantak *et al.,* (2014) noted 12.20% moisture content which is higher than our result. The ash content of banana peel was 10.65% which is in the accordance with the report of Anhwange and Joseph, (2009) who reported 8.50%, but Raymundo *et al.,* (2014) noted 19.98%, which is very high.

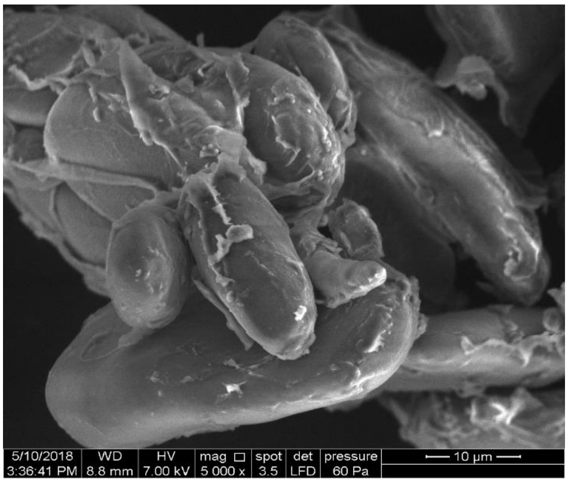

Fig.1. SEM image of banana peel before adsorption

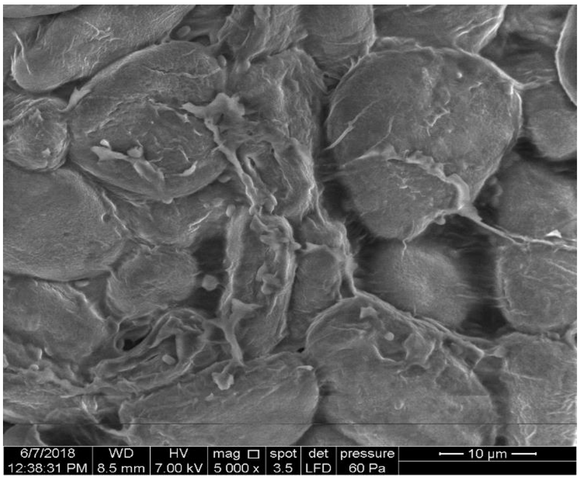

Fig.2. SEM image of banana peel after adsorption of Cd ionst

Total N, P and K was estimated 16.8 mg/g, 6.61 mg/g and 64.5 mg/g in banana peel but Anhwange and Joseph, (2009) was noted 78.10 mg/g potassium in banana peel which is higher than our estimation. Calcium and magnesium was evaluated 20.45 mg/g, 6.56 mg/g and Anhwange and Joseph, (2009) reported 19.20 mg/g Ca in banana peel, which is the same result with our estimation. The total Na, Fe, Mn and Zn content of banana peel were estimated 19.5 mg/g, 0.29 mg/g, 3.54 mg/g, and 0.16 mg/g respectively but Anhwange and Joseph, (2009) examined 24.30 mg/g Na, 0.61 mg/g Fe and 76.20 mg/g Mn in banana peel.

Table 3. Chemical composition of banana peel before and after adsorption of Cd ions by EDX analyzer

Element	Wt. before adsorption (%)	Wt. after Cd adsorption (%)	Element	Wt. before adsorption (%)	Wt. after Cd adsorption (%)
C	69.13	48.37	P	00.28	00.00
N	05.36	04.64	S	00.30	00.37
O	23.41	39.38	Cd	00.00	03.04
Zn	-	00.30	Pb	00.00	-
Na	00.27	00.29	Cl	00.53	00.30
Mg	00.08	00.32	K	00.24	02.13
Al	00.24	00.09	Ca	00.00	00.76
Si	00.16	00.00			

Surface characteristics of banana peel

The surface morphology of banana peel before and after adsorption of Cd was studied by SEM micrograph (Fig.1) and (Fig.2). The micro porous structure was observed with 10000 X resolution and the image was taken with a particle size of 10 µm. The SEM images of banana peel showed that contain irregular porous surface. Suantak *et al.,* (2014) also determined the same result from the SEM analysis of banana peels to have irregular and porous morphological surface area.

EDX analysis

EDX analysis was observed the chemical composition presence on the surface of banana peel before and after adsorption. The chemical composition of banana peel before and after adsorption of Cd by EDX as given in table 3 and the micrographs have been represented in (Fig.3) and (Fig.4). It shows that the weight % of Cd and Pb in banana peel is zero (0.00) before adsorption, but after adsorption their weight % increased to 3.04% and 1.31%, respectively.

Suantak *et al.,* (2014) estimated the percentage weight of chemical composition in banana peel as follows: C 30.12%, O 41.81%, K 15.60%, Si 1.32%, Ca 0.32%, Na 2.02%, Al 0.8% and Mg 2.33%.

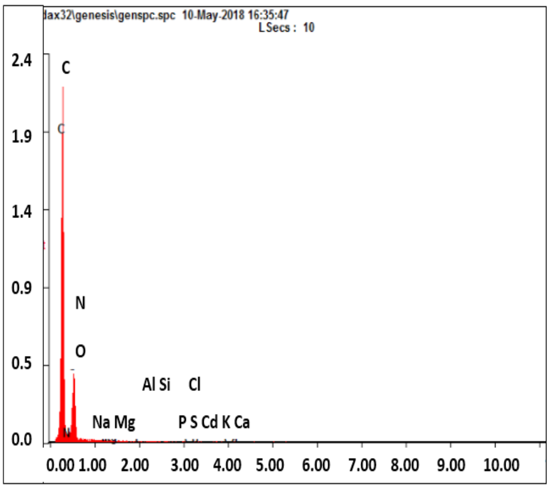

Fig.3. EDX micrograph of banana peel before Adsorption

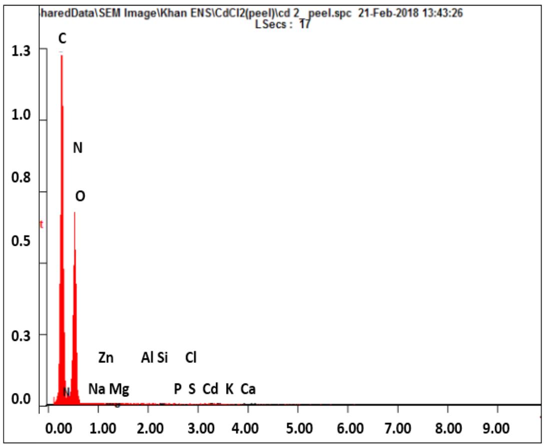

Fig.4. EDX micrograph of banana peel after Cd adsorption

Functional characteristic of banana peel

FTIR spectroscopy method used to show the functional groups present in the surface of banana peel before and after adsorption of Cd ions. The FTIR spectrum of banana peel made some peaks within the interval of 4000-400 cm^{-1}; which was only a sign of the complex chemical nature, the graphs are given in (Fig.5) and (Fig.6). Alcohol functional group in banana peel with H- bonded (O-H) has been recorded at 3275.5 cm^{-1} before adsorption, and after adsorption of Cd the adsorption band was changed to 3297.97 cm^{-1}. The band corresponding to alkane (C-H) was detected at 2922.59 cm^{-1} before adsorption, and after adsorption of Cd it was changed to 2923.56 cm^{-1}. The variable intensity alkene functional group with (C=C) band was detected at 1622.8 cm^{-1} before adsorption, and after Cd adsorption it was changed to 1629.55cm^{-1}. The strong intensity alkene functional group with (=C-H) band was detected at 999.91 cm^{-1} before adsorption, and after adsorption of Cd it was changed to 997.982 cm^{-1}. The functional group of allyl halide with (C-F) band was shown at 1313.29 cm^{-1} frequency before adsorption, and after adsorption of Cd it was changed to 1337.39 cm^{-1}. The band corresponding to allyl halide with (C-Cl) band determined at 769.458 cm^{-1} adsorption frequency before adoption, after adsorption of Cd the peak frequency was not detected (Fig.3). Suantak *et al.,* (2014) also determined the hydroxyl group around 3421.57 cm^{-1} broad peak, 2923.06 cm^{-1} peak was due to stretching vibration of CH, CH and CH3 groups, 1637.45 peak was characteristic of (C=C) band in aromatic rings and 1383.45 cm^{-1} peak due to (C-O) carboxyl band in banana peel. Similar peaks were detected by Khormaei *et al.,* (2007) and Lai *et al.,* (2010) for biosorption of copper ions in orange residue.

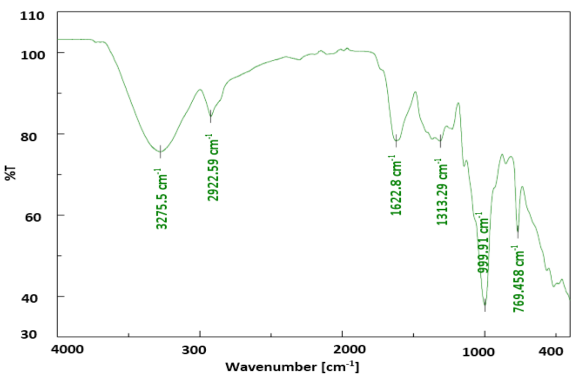

Fig.5. FTIR analysis of banana peel before adsorption

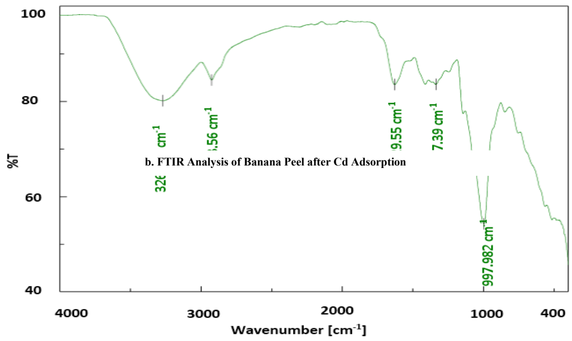

Fig.6. FTIR analysis of banana peel after Cd adsorption

Adsorption parameters

Effect of pH

The effect of pH on Cd adsorption was studied from pH 4 to 8 (Fig.7). The adsorption of Cd increased with increase in pH from 4 to 6, then decreased. The highest adsorption (88.01%) was at pH 6, which followed by 85.97%, 81.20%, 80.00% and 55.23% in pH range 7, 8, 5 and 4 respectively, and the minimum adsorption was noted at pH 4. The less removal percentage of Cd in high acidic condition may be due to the high mobility and high concentration of H^+, because H^+ ions are adsorbed in more amount compare to metal ions. Hossain *et al.,* (2012) suggested the similar result to increase the Cu adsorption by banana peel with the increasing of pH from 2 to 6. Abbasi *et al.* (2013) also reported that adsorption of Ni^{+2} and Co^{+2} by banana peel increased with the increasing pH form 1.0 to 6.0. The same

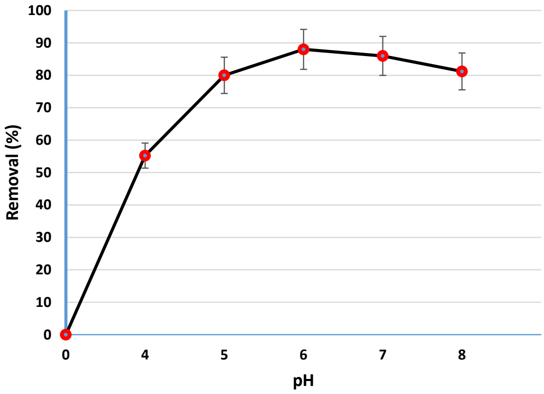

Fig.7. Cd removal efficiency (%) based on pH

result was observed by Demirbas *et al.,* (2009) in the much lowered pH (H_3O^+) the hydrogen doing competition with Cu^{2+} for binding onto adsorbent sites in the result decreasing the adsorption capacity of biosorbents. The same observations were observed by Kaewsarn *et al.,* (2008) who studied the Cd^{2+} ions adsorption by banana peel and determined to adsorption of Cadmium ions increased with the increasing of pH from 1 to 5. Shafaghat *et al.* (2012) also reported that in high acidic condition, the adsorption capacity of biosorbents are lower. The surface functional groups (mainly oxygen containing groups) bind to the H^+ at lower pH and making these inaccessible for metal ions. With increasing pH, the deprotonating functional groups provided the chance to co-ordinate with Cd and Pb ions resulting in higher removal percent (Liu and Zhang, 2010).

Effects of metal ions concentration

The effect of metal ion concentration on the adsorption of Cd by banana peel was determined for 25 ppm, 50 ppm, 75 ppm and 100 ppm (Fig.8). The removable efficiency of Cd increased with the

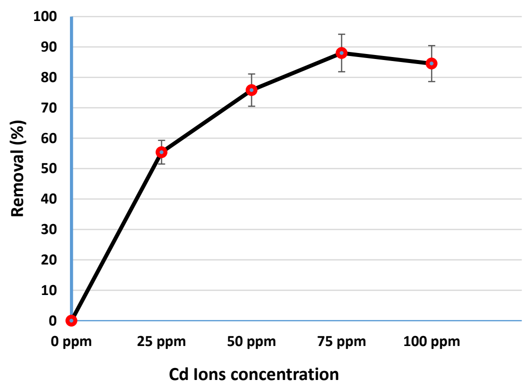

Fig.8. Cd removal efficiency (%) based on ions concentration

increasing of initial concentrations from 25 to 75 ppm, it was ranged between 55.39% to 88.01%, then decreases with the increase of initial concentration. The highest adsorption (88.01%) was observed at 75 ppm and the lowest (55.39%) was at 25 ppm. Abbasi, *et al.* (2013) reported the same result that Co^{+2} and Ni^{+2} adsorption capacities of banana peel increased with the increasing of equilibrium concentration, but Priyanka (2017) reported a contractor result for the Pb adsorption. She reported that the removable efficiency of Pb (II) decreases with increasing initial concentration from 10 to 100 mg L^{-1}. The capacity of banana peel increases with increasing concentration of metal ions. But if the substrate dose remains constant the removal efficiency may be reduced even if the metal concentration increases (Zhou *et al*. 2007). At higher dose, overcrowding of adsorbent particle leads to overlapping and aggregation at adsorption sites reduces the amount sorbed.

Conclusion

Lead and Cadmium are the most hazardous metals accumulate in the human body causing severe damage. To avoid health hazards it must be remove from waste water before its disposal. Hence biosorption is one of the economically method for the removal of heavy metals from waste water compared to other techniques. Based on the results and discussion concluded that banana peel is the cheap and effective adsorbent for the removal of Cd(II), because 1g of banana peel can adsorb 88.01% Cd ions form 100 ml solution. The maximum adsorption was observed at pH 6 and 75 ppm initial concentration. The present study also determine that instead of chemical, we can use pectin rich agricultural waste materials as heavy metal removers from wastewater to overcome water pollution.

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