Research Article

Integrated Waste-Metal-Bioenergy: An Operative Approach for Water Remediation

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ABSTRACT

Increasing levels of agricultural waste, water pollution and energy crisis led us to integrate the process of water remediation with agricultural waste and generation of renewable energy for sustainable growth of society. Present paper deals with removal of metal ions on bio-adsorbent and generation of bio-energy from discarded generated by the process. Adsorption of copper (II) on nano-sized tea waste was done using flame atomic absorption spectroscopy. Effectiveness of tea waste for copper removal was 91.98% and used tea waste after adsorption produced 58.08% methane. Adopted approach presents suitable and sustainable route to grow the society, maintaining environmental ethics and compensating energy demand, initiating Waste-Metal-Biogas (WMB) technology for scaled up processes.

Keywords: Tea waste; heavy metals; adsorption; biogas production; toxic.

INTRODUCTION

Industries are the major sources of water pollution due to discharge of number of heavy metal ions and dyes along with their effluents. Toxicity caused by the heavy metal ions in this type of discharge is a major concern worldwide. Lead, mercury, arsenic, cadmium, iron and copper are main cations which impose hazardous effect on human and environmental health.

These metals have extensively been studied and their effects on human health regularly reviewed by international bodies. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones[1]. Copper, particularly becomes responsible for mental disorders, anaemia, arthritis/rheumatoid arthritis, hypertension, nausea/vomiting, hyperactivity, schizophrenia, insomnia, inflammation and enlargement of liver, heart problem, and cystic fibrosis[2]. Among the available methods for copper removal[3-6], bio-technological method is advantageous being cost effective, simple to use and environmentally benign. A wide range of agro-wastes, such as banana peels[7-8], rice straw[9], seaweed[10], wood and bark[11], maize corn cob[12-13], sugarcane bagasse[14-18], tamarind hull[19-20], sawdust[21-23], rice husk[24-26], and others may be the potential sources for producing bio-adsorbents for heavy metal removal[27-38].

Besides other agricultural stuff, tea is an important part of our daily life and is the product of the leaves, leaf buds, and internodes of the Camellia sinensis plant. As per a report, worldwide annual tea production was 4.52 million tons in 2011 and is continuously increasing with an average rise of around 4% per year[39]. With this large amount, it can be estimated that a huge quantity of tea waste is generated per annum, which can be potentially employed for other purposes. Keeping in view this aspect, various researchers have investigated waste/spent tea as adsorbent for the removal of different types of pollutants from water. Tea waste has been used for the removal of lead, iron, zinc & nickel[40-41], and chromium (VI) by Mozumder.[42] Copper and lead ions have also been efficiently removed over tea waste by Amarasinghe and Williams[43]. The highest metal uptake of 48 and 65 mg/g was observed for Cu and Pb, respectively. The adsorption ability of Turkish tea waste (fibrous) was investigated for the removal of Cu(II) and Cd(II) from single (non-competitive) and binary (competitive) aqueous systems[44-45]. Adsorption of the investigated heavy metal ions by tea waste was found to be strongly dependent on pH, contact time, initial concentration of the heavy metal ions and adsorbent dosage. The maximum adsorption capacities of Cu(II) and Cd(II) were calculated as 8.64 and 11.29 mg/g for single and 6.65 and 2.59 mg/g for binary systems, respectively.

Looking at the prospects of vital availability, potential to adsorb heavy metal ions, waste management, and also crucial dependability on fossil fuels, effort has been made to utilize tea waste from local tea making outlets for removal of copper ions from textile industry and generation of bioenergy from the spent after water purification.

MATERIALS AND METHODS

Industrial effluent was collected from four different textile industries based in Punjab, India. Copper sulfate, $CuSO_4.5H_2O$ (AR Grade, Rankem Fine Chemicals) and de-ionized distilled water of HPLC grade were used in the analysis. Standard solution of copper sulfate was prepared by dissolving weighed amount of copper sulfate in distilled water. The tea waste was collected from the tea making outlets of different departments of the organization.

Experimental

Preparation & Characterization of Bio-adsorbent

Hydrolysable tannins were removed from the used tea waste and the tea waste powder of particle size (150 µm) was primed to prepare bio-adsorbent. State-of-art techniques, viz. surface area studies (Accelerated Surface Area and Porosimetry System, Micromeritics, ASAP 2020), X-ray diffraction (Rigaku XPert Pro X-ray diffractometer with Cu K@ radiarion -1.541Å) and FTIR (Perkin Elmer Frontier) and were used to characterize the bio-adsorbent for its surface area, pore volume & average particle size, crystallinity and structural features respectively.

Removal of Metal from Industrial Sewage

As per the optimized reaction conditions from our previous work, discharges collected from textile industries were incubated at 120 rpm in orbital shaker (Spectralab, HM8T) containing 3g bio-adsorbent (particle size 150µm) at 40°C, pH 5 for 2 hrs[46]. The solutions were then filtered and analyzed for copper concentration using Atomic Absorption Spectrophotometer (Thermo Scientific Works, ICE 3000 series).

Renovation of Waste to Energy

Many researchers have worked for the removal of heavy metals using variety of waste, but none of them have provided attention to the hazardous waste generated after loading of metal on it. This particular section is the novelty of the experimental sequence in which tea waste obtained after loading of copper metal has been subjected to bio-methanation under anaerobic and mesophilic conditions for the production of biogas as an alternative source of bio-energy. Copper loaded bio-adsorbent was assimilated under anaerobic conditions in batch mode reactor at 250 rpm, 35°C and pH 6.0. Hydraulic retention time (HRT) for the reaction was maintained as 24 hrs. The gas produced was analyzed on Gas Chromatograph equipped with flame ionization detector (Nucon 5700).

RESULTS AND DISCUSSION

Physico-chemical characteristics of tea waste are given in Table 1.

BET Studies

For surface area measurement, adsorbent was heated up to 150°C at a ramp rate of 1/6 K/s. Degassing was done by flowing helium at 150°C for 3 hrs and the adsorbent was analyzed by liquid nitrogen. Graph of BET surface area for the bio-adsorbent is shown in figure 1. The straight line of BET curves indicates that BET equation holds good for the adsorption of metal ions on the surface of bio-adsorbent. The relative pressure of gas (p/p_o) is the ratio of absolute pressure of gas i.e, p, to the saturated vapor pressure p_o. It has a value between 0 and 1. Type IV isotherms were obtained for all the samples[47]. Limiting adsorption at high P/P_o was not exhibited and the isotherm comprised of H3 type hysteresis loops. This suggested the existence of aggregates of plate like particles creating slit shaped pores. Results indicate the formation of mesoporous samples[48]. The existence of conspicuous hysteresis loops at high relative pressure also indicates the presence of mesoporous material, being related to capillary condensation associated with large pore channels[49]. Studies suggest the mesoporous nature of material associated with very high surface area (485.6445 m^2/g) and high pore volume (0.4322 cc/g). The average particle size of the material is 12.3547 nm.

Table 1: Physico-chemical properties of Tea waste

S. No.	State-of art study	Inference
1.	**BET Study**	
	Surface Area	485.6445 m^2/g
	Pore volume	0.4322 cc/g
	Average particle size	12.3547 nm
2.	**XRD**	Crystalline material
3.	**FTIR**	
	3376.33 (w) cm^{-1}	-NH
	1516.29 (s) cm^{-1}	-NH
	1240.12 (s) cm^{-1}	=CO, -CN
	1147.27 cm^{-1}	=CO, -CN
	1370.75 cm^{-1}	Cu metal
	1100.6 cm^{-1}	Cu metal

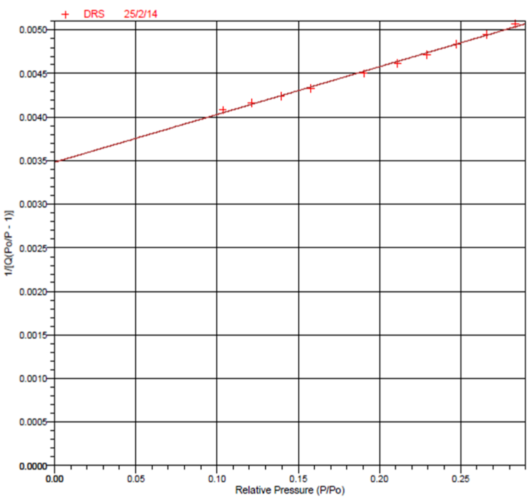

Figure 1: BET Surface Area Plot of Bio-adsorbent

XRD Study of the Bio-adsorbent

It was found from PXRD pattern analysis that the sample of bio-adsorbent possesses sharp line around 2θ range 50°, which may be due to its crystalline nature comprising of large number of vacant sites to be involved in the adsorption of metal ion (Figure 2).

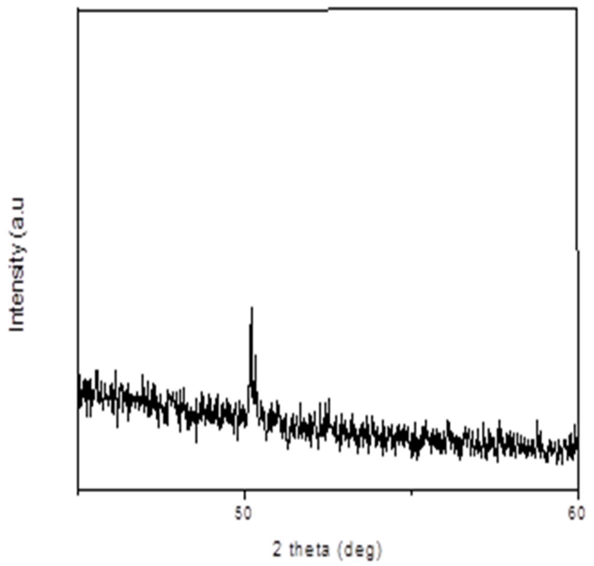

Figure 2: XRD of bio-adsorbent

FTIR Studies

Structural features of bio-adsorbent were studied with FTIR spectrum, which could be responsible for its adsorption ability. Figure 3 shows the FTIR spectra of tea waste before and after adsorption of copper ions. Before adsorption, tea waste showed characteristic absorption bands at 3376.33 (w) & 1516.29 (s), 2919.7 (s) & 2847.5 (s), 1318.82 (w), 1240.12 (s), 1147.27 (s), 1036.89 (m) and 823.47 (m) & 767.25 (m) cm^{-1}, corresponding to the presence of –NH, -CHO, -OH, =CO & -CN, =CO, -OH & -CN and –CH for aromatic ring, respectively[50]. After adsorption, some peaks showed lowering in vibration frequencies indicating the involvement of respective functional groups (-NH, =CO and –CN groups) in co-ordination with Cu(II) ions during bio-adsorption process[51]. Cu(II) ions were confirmed by the presence of two new bands at 1370.75 and 1100.6cm^{-1} [52-53].

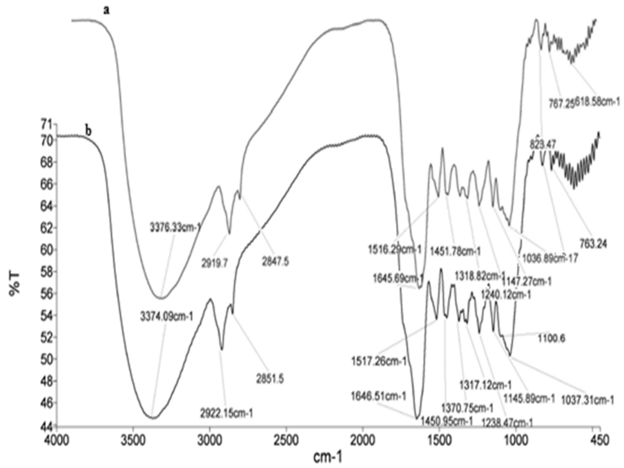

Figure 3: FTIR of Bio-adsorbent (a) Before adsorption (b) After adsorption

Removal of Metal from Industrial Sewage

Sewages received from textile industries (1, 2, and 3) were found to contain high concentration of copper ions, which could be reduced to a considerable extent (~1.0 ppm) after treatment under optimized conditions (Table 2), viz. 3g bio-adsorbent, temperature 40°C, 2 hrs, pH 5, and particle size 150µm.

Comparison of Adsorption Ability of Tea Waste for Copper Ions with Other Adsorbents

Tea waste possesses more adsorption ability for copper ions as compared to other materials (Table 3).

Table 2: Copper ions concentration in sewages of textile industries

Cu^{+2} concentration (ppm)	Industry 1	Industry 2	Industry 3
Before treatment (ppm)	11.98	10.78	11.56
After treatment (ppm)	1.09	0.67	1.01
Removal extent (%)	90.90	93.78	91.26

Table 3: Comparative adsorption abilities of various materials for copper ions

S. No.	Adsorbent	Adsorption ability for Cu(II) (mmol/g)	Reference
1.	AMP modified silica gel	0.447	[53-54]
2.	Expended perlite	0.136	[55]
3.	Herbicide-modified silica gel	0.442	[56]
4.	Minced banana peels	0.330	[8]
5.	Modified peanut husk	0.159	[57]
6.	Na-bentonite	0.108	[58]
7.	Sawdust	0.104	[57]
8.	Tea waste	1.12	Present study

Production of Bio-Energy

Successive operation and investigation of waste in batch reactor followed by analysis on GC indicated that biogas was produced with the composition 58.08% methane, 40.16% carbon dioxide, 0.64% hydrogen sulphide and 1.12% nitrogen (Figure 4). Standard biogas contains 65% methane. Obtained results were good enough to effectively convert a waste to an energy resource, which can be utilized for house-hold usage and also for electricity generation, if done at very large scale.

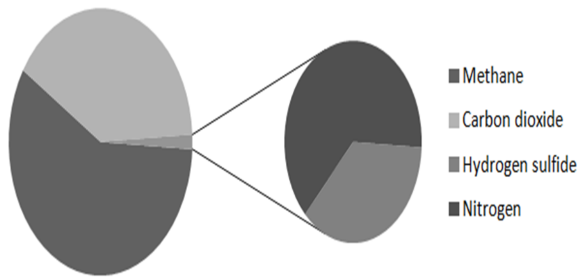

Figure 4: Biogas production from waste

Technological Aspect of the Study

Removal of heavy metals through bio-adsorbents is an effective and low cost method for water purification. In the present study efforts have been made for studying the efficiency of tea waste for the removal of copper. Similarly, studies can be combined for the removal of other noxious metals also, such as arsenic, lead, mercury, etc. and the complete package including the removal of all the harmful metals on to a single adsorbent can be scaled up and converted to a technology for industries. This can bring in the development of an integrated Waste-Metal-Biogas (WMB) technology (Figure 5), which will be helpful in effective remediation of contaminated water along with the generation of bio-energy.

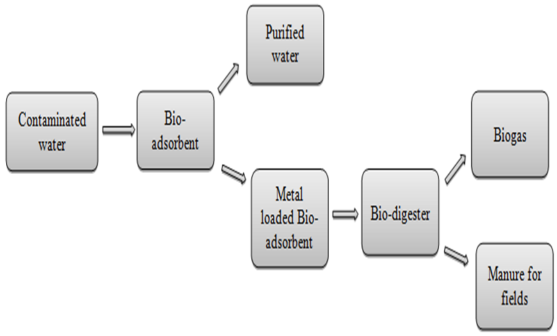

Figure 5: Schematic representation of WMB Technology

CONCLUSION

WMB technology is an appropriate choice to manage the industrial sewage. This technology fulfills three major objectives required for the sustainable development of the society, viz. proper low cost treatment of the sewage, safe disposal to the environment and generation of renewable energy. In the present work, copper removal has been achieved by tea waste as bio-adsorbent along with the generation of bio-energy. Under optimized process parameters (bio-adsorbent dose of 3g, particle size 150µm, 40°C, 120rpm, 2 hrs, pH 5), removal of copper ions from textile sewage was around 92%. The study signifies the maximum adsorption capacity as 1.12mg of copper/g of tea waste and 58.08% methane content in the biogas produced by the anaerobic digestion of waste obtained. Thus, WMB technology is recommended as a package for managing waste, recycling water and harvesting renewable energy for society.

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