

A Green Route for Copper Ions Removal from Textile Industry Effluent

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Abstract: The adsorption of copper(II) on tea waste has been studied in batch mode using flame atomic absorption spectroscopy for metal estimation. Important process parameters like adsorbent dose, pH, contact time, reaction temperature, shaking speed and particle size were investigated. Adsorption was found to be in accordance with Freundlich and Langmuir isotherms. The maximum amount of copper(II) adsorbed (qm), as evaluated by Langmuir isotherm, was approximately 1.33 mg per gram of powder of tea waste per litre of solution. The optimized process parameters were observed to be 3 g adsorbent, pH 5, 40°C temperature, 120 rpm shaking speed and 150 µm particle size.

The effectiveness of tea waste for copper removal from industrial effluent was observed to be around 95.345%. The used tea waste after adsorption produced 51.76% methane as biofuel.

Key words: Teawaste, heavy metals, adsorption, biogas production.

Introduction

Textile industries are the major sources of pollution since they discharge a number of heavy metal ions and dyes along with their effluents. This type of pollution has become a major issue worldwide due to their possible toxic effects. Among various heavy metals, copper has its own concerns and harmful effects on health, which creates the requirement for its removal from effluent before disposing it off in running water. Although copper is an essential trace element for plants, animals and human health, its excess is extremely hazardous. Recommended dietary intake of copper for body is only 2 mg/day and more than this even upto only 10 mg is highly toxic in nature.

An excess of copper in body damages protein, lipids and DNA (Brewer, 2010) and also causes early aging factor, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases (Brewer, 2010; Faller, 2009; Haureau and Faller, 2009). In water, it damages marine ecosystem and affects the gills, liver, kidneys and nervous system of water animals. It also has an adverse effect on sexual life of fish (Van Genderen et al., 2005; Flemming and Trevors, 1989). Keeping its adverse effects in mind, it becomes necessary to remove copper from water which becomes the major source to its exposure.

Among the available methods for copper removal, bio-technological method is advantageous being cost effective, simple to use and environmentally benign.

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Huge and abandoned agro-wastes may be the potential sources for producing bio-adsorbents for heavy metal removal. Different bio-adsorbents have been developed from agro-wastes as rice straw (Gao et al., 2008), seaweed (Basha et al., 2008), wood and bark (Mohan et al., 2007), maize corn cob, sugarcane bagasse (Garg et al., 2007), tamarind hull (Verma et al., 2006), sawdust (Memon et al., 2005), rice husk (Kumar and Bandyopadhyay, 2006), etc.

Adsorption ability of tea waste was investigated for the removal of Cu(II) and Cd(II) from single (non-competitive) and binary (competitive) aqueous systems (Cay et al., 2004; Malkoc and Nuhoglu, 2005). Amarasinghe and Williams (2007) used the tea waste as a low cost adsorbent for the removal of copper and lead from waste water. Various studies indicate the potential of agro-wastes, discarded abruptly, for the removal of heavy metals from waste or dirty water, but no researcher has thought of how to dispose off the bio-adsorbent contaminated with heavy and toxic metals. The present paper includes the optimization of reaction conditions for removal of Cu^{+2} ions from copper sulfate solution and applying the prescribed conditions for different textile industry effluents collected. Concern has also been given to use the waste, generated after metal loading effectively for its conversion to biogas, which is an excellent means of waste management, also helping in meeting the emerging energy demand to a considerable extent.

Materials and Methods

Textile industry effluent was collected from four different industries based in Amritsar (Punjab), India. Copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR Grade, Rankem Fine Chemicals) and de-ionized distilled water of HPLC grade were used in the analysis. A standard 100 ppm stock solution of copper sulfate was prepared. Solutions of various concentrations viz. 1 ppm, 5 ppm, 10 ppm, 20 ppm and 30 ppm were prepared by diluting the stock solution. The tea waste was collected from the tea making outlets of different departments of the organization.

Experimental

Preparation of Bio-adsorbent

Tea waste was washed with hot water for an hour to remove hydrolysable tannins followed by drying in hot air oven (Perfit India) at 110°C for constant weight. It was then grounded to powder of various particle sizes,

viz. 150, 200, 300, 400, 500, 600 μm . The dried and ground tea waste was analyzed for various functional groups by FTIR (Perkin Elmer Frontier), both before and after adsorption.

Treatment of Standard Copper(II) Ion Solution

Hundred ml of standard copper sulfate solution was incubated in batches at 120 rpm in orbital shaker (Spectralab, HM8T) for different adsorbent doses (1 g, 2 g, 3 g, 4 g, 5 g and 8 g), temperature (30 – 50°C), contact time (1–6 hr), pH (3–10) and particle size of tea waste (150, 200, 300, 400, 500 and 600 μm) followed by filtration. The resulting filtrates were analyzed for copper concentration using Atomic Absorption Spectrophotometer (Thermo Scientific Works, ICE 3000 series).

Treatment of Textile Industry Effluent under Optimum Conditions

Effluents collected from textile industries were analyzed for the presence of copper ions. They were then treated with processed tea waste under reaction conditions optimized for the standard solution of copper sulfate, i.e. 3 g bio-adsorbent (particle size 150 μm) at 40°C and pH 5 for 2 hrs.

Conversion of Copper-loaded Bio-waste to Biogas

Copper loaded tea waste was digested under anaerobic conditions in continuous stirred tank reactor (CSTR) at 200 rpm, 37°C and pH 6.5. HRT (Hydraulic retention time) for the reaction was 36 hrs. The gas was collected in a balloon and analyzed on Gas Chromatograph equipped with flame ionization detector (Nucon 5700).

Result and Discussion

FTIR Spectra of Bio-adsorbent

FTIR spectra of tea waste was obtained to understand the structural features of the bio-adsorbent responsible for its adsorption ability. 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 $-\text{NH}$, $-\text{CHO}$, $-\text{OH}$, $=\text{CO}$ & $-\text{CN}$, $=\text{CO}$, $-\text{OH}$ & $-\text{CN}$ and $-\text{CH}$ for aromatic ring, respectively (Ashraf et al., 2012). After adsorption, some peaks showed lowering in vibration frequencies indicating the involvement of respective functional groups ($-\text{NH}$, $=\text{CO}$ and $-\text{CN}$ groups) in co-ordination with Cu(II) ions during bio-adsorption process (Gupta, 2003). Two new bands

also appeared at 1370.75 and 1100.6 cm^{-1} showing the presence of Cu(II) ions (Markova-deneva, 2010; Miller and Wilkins, 1952).

Optimization of the Process with Standard Copper(II) Solution

With 100 ml standard solutions of variable concentrations, adsorption was found to increase with an increasing amount of bio-adsorbent, which however decreased after 3 g (Figure 1a). Increased extent of metal removal with the amount of adsorbent was due to an increased surface area. Thereafter, the adsorption decreases probably due to partial aggregation among the available active binding sites, making them no more available for adsorbing the metal ion from the solution (Anwar et al., 2010; Karthikeyan et al., 2007).

The experiments were repeated for different temperatures using 3 g of bio-adsorbent. Results indicated that adsorption increased initially till 40°C, after which it decreased again (Figure 1b). An increase in temperature initially may have induced swelling within the internal structure of the tea waste which made more active sites available for adsorption.

To study the effect of contact time, standard solution was treated with 3 g bio-adsorbent at 40°C for 1 hr, 2 hr, 4 hr and 6 hr. The maximum removal of copper ions was reported to occur in 2 hrs (Figure 1c). The reason can be explained on the basis of initial large number of vacant active binding sites in tea waste available, as a result of which large amount of copper ions were bound rapidly onto the bio-adsorbent. Shortly, the binding sites become limited, making it difficult to make the remaining vacant sites occupied by metal ions due to

the formation of repulsive forces between metal on the solid surface and the liquid phase (Srivastava et al., 2006; Achak, 2009). Further, the metal ions have to pass through the deeper surface of the pores for binding and encounter much larger resistance which slows down the adsorption during the later phase of adsorption (Srivastava et al., 2006).

pH varied between 2.0 and 9.0 to study its effect on the bio-adsorption process. The adsorption was found to increase with pH with the optimum removal at pH 5.0 (Figure 1d). This is due to the fact that at low pH, adsorbent (negatively charged) remains more closely attached with protons than the metal ions which remain less accessible as a repulsive force is generated. On increasing the pH, removal efficiency increases as number of ligands with negative charge increase. This is again followed by a decrease in the percentage removal till pH 9. This can further be explained as the binding site may not activate in alkaline condition due to the precipitation of copper as copper hydroxide (Cay et al., 2004).

Particle size of the bio-adsorbent was also found to affect the efficiency of the process. Extent of copper removal increased with decreasing size of the bio-adsorbent particles (Figure 1e). The reason being that as particle size decreases the effective surface area for bio-adsorption increases thus facilitating removal with greater efficiency.

Process Parameters as Applied for Textile Industry Effluents

Effluents collected from various textile industries (1, 2, 3 and 4) were found to contain 9.92, 8.68, 9.02 and

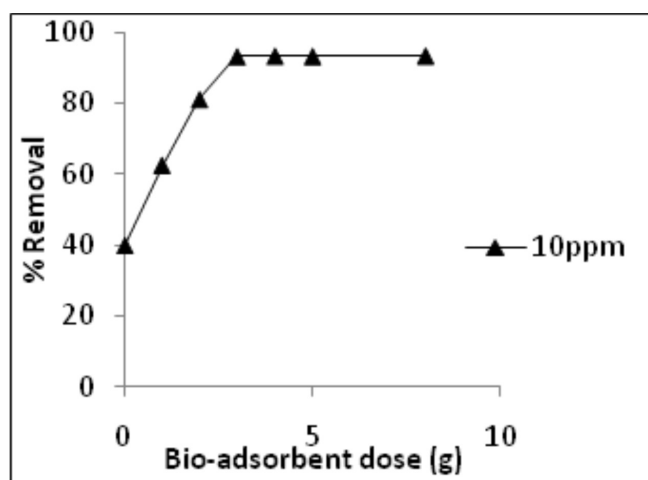


Figure 1a: Effect of adsorbent dose on bio-adsorption.

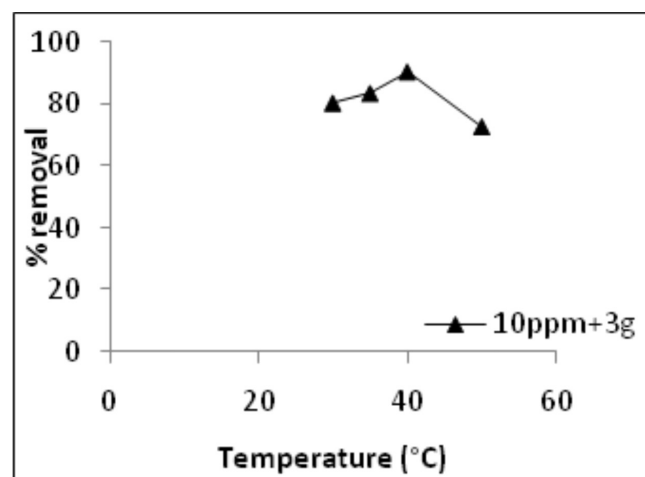


Figure 1b: Effect of temperature on bio-adsorption.

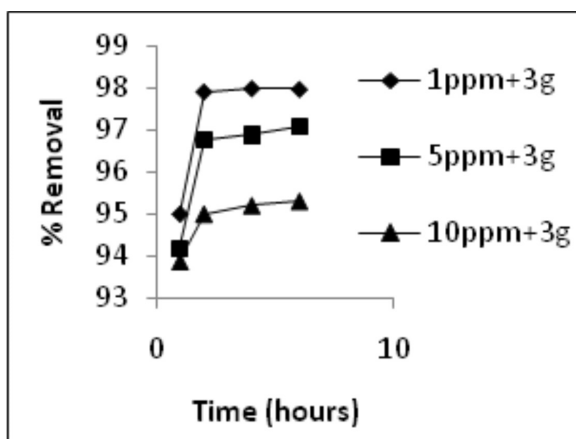


Figure 1c: Effect of contact time on bio-adsorption.

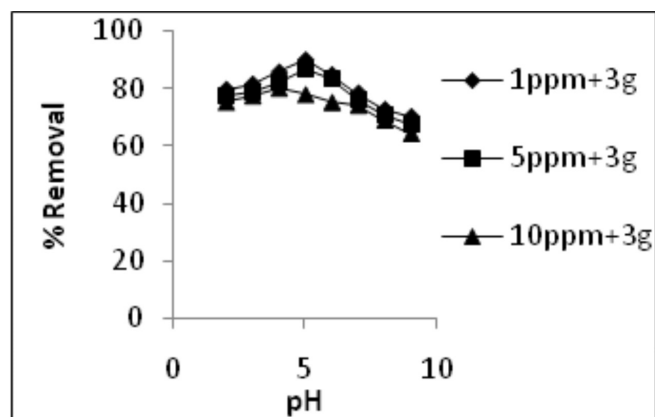


Figure 1d: Effect of pH on bio-adsorption.

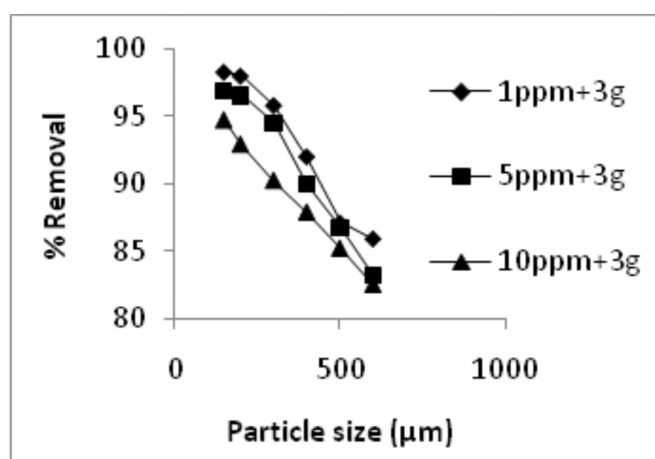


Figure 1e: Effect of particle size on bio-adsorption.

7.98 ppm Cu^{+2} ions, respectively before treatment. On treating the effluents with tea waste under optimized conditions, an efficient removal was observed as summarized in Table 1.

Acceptable limit of copper ions in industrial waste is <1.0 ppm (FEPA, 1991). It is clear from the statistics that the effluent collected was contaminated with high amount of copper, which after treatment under optimized conditions showed its significant removal bringing it in a permissible range.

Adsorption Isotherm of the Process

The optimized conditions of pH, bio-adsorbent dose, temperature and contact time (pH 5, 3 g, 120 rpm, 40°C, 2 hrs) were adopted to study Langmuir and Freundlich adsorption isotherms in Cu(II) solutions of 1, 5, 10, 20 and 30 ppm.

$$q_e = \frac{(C_o - C_e)V}{m}$$

where C_o and C_e are the initial and equilibrium concentrations of the metal ion in solution (mg/l), V is

Table 1: Copper ions concentration in textile industries from Amritsar region

Cu^{+2} concentration (ppm)	Industry 1	Industry 2	Industry 3	Industry 4
Before treatment (ppm)	9.92	8.86	9.02	7.98
After treatment (ppm)	0.46	0.36	0.35	0.48
Removal extent (%)	95.36	95.93	96.11	93.98

the solution volume (l) and m is the mass of tea waste (g).

The Freundlich adsorption isotherm model assumes that the adsorption occurs on heterogeneous surfaces and, for linear form, is expressed as,

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where C_e is the equilibrium concentrations of the metal ion in solution (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), K_f is Freundlich isotherm constant (l/mg) related to adsorption capacity and n is Freundlich isotherm exponent related to adsorption intensity. The straight line and correlation coefficient ($R^2 = 0.9911$) show that the results are adequate for the Freundlich equation. Values of K_f and $1/n$ were calculated from the intercept and slope of plots $\ln q_e$ vs $\ln C_e$ (Figure 2a).

Langmuir isotherm assumes the formation of monolayer of metal on the adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir equation for adsorption isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/l) and b is adsorption equilibrium constant related to the apparent energy of adsorption (l/mg). q_m is the mass of solute adsorbed per unit mass of adsorbent (mg/g) at equilibrium. The graph between (C_e/q_e) and C_e shows straight line (Figure 2b) q_m and b can be determined by the slope and intercept respectively.

The regression constants are given in Table 2. High value of correlation constant ($R^2 = 0.9809$) indicates a good agreement between the experimental value and adsorption isotherm model.

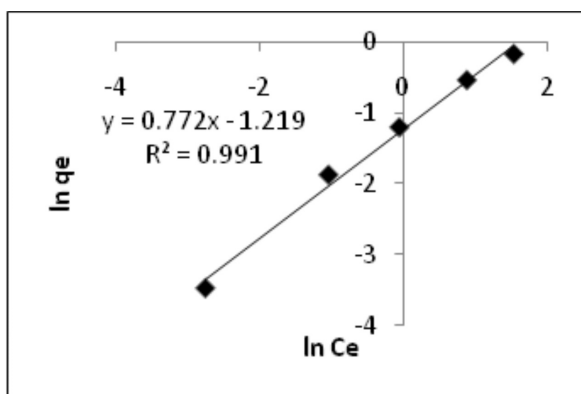


Figure 2a: Freundlich adsorption isotherm for biosorption of Cu(II) on tea waste.

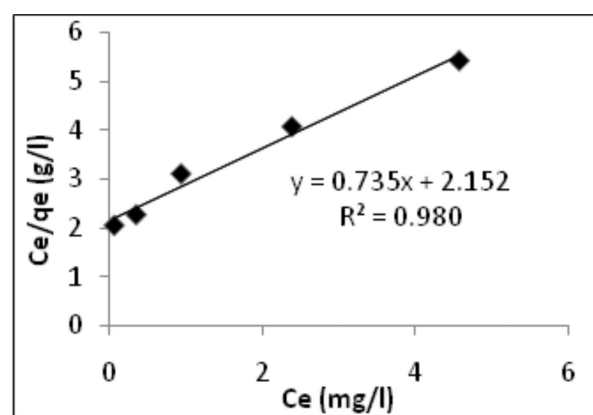


Figure 2b: Langmuir adsorption isotherm for bio-adsorption of Cu(II) on tea waste.

The results revealed that the active sites are distributed in homogeneous manner on the tea waste surface, since it is the basic assumption of Langmuir isotherm that the surface of adsorbent is homogeneous and adsorption is mono layer rather than in multilayer fashion.

Effect of Temperature and Thermodynamic Parameters

The effect of temperature on the adsorption of Cu(II) ions on tea waste was investigated by conducting experiments on solutions with 10 mg/l of initial Cu(II) ion concentrations at 303, 313 and 323 K keeping rest of the conditions constant. It was found that removal of Cu (II) ions from the solution increased with the rise of temperature, showing the endothermic nature of the adsorption process. The thermodynamic parameters Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$\ln \left(\frac{q_e m}{C_e} \right) = \frac{\Delta S^\circ}{R} + \frac{-\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

where m is the adsorbent dose (g/l), C_e is concentration of metals ion (mg/l) at equilibrium and q_e is the amount of metals ion at equilibrium per unit mass of adsorbent (mg/g). ΔH° , ΔS° and ΔG° are changes in enthalpy (kJ/mol), entropy (J/K/mol) and free energy (kJ/mol) respectively. R is the gas constant (8.314 J/K/mol) and T is the temperature (K).

A linear line was obtained on plotting the graph of $\ln (q_e m/C_e)$ vs. $1/T$. The values of ΔH° and ΔS° were obtained from the slopes and intercepts respectively, thereafter ΔG° values were determined. The values of thermodynamic parameters are given in Table 2.

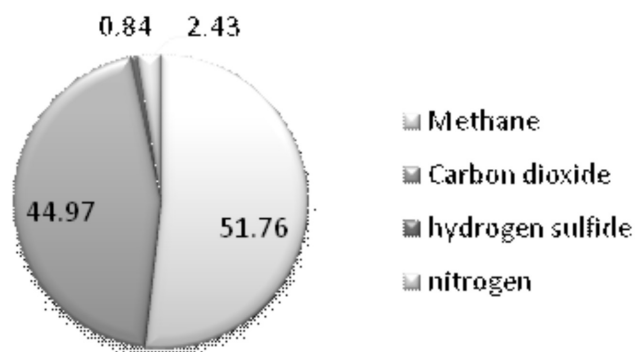
Table 2: Thermodynamic parameters for adsorption of Cu(II) ions on tea waste

ΔH° (kJ/mol)	ΔS° (kJ/mol)	$-\Delta G^\circ$ (kJ/mol)		
		303 K	308 K	313 K
62.98	20.785	69.27	69.38	69.48

The results showed that ΔG° values are negative showing the spontaneity of the process. Further their absolute values increase with temperature (Akmil et al., 2005). This result suggests that a high temperature favours the adsorption of Cu(II) ions on the tea waste. Endothermic nature of the process is also confirmed by the positive value of ΔH° . A positive ΔS° suggested that Cu(II) ions are not very stable on the adsorption sites of tea waste probably due to the increase in translational energy of the metals ion.

Biogas Production

Running the generated waste in CSTR followed by analysis on GC indicated that gas was produced with the composition 51.76% methane, 44.97% carbon dioxide, 0.84% hydrogen sulphide and 2.43% nitrogen (Figure 3). Standard biogas contains 65% methane. Obtained results were good enough to effectively convert a waste to an energy resource, which can be utilized for household usage and also for electricity generation if done at very large scale.

**Fig. 3: Biogas production from waste.**

Conclusion

Tea waste has been found to be effective for the removal of copper with a bio-adsorbent dose of 3 g (particle size 150 μm) at 40°C, 120 rpm for 2 hrs and pH 5. Maximum adsorption capacity of tea waste indicates that 1 g of tea waste can adsorb around 1.33 mg of copper from solution. The negative value of ΔG° suggested the adsorption to be spontaneous in nature. The optimized conditions removed 95.36, 95.93, 96.11

and 93.98% copper ions from effluents of industry 1, 2, 3 and 4, respectively. One important feature of this study is the production of 51.76% methane as biofuel from the metal loaded bio-waste generated after the experiments, thereby providing a zero waste route.

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Calendar of Events

3rd Annual International Conference on Water

13th to 16th July 2015

Athens, Greece

Website: <http://www.atiner.gr/water.htm>

Contact person: Dr. Gregory T. Papanikos

Organized by: Athens Institute for Education and Research (ATINER)

Water and Society 2015 – 3rd International Conference on Water and Society

15th to 17th July 2015

A Coruna, Spain

Website: <http://www.wessex.ac.uk/watersoc2015>

Contact person: Irene Moreno Millan

Organized by: Wessex Institute, UK

4th International Conference on Geological and Environmental Sciences (ICGES 2015)

5th and 6th August 2015

Paris, France

Website: <http://www.icges.org/>

Contact person: Ms. Eve Li

Organized by: CBEES

2nd International Conference on Substantial Environmental Technologies – ICSET 2015

17th to 18th August 2015

Toronto, Canada

Website: <http://icset.org/>

Contact person: Cindy Lau

Organized by: SCIEI

International Conference on Clean Water, Air & Soil (CleanWAS)

25th to 28th August 2015

Kuala Lumpur, Malaysia

Website: <http://www.cleanwas.aconf.org>

Contact person: Chris Chen

Organized by: The International Water, Air and Soil Conservation society (INWASCON)

5th International Conference on Energy and Environmental Science (ICEES 2015)

3rd and 4th September 2015

Penang, Malaysia

Website: <http://www.icees.org/>

Contact person: Ms. Rebecca Yang

Organized by: IACT

3rd International Conference on Renewable Energy and Environment (ICREE 2015)

5th and 6th September 2015

Shanghai, China

Website: <http://www.icree.org/>

Contact person: Ms. Eve Li

Organized by: CBEES

ICE Coastal Management

9th to 11th September 2015

Netherlands

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