Ultrasound Pretreatment Of Cotton Gin Waste For Methane Production And Adsorption Of Metals

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Abstract In the present study, ultrasound irradiation was applied to cotton gin waste. The scope of this procedure was to evaluate the use of the obtained pretreated materials as substrates for anaerobic digestion for methane production and as adsorbents for metal (Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}) removal from aqueous solutions. Results showed a limited effect of pretreatment on material solubilization, however an increase in methane yield was obtained for a pretreatment duration of 60 min. Adsorption assays revealed a greater affinity of the investigated adsorbents for Pb^{2+} and Cu^{2+}, compared with Ni^{2+} and Cd^{2+}, with the samples produced after 30 and 15 min of pretreatment being more effective for metal removal.

Keywords: ultrasound, cotton, waste, anaerobic digestion, adsorption

1. Introduction

Cotton gin waste accounts for approximately 10% of the quantity of seed cotton originally processed during the ginning process and it usually includes a variety of plant materials, such as burs, stems, immature cottonseed, cotton lint, sticks and leaves. Cotton gin waste can be neither incinerated nor directly returned to the field, due to potential hazards. Therefore, the options concerning its management are limited and require further research (Hamawand *et al*., 2016).

Anaerobic digestion represents a viable solid waste management method, since it results not only in waste treatment and stabilization, but also in a materials and energy recovery option. In fact, anaerobic digestion offers both alternative energy generation through biogas exploitation and recovery of nutrients through the use of digestate, mainly as a soil conditioner (Boni *et al*., 2016). Nevertheless, if the waste being treated is composed of recalcitrant compounds, such as lignocelluloses, then the performance of the anaerobic digestion process is limited. In those cases, pretreatment methods are often applied, in order to increase the biodegradability of waste materials. These methods include physical, chemical, physico-chemical, as well as biological processes (Bayr *et al*., 2013).

On the other hand, the use of waste biomass as adsorbents for removing pollutants from water and wastewater has also been intensively investigated lately, as a viable management option. Especially as far as metal removal is concerned, different types of waste materials, in particular agricultural and agroindustrial waste, have been studied for such a purpose (Abdolali *et al*., 2016; Pellera *et al*., 2012; Vijayaraghavan *et al*., 2016).

This study focused on applying ultrasound irradiation to cotton gin waste. The main objective was to determine the manner in which such a pretreatment affects the ability of the obtained materials to be used either as substrates for anaerobic digestion for methane production, or as adsorbent materials for metal removal from aqueous solutions.

Ultrasound irradiation consists in the transfer of energy in the form of sound waves of frequencies greater than 16-20 kHz. This process has been reported to be able to alter the morphology of lignocellulosic biomass particles that are suspended in a fluid and its main mechanisms are affected by factors such as specific energy, ultrasonic frequency, exposure time and the characteristics of the substrate (Fernández-Cegrí *et al*., 2012; Ur Rehman *et al*., 2013).

In the present study, pretreatment was carried out by exposing cotton gin waste to ultrasound irradiation for different durations, using an ultrasonic bath. Initially, the effect of pretreatment on the solubilization of cotton gin waste was determined by measuring soluble chemical oxygen demand (sCOD) and total phenols (TPH) concentrations in the liquid phase obtained after pretreatment. Subsequently, pretreated samples were used in anaerobic digestion assays and in adsorption assays. The former assays (Biochemical Methane Potential (BMP) assays) aimed at determining the effect of pretreatment on methane production from the samples. On the other hand, in the latter assays pretreated samples were evaluated regarding their capability of adsorbing a mixture of different metal ions, i.e. Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}, from aqueous solutions.

2. Materials and Methods

2.1. Material preparation

The material being used in the present study is cotton gin waste (CGW), which comprised of cotton fiber, stalks, bur and leaves. CGW was initially dried at 60 °C, then comminuted to a particle size less than 500 μm and finally stored in a closed container until use. CGW was

characterized by total solids (TS) and volatile solids (VS) contents of 70.6 and 52.9%, respectively, as well as by a slightly acidic pH of 6.9.

2.2. Ultrasound pretreatment

Ultrasound pretreatment was carried out by initially inserting 1 g of dried CGW in 50 mL capacity centrifuge tubes, to which 20 mL of deionized water were then added. Subsequently, the tubes were placed in a low frequency (37 kHz) ultrasonic bath (ultrasonic density 4 W/mL) and were kept there for varying pretreatment durations (15, 30, 60 and 120 min). At the end of the pretreatment, the final pH of the slurries was measured. Afterwards, the samples were centrifuged at 3,500 rpm for 15 min and the solid and liquid fractions were collected separately. The liquid fractions were filtered through a 0.45 μm pore size membrane filter in order to determine sCOD (soluble Chemical Oxygen Demand) and TPH (Total Phenols) concentrations, while the solid fractions were dried at 60 °C for further analyses. All experiments were performed in triplicate.

2.3. Biochemical methane potential assays

Biochemical methane potential (BMP) assays were conducted for both untreated (Raw) and pretreated (US15, US30, US60 and US120) CGW samples. More specifically, the assays were performed in 250 mL conical flasks covered with rubber stoppers, the latter being equipped with three PVC (Polyvinyl chloride) tubes, which allowed N_2 flushing in the flasks, daily methane measurement and weekly digestion slurry sampling.

BMP assays were carried out by firstly introducing the inoculum in the flasks at a concentration of 15 gVS/L. The inoculum used in the present study consisted of anaerobic sludge originating from a mesophilic anaerobic digester of the Municipal Wastewater Treatment Facility of Chania, Crete, with TS and VS contents of 2.09 and 1.48%, respectively, and a pH of 7.35. Subsequently, the substrates were added to the flasks in appropriate amounts, in order to achieve a substrate to inoculum ratio (SIR) of 0.25 (on a VS basis, i.e. $gVS_{substrate}/gVS_{inoculum}$), which was chosen considering the results of a previous study (Pellera and Gidarakos, 2016). Blank assays (SIR=0), containing only the inoculum were also performed, in order to determine the residual methane potential of the inoculum. The working volume in the flasks was set to 100 mL. Where needed, this value was achieved by adding deionized water to the mixture. After adjusting the pH of the mixture at 7.8±0.05, the flasks were covered with the rubber stoppers, flushed with N_2 for 2 min and finally placed in an incubator set at 35 °C. Methane production was measured daily for the first seven days of incubation and subsequently every two days. BMP assays were terminated when methane production was undetectable or less than 5% of the total amount. All the assays were performed in duplicate.

2.4. Metal adsorption assays

The capability of CGW samples of removing metals from aqueous solutions was determined through batch adsorption assays. More specifically, the assays were carried out using plastic flasks, in which a determined amount of sample (5 g/L) and 20 mL of metal solution, containing equal concentrations (1 mM) of Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}, were added. The pH inside the flasks was adjusted to a value of 6. The flasks were then agitated at a speed of 250 rpm on an orbital shaking table for 24 h, after which, the pH of the slurries was measured and their contents were filtered through a nylon 0.45 μm filter to separate the solids from the liquids. The filtrates were acidified with concentrated (65%) HNO_3 to pH<2 and stored at 4 °C.

2.4. Analytical methods

TS and VS contents were determined according to APHA (American Public Health Association) method 2540G. pH was determined using a portable pH-meter. The sCOD concentrations in the liquid fractions obtained after pretreatment were determined through APHA method 5220C, while TPH concentrations were determined according to Folin-Ciocalteu's method (Singleton *et al*., 1999). Methane production was determined by means of volume displacement using an 11.2% KOH solution. Metal concentrations in the aqueous phase obtained from adsorption assays, was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3. Results and discussion

3.1. Effect of pretreatment on material solubilization

As it can be seen in Figure 1, one of the immediate effects of ultrasound pretreatment was an increase in the temperature of the slurry. This phenomenon has been mentioned in other studies as well (Oz and Uzun, 2015) and it can be attributed to the dissipation of the ultrasound energy as heat (Ur Rehman *et al*., 2013) In fact, for increasing pretreatment durations, temperature progressively increased from ambient temperature to a maximum average value of 45.43 ºC. Moreover, a decrease in pH was noticed as a function of time, which however was slight, with the values ranging from 6.88-6.79. This decreasing trend is most likely related to organic acids release during pretreatment (Pecorini *et al*., 2016).

As far as organic material release from CGW is concerned, Figure 2 depicts the variation in sCOD and TPH concentrations during pretreatment. A similar pattern is noticed for both parameters, and is characterized by an initial increasing trend for pretreatment durations between 15 and 60 min, and a following slight decrease for a pretreatment lasting 120 min. The latter could also be interpreted as a stabilization trend. Such an increase in COD solubilization as a function of sonication time has also been observed in previous studies (Fernández-Cegrí *et al*., 2012; Kim *et al*., 2003; Naddeo *et al*., 2009). In one of these studies, Naddeo *et al*. (2009) also observed that at

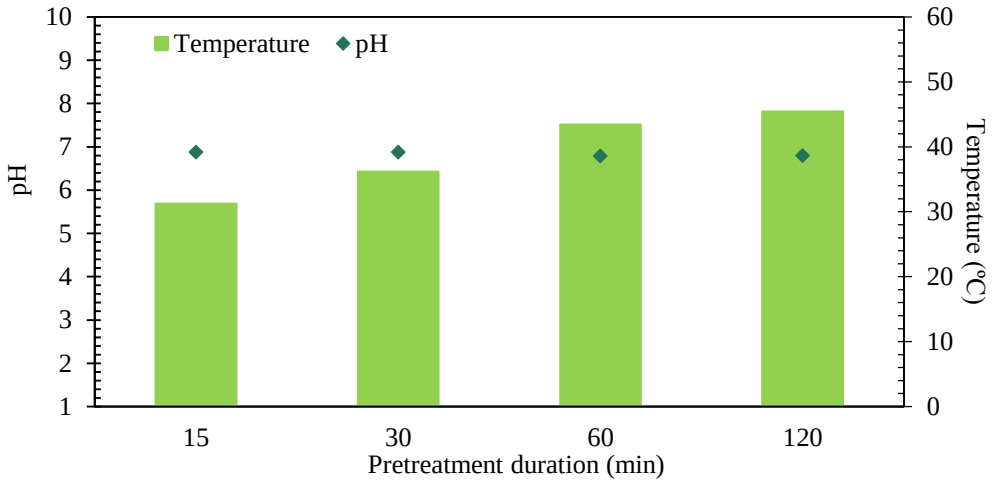

Figure 1. Effect of ultrasound pretreatment on pH and temperature

higher ultrasonic densities, the curve representing COD solubilization would gradually lose its linearity and gain a tendency towards stabilization. Considering that in the above mentioned study the maximum density being investigated was of 0.2 W/mL, the behavior of the COD curve of the present study seems reasonable, since experiments were conducted at a density of 4 W/mL. Moreover, in the study conducted by Cesaro *et al*. (2012), the highest COD solubilization value was obtained at a sonication time of 60 min, similarly to what was observed in the present study. Interestingly, while TPH concentrations are found to vary within a close range (2.41-2.91 mgGAE/gVS), the variations in sCOD concentrations are much more pronounced, especially between 30 and 60 min. Nevertheless, considering the theoretical oxygen demand (TOD) for CGW (1120 mgO_2/gVS), these concentrations correspond to quite low solubilization values, i.e. 3.57, 4.18, 5.79 and 5.48%, for pretreatment durations of 15, 30, 60 and 120 min, respectively, with the highest solubilization being achieved after 60 min of pretreatment.

3.2. Effect of pretreatment on methane production

BMP assays were conducted on both Raw and pretreated CGW, in order to evaluate the effect of ultrasound pretreatment on methane production. Figure 3 depicts the cumulative methane production patterns that were obtained during an incubation period of 23 days, while Table 1 presents the specific methane yields (SMY) of the samples. The SMY were calculated by subtracting the ultimate cumulative methane production of the blank-assay (mL CH_4) from the ultimate cumulative methane production of each sample-assay, and by subsequently dividing it by the added amounts of VS. These values were then converted to STP conditions.

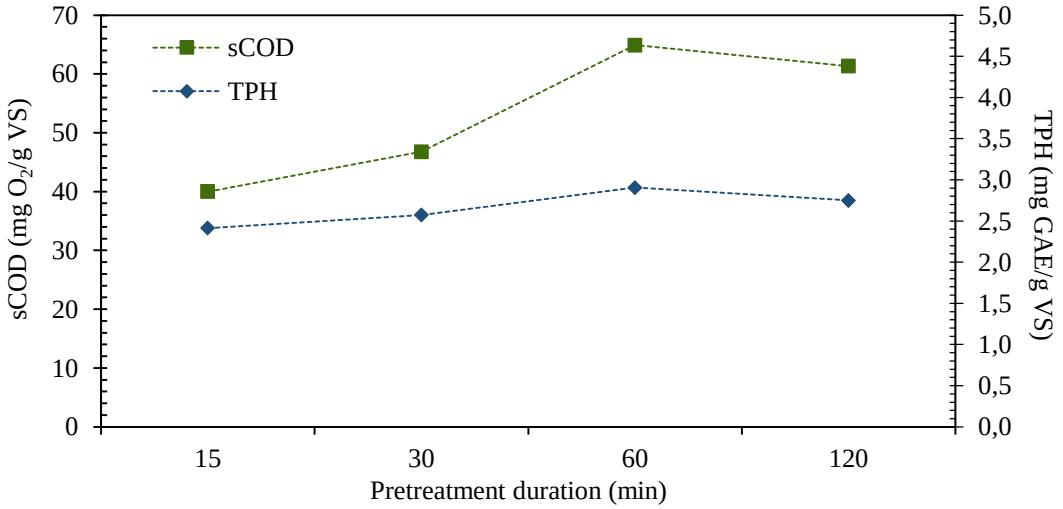

Figure 2. Effect of ultrasound pretreatment on sCOD and TPH concentrations

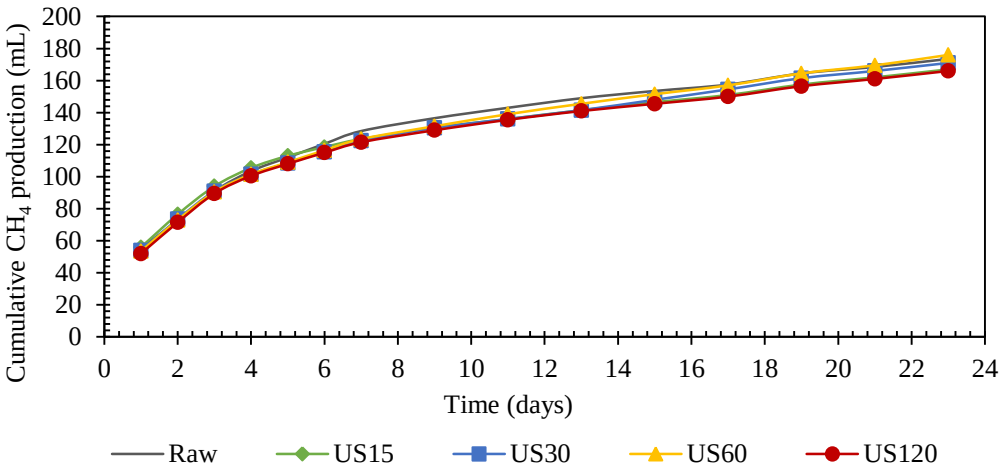

Figure 3. Cumulative methane production

It is evident from the results that pretreatment did not have a very pronounced effect on methane production, since both the produced methane volumes (mL CH_4) and methane yields (mL CH_4/g VS) vary within a close range. Nevertheless, although most pretreated samples yielded lower methane quantities than Raw CGW, US60 ultimately yielded a slightly higher methane quantity. Among pretreated samples, the second best SMY was provided by US30, however it was lower than that of the untreated substrate. In a similar study (Fernández-Cegrí *et al.*, 2012), the authors obtained the two highest methane yields for ultrasound pretreatment durations of 16.6 and 60.6 min, however only the former value exceeded the value that had been obtained for the untreated substrate.

Table 1. Specific methane yields of Raw and pretreated CGW samples

Samples	SMY (mL $CH_{4,\ STP}$/g VS)
Raw	136.50
US15	121.14
US30	130.55
US60	142.47
US120	118.48

3.3. Effect of pretreatment on metal adsorption

Table 2 and Table 3 present the results of the adsorption assays performed on Raw and pretreated CGW samples, expressed in terms of adsorption capacity (mmol/g or mg/g) and metal removal (%). These two parameters were calculated according to Equation 1 and Equation2, respectively (Pellera *et al.*, 2012):

$$q = \frac{(C_i - C_f)\cdot V}{m} \quad (1)$$

$$R = \frac{(C_i - C_f)}{C_i}\cdot 100 \quad (2)$$

where, q is the adsorption capacity (mmol/g or mg/g), C_i and C_f are the initial and final metal concentrations (mmol/L or mg/L) in the solution, respectively, V is the solution volume (L) and m is the mass of adsorbent (g).

All samples showed a higher affinity towards Pb^{2+} and Cu^{2+}, manifested by higher adsorption capacity and removal percentage values. More specifically, the adsorption capacity results expressed in mmol/g follow the order: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+}$, for Raw CGW, US15, US60 and US120, and $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$ for US30. On the other hand, the metal removal results follow the former order for all adsorbent samples. In fact, while removals for Ni^{2+} and Cd^{2+} were noticed in the ranges of 29.8-36.7% and 23.4-35.6%, respectively, in the cases of Cu^{2+} and Pb^{2+} the respective ranges were 70.7-77.4% and 92.0-94.4%. The above mentioned orders of affinity agree with those observed in previous studies (Cutillas-Barreiro *et al.*, 2014; Vijayaraghavan *et al.*, 2016). Moreover, the US30 pretreated sample was found to have a better performance compared with the other samples, since its use resulted in higher metal removal percentages for all four investigated metals. Nevertheless, the US15 sample showed a higher adsorption capacity than US30 in the cases of Cu^{2+} and Pb^{2+}. The adsorption capacities obtained in this work are found mostly comparable with the results reported in previous studies (Abdolali *et al.*, 2016; Vijayaraghavan *et al.*, 2016; Riaz *et al.*, 2009), albeit lower than the majority of these literature values. Furthermore, it was observed that the use of pretreated materials resulted in generally higher metal removal compared with the use of untreated CGW.

4. Conclusions

The objective of this study was to evaluate the effect of ultrasound pretreatment of cotton gin waste on the performance of this material as a substrate for methane

Table 2. Adsorption capacity of Raw and pretreated CGW samples for Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} ions

Metal ions	Adsorbents									
	Raw		US15		US30		US60		US120	
	[mmol/g]	[mg/g]	[mmol/g]	[mg/g]	[mmol/g]	[mg/g]	[mmol/g]	[mg/g]	[mmol/g]	[mg/g]
Ni^{2+}	59.53	3.495	70.94	4.165	72.88	4.279	68.48	2.623	66.00	3.875
Cu^{2+}	148.8	9.455	149.8	9.517	119.5	7.593	141.0	8.959	146.8	9.331
Cd^{2+}	58.13	6.534	63.09	7.092	92.49	10.40	46.69	5.249	61.74	6.940
Pb^{2+}	185.1	38.34	185.1	38.36	129.5	26.84	183.7	38.05	184.6	38.25

Table 3. Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} ions removal (%) for Raw and pretreated CGW samples

Metal ions	Adsorbents				
	Raw	US15	US30	US60	US120
Ni^{2+}	29.8	35.6	36.7	34.4	33.2
Cu^{2+}	74.4	75.2	77.4	70.7	73.9
Cd^{2+}	29.1	31.7	35.6	23.4	31.1
Pb^{2+}	92.6	92.9	94.4	92.0	93.0

production and as an adsorbent for metal removal from aqueous solutions. According to the obtained results, the applied ultrasound pretreatment was not highly effective in solubilizing cotton gin waste. Nevertheless, anaerobic digestion assays showed that an ultrasound pretreatment of 60 min, a duration at which the highest material solubilization was noticed, resulted in a maximum methane yield. On the other hand, pretreatment durations of 30 and 15 min appeared to be more effective in terms of metal removal from aqueous solutions. Therefore, it may be concluded that ultrasound pretreatments carried out for more than 60 min would not offer any additional benefit towards neither methane production, nor metal adsorption, while they would also be economically unattractive.

References

Abdolali A., Ngo H.H., Guo W., Lu S., Chen S.S., Nguyen N.C., Zhang X., Wang J. and Wu, Y. (2016), A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study, *Science of the Total Environment*, **542**, 603–611.

Bayr S., Kaparaju P. and Rintala J. (2013), Screening pretreatment methods to enhance thermophilic anaerobic digestion of pulp and paper mill wastewater treatment secondary sludge, *Chemical Engineering Journal*, **223**, 479-486.

Boni M.R., D'Amato E., Polettini A., Pomi R. and Rossi A. (2016), Effect of ultrasonication on anaerobic degradability of solid waste digestate, *Waste Management*, **48**, 209-217.

Cesaro A., Naddeo V., Amodio V. and Belgiorno, V. (2012), Enhanced biogas production from anaerobic codigestion of solid waste by sonolysis, *Ultrasonics Sonochemistry*, **19**, 596-600.

Cutillas-Barreiro L., Ansias-Manso L., Fernández-Calviño D., Arias-Estévez M., Nóvoa-Muñoz J.C., Fernández-Sanjurjo M.J., Álvarez-Rodríguez E. and Núñez-Delgado A. (2014), Pine bark as bio-adsorbent for Cd, Cu, Ni, Pb and Zn: Batch-type and stirred flow chamber experiments, *Journal of Environmental Management*, **144**, 258–264.

Fernández-Cegrí V., De La Rubia M.A., Raposo F. and Borja R. (2012), Impact of ultrasonic pretreatment under different operational conditions on the mesophilic anaerobic digestion of sunflower oil cake in batch mode, *Ultrasonics Sonochemistry*, **19**, 1003-1010.

Hamawand I., Sandell G., Pittaway P., Chakrabarty S., Yusaf T., Chen G., Seneweera S., Al-Lwayzy S., Bennett J. and Hopf, J. (2016), Bioenergy from Cotton Industry Wastes: A review and potential, *Renewable and Sustainable Energy Reviews*, **66**, 435–448.

Kim J., Park C., Kim T.-H., Lee M., Kim S., Kim S.-W. and Lee J. (2003), Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, *Journal of Bioscience and Bioengineering*, **95**, 271-275.

Naddeo V., Belgiorno V., Landi M., Zarra T. and Napoli R.M.A. (2009), Effect of sonolysis on waste activated sludge solubilisation and anaerobic biodegradability, *Desalination*, **249**, 762-767.

Oz N.A. and Uzun A.C. (2015), Ultrasound pretreatment for enhanced biogas production from olive mill wastewater, *Ultrasonics Sonochemistry*, **22**, 565–572.

Pecorini I., Baldi F., Carnevale E.A. and Corti A. (2016), Biochemical methane potential tests of different autoclaved and microwaved lignocellulosic organic fractions of municipal solid waste, *Waste Management*, **56**, 143-150.

Pellera F.-M., Giannis A., Kalderis D., Anastasiadou K., Stegmann R., Wang J.-Y. and Gidarakos E. (2012), Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products, *Journal of Environmental Management*, **96**, 35-42.

Pellera F.-M. and Gidarakos E. (2016), Effect of substrate to inoculum ratio and inoculum type on the biochemical methane potential of solid agroindustrial waste, *Journal of Environmental Chemical Engineering*, **4**, 3217-3229.

Riaz M., Nadeem R., Hanif M.A., Ansari T.M. and Rehman K.-u.- (2009), Pb(II) biosorption from hazardous aqueous streams using Gossypium hirsutum (Cotton) waste biomass, *Journal of Hazardous Materials*, **161**, 88–94.

Singleton V.L., Orthofer R. and Lamuela-Raventós R.M., (1999), [14] Analysis of total phenols and other oxidation substrates

and antioxidants by means of folin-ciocalteu reagent, *Methods in Enzymology*, **299**, 152-178.

Ur Rehman M.S., Kim I., Chisti Y. and Han J.I. (2013), Use of ultrasound in the production of bioethanol from lignocellulosic biomass, *Energy Education Science and Technology Part A: Energy Science and Research*, **30**, 1391-1410.

Vijayaraghavan K., Rangabhashiyam S., Ashokkumar T. and Arockiaraj J. (2016), Mono- and multi-component biosorption of lead(II), cadmium(II), copper(II) and nickel(II) ions onto coco-peat biomass, *Separation Science and Technology*, **51**, 2725–2733.