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Production and characterisation of biochar from tea waste and its nickel removal capacity from aqueous solutions

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Abstract: Biochar, a carbon-rich solid product of slow pyrolysis of biomass, has gained interest due to its application in the various aims. Investigating of adsorption properties of biochar for removing pollutants from waste water is current research areas. The objective of this study is to obtain biochar from industrial tea waste, characterise it in detail and determine biochar's heavy metal adsorption potential to Ni(II) ions. Biochar prepared at 300°C and 400°C and characterised by various methods; elemental analysis, TGA, XRD, XRF, SEM and FTIR. The surface area and pH were determined as well. It was found out that biochar is mesoporous and the structures show more cellulosic characteristics. Carbonisation and aromaticity increase with increasing temperature. The magnitude of adsorption potential is between 500 J/mol and 4000 J/mol and decreases with increasing Ni concentration from 85 ppm to 205 ppm. The adsorption capacities of biochar are much lower than origin of biomass.

Keywords: biochar; tea waste; nickel; adsorption.

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1   Introduction

Biochar has been attracting increasing attention due to its ability to sequestrate carbon to improve soil quality and therefore can be beneficial for land reclamation, water remediation and soil amendment (Barrow, 2012; Meyer et al., 2011). As the energy content of biochar is higher than original biomass, it could be used as solid fuel in boilers as well. Furthermore, heavy metal sequestration is an important aspect of biochar for soil fertilisation and environmental remediation which are encountered in wastewater streams from industries.

Biochar is a carbonaceous material, derived from biomass by pyrolysis. During the pyrolysis, the biomass feedstock is heated up to desired in the partial or total absence of oxygen conditions. At that point, the molecules in the biomass as organic waste reorganise to form biochar, the feed stocks carbonise and volatile molecules leave the biomass. Furthermore, carbonisation stabilise the molecules causing hysteresis behaviour when biomass is used in raw state as biosorbent.

Biochar is a generic term and the characteristics are very variable depending on composition of the source material biomass and pyrolysis conditions (Chowdhury et al., 2016). Biomass mainly comprised cellulose, hemicellulose, lignin and small amount of volatiles, which have different thermogravimetric behaviours by pyrolytic decomposition (Burhenne et al., 2013). To this end, biochar from various biomass feed stocks shows different characteristics and physicochemical properties such as surface functionalities, cation exchange capacity, porosity or surface area even if they have similar carbonisation ratio (Xie et al., 2014; Lei and Zhang, 2013). Therefore, standards have not been established yet for biochar.

Among a number of available methods for the removal of heavy metal ions, adsorption by low-cost biomass or by-products (natural materials from agricultural or industrial activities) are the cheapest and most effective (Pereira et al., 2015). It has been also reported that biochar has a strong sorption capacity to organic and inorganic contaminants (Ahmad et al., 2014; Tan et al., 2015; Rajapaksha et al., 2014; Mohan et al., 2014). Sometimes, the adsorption capacities of biochar could be similar or even better than commercial activated carbon. There can be found various studies on activated carbon applications on pollutant remediation (Ahmadpour et al., 2013; Hadi et al., 2015; Kim et al., 2012) but the cost of preparation of activated carbon is relatively high.

Elaigwu et al. (2014) measured the adsorption of two heavy metal ions, Pb^{2+} and Cd^{2+} by biochar prepared by pyrolysis of a *Prunus africana* shell. It was found that the adsorption occurs in a short time period, such as 30 min, and the maximum adsorption capacities for biochar are as high as those for activated carbon.

The biochar production conditions and feedstock type influence the physical and chemical properties and thus heavy metal fate in the biochar body (Kim et al., 2012; Jin et al., 2014; Kim et al., 2013). Han et al. (2013) studied the adsorptive properties of heavy metals, Zn^{2+}, Cu^{2+} and phenol onto the biochar derived from three types of biomasses; switch grass, hardwood and softwood, through both fast and slow pyrolysis. It was found that the adsorption capacity with respect to biomass type followed the order: switch grass, hardwood and softwood biochar, proportional to the pore size and surface functional groups. Tan et al. investigated the Cd^{2+} adsorption potential of biochar derived from municipal sewage sludge at pyrolysis temperature ranged from 500°C to 900°C (Chen et al., 2014). A better adsorption capacity was determined for biochar produced at higher temperatures.

Since biochar derived from various biomass resources exhibit different physical and chemical properties, the potential use of biochar as a heavy metal adsorbent for the remediation of wastewater should be evaluated for various biomass types. There have been many studies related to biochar derivation from various biomasses, such as agricultural residues, wood, various leaves, coconut, etc. and their application for the improvement of soil quality. However, studies relating to biochar from industrial tea waste, which is mostly comprised of the separated waste tea leaves from various stages of production, and the accumulation of dust and stalks, its characterisations and adsorption behaviours are researched to a limited extent (Uzun et al., 2010). This study aims to investigate the adsorption capacity of biochar derived from industrial tea waste and the relation of adsorption capacity to the physical and chemical characteristics of biochar produced at different pyrolysis temperatures.

2 Experimental

2.1 Preparation of biochar

Tea waste was collected from a tea plant in Salarha-Rize/Turkey located in the Black Sea Region. The waste, the useless end product called sorting waste (SW), was grinded by a rod mill from original particle size of <2.36 to <1.00 mm. The SW was dried in a drying oven at 80°C for 24 h. The tea waste was used without any pre-treatments such as washing.

The biochar was prepared by crucible with limited air conditions. Five grams samples were put in to several 18 ml porcelain crucibles, closed with covers, settled into a muffle furnace (Nabertherm-controller P 320) at 25°C and heated with 10°C/min until the desired temperatures of 300°C and 400°C which were reached after 30 min and 40 min, respectively. All the produced samples were collected in sample vessels for 300°C and 400°C, separately. It was determined by weighing that 36–40% is removed from the biomass at 300°C and 400°C. The derived biochar is assigned the names SWC300 and SWC400 (Sorting Waste Crucible-experiments at 300°C and 400°C). The maximum temperature setup was adjusted to 400°C. The biochar was crushed in a porcelain mortar and sieved through a 0.125 mm sieve and used within this particle size in all experiments.

2.2 Characterisations of tea waste and biochar

The pH values of the biochar in deionised water were determined (1 : 50, w/v) by Chebios-640 type pH meter.

Specific surface areas and total pore volumes of all samples were determined (Quantachrome Autosorb 1C). The ash content of the SW was determined by heating the samples in the muffle furnace at 550°C for 3 h (DIN 51719, http://www.european-biochar.org/en/analytical%20methods). Fourier-transform infrared spectroscopy (FTIR, Bruker Optics-Alpha) analyses were performed to determine the surface functional groups of biomass and biochar samples. Thermogravimetric analyses (TGA) were carried out using the TGA-50 analyser (Shimadzu). X-ray diffraction (XRD, Rigaku SmartLab X-ray diffractometer using non-monochromatographic Cu Kα1-radiation (40 kV, 30 mA, $\lambda = 1.5$). Scanning was in the range 5–65° of 2θ) patterns were recorded. Elemental analyses were realised by CHNS analyser (Leco, TrusPec Micro) according to ASTM D3176. The mineral composition of SW determined by ED-XRF (PANalytical, EPSILON 5 Model X-Ray Fluorescence Spectrometer). The morphology of the samples was scanned by a scanning electron microscope (SEM) (JEOL/JSM-6610). Calorific values were measured by a bomb calorimeter (Parr, 6200 Calorimeter).

2.3 Adsorption experiments

A 1 g/l stock solution of Ni(II) was prepared with $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich). The stock solution was diluted further to prepare various concentrations between 75 ppm and 200 ppm. The adsorbent concentration was kept constant as 0.6 g/l for all experiments. The sorption experiments were performed in 50 ml Erlenmeyer flasks at room temperature. The flasks were stirred on a magnetic shaker at a constant agitation rate of 200 rpm for different periods of time up to 360 min. After the reaction, suspensions were centrifuged at 5000 rpm for 3 min in order to separate the solution and the solid. The initial and non-adsorbed concentrations of Ni in supernatants were determined by an Atomic Absorption Spectrometer (AAS, GBC A 4382).

The amount of metal ion uptake by adsorbents was calculated, as in equation (1):

$$q_e = (C_0 - C_e)\frac{V}{m}, \tag{1}$$

where C_0 is the initial metal concentration (mg/l), C_e is the metal concentration remaining in the solution at a given time (mg/l), V is the volume of solution in the flask (l), m is the adsorbent mass (g) and q_e is the metal ion uptake (mg/g).

3 Results and discussion

3.1 Characterisations of samples

The physical and chemical properties of samples are given in Table 1. The moisture and ash contents of SW were determined as 7.20% and 5.03%, respectively. The pH values of SW, SWC300 and SWC400 were measured as 5.09, 9.15 and 9.28, respectively. The surface areas of samples were determined as 12.7, 3.9 and 6.9 m²/g.

Table 1   Properties of SW, SWC300 and SWC 400

| Property	SW	SWC300	SWC400	Reference
Moisture (%)	7.20	–	–	This work
	7.26			Uzun et al. (2010)
Ash (%)	5.03	–	–	This work
	3.48			Uzun et al. (2010)
pH	5.09	9.15	9.28	This work
Surface area (m²/g)	12.7	3.9	6.9	This work
C (%)	45.4	60.5	66.4	This work
	48.6			Uzun et al. (2010)
H (%)	5.7	4.1	3.7	This work
	5.3			Uzun et al. (2010)
N (%)	2.9	3.4	3.6	This work
	3.8			Uzun et al. (2010)
S (%)	0	0	0	This work
O (%)	46.0	32.0	26.3	This work
	42.2			Uzun et al. (2010)
Calorific value (MJ/kg)	18.31	24.50	25.42	This work
	16.19			Uzun et al. (2010)
Volatile matter (%)	70.29			Uzun et al. (2010)
Lignin (%)	25.68			Uzun et al. (2010)
Holocellulose (%)	31.05			Uzun et al. (2010)
Extractives (%)	13.97			Uzun et al. (2010)

Biochar's surface areas are smaller than tea waste biomass (SW) that can be due to collapsing the structure during carbonisation. On the other hand, surface area increases with an increase in pyrolysis temperature. SWC400 has a higher surface area than SWC300. The further release of volatile compounds can lead to enlargement of internal cavities and also the decomposition of various structures at higher temperature can cause

coalescence of pores. Biochar features mesoporous structure and functional sites are indicated mostly along the external surface (Rajapaksha et al., 2014).

Figure 1 indicates the development of aromatisation and de-polymerisation in the biochar structure by a diagram of H/C–O/C atomic ratios (Van Krevelen diagram). The decreasing hydrogen and oxygen ratios at higher temperatures results in enrichment of the carbon content in the biochar. As the temperature increases, O/C and H/C ratios decrease which indicates that the dehydration and deoxygenating occur.

The calorific values of the samples given in Table 1 are between 17 MJ/kg and 25 MJ/kg. Notably the biochar's energy levels are in the range of higher-rank coals. Toptas et al. (2015) investigated the combustion behaviours of torrefied lignocellulosic biomass and showed that biomasses improved the burnout performance of lignite since their reactivity is similar. Liu (2013) reported that biochar provides better fuel qualities than their parent biomass of wood and also that mixing biochar with lignite enhances the blend reactivity.

Figure 1   Van Krevelen diagram of SW, SWC300 and SWC 400
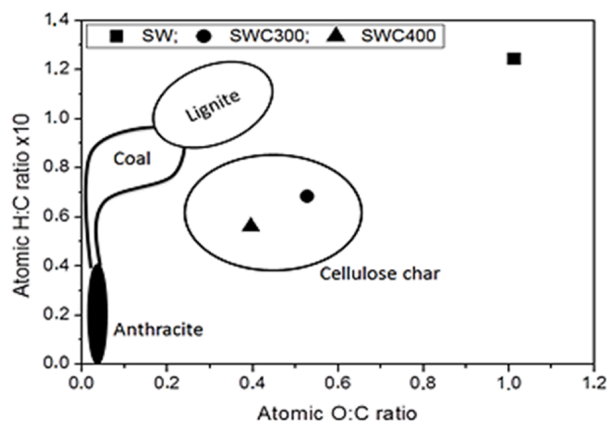
The XRD patterns show one main peak for each sample around 22° of 2θ, indicating cellulose region (Figure 2). The peak shifts higher values of 2θ (24°) for biochar samples and become broader and less intense when the temperature increases from 300°C to 400°C, which corresponds with the decomposition of cellulose and carbonisation (Elyounssi and Halim, 2014).

The FTIR spectra of the samples are given in Figure 3. The broad band at around 3600–3200 cm^{-1} represents –OH stretch (concentrated). The width of the band indicates the strength of –OH groups. SWC300 has the largest –OH peak intensity. The bands observed at ~956–2856 cm^{-1} could be assigned to the aliphatic (alkanic) C–H group. A small peak is formed around 2350–2317 cm^{-1} for SWC300 and SWC400 corresponds to the amine group. The broad band around 1617–1599 cm^{-1} corresponds to C = O and aromatic C = C stretch. The shoulder form at 1699 cm^{-1} for SWC300 is for C = O stretching. Symmetric bending of CH_3 is observed around 1454–1446 cm^{-1} for SWC300 and SWC400. 1366 cm^{-1} and 1311 cm^{-1} peaks of SW show CH_3, CH_2 or C-X stretching. The peaks at 1234 cm^{-1} and 1136 cm^{-1} for SW is assigned to etheric C–O stretching, respectively. The peak at 1030 cm^{-1} is responsible for C–N stretch and shielded by the aromatically peaks of the SWCs. The peaks between 877 cm^{-1} and 787 cm^{-1} indicate inorganic bonds such as Si–O–Si which are more intensive in biochar samples.
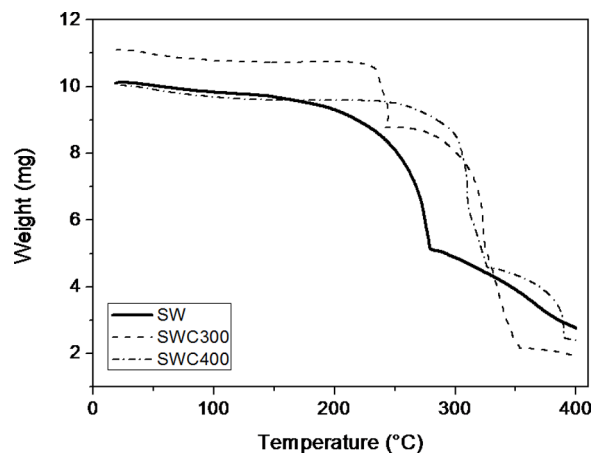
Figure 2 XRD analyses of SW, SWC300 and SWC 400
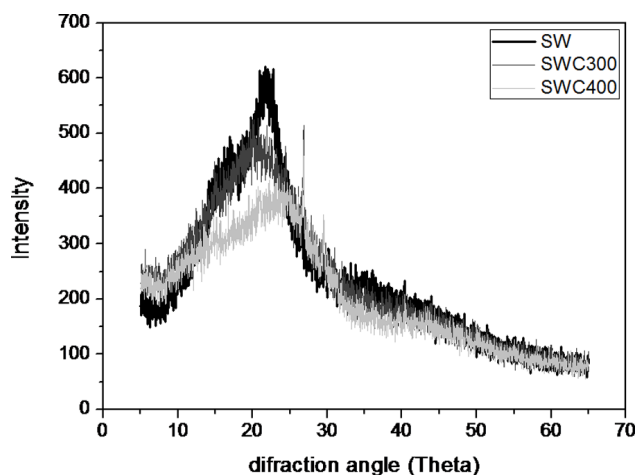
Figure 3 FTIR spectra of SW, SWC300 and SWC 400
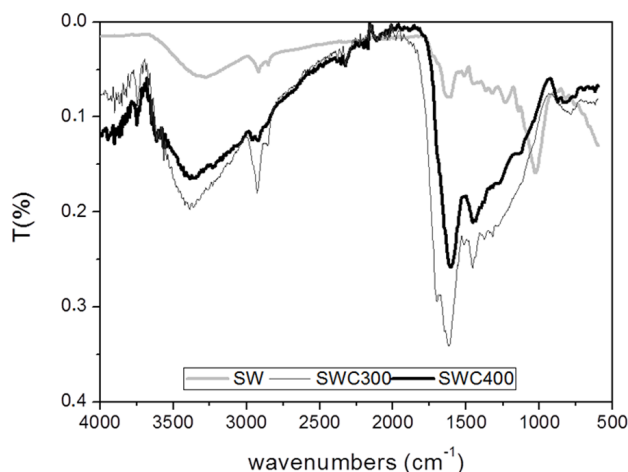
By converting the SW to its biochar forms, the single bonds turn to aromatic bonds. The biochar samples contain more –OH, C=O, C=C than C–H and C–O. On the other hand, Uzun et al. (2010) and Rajapaksha et al. (2014) showed that biochar prepared from tea waste at 700°C has more aromatic polymeric carbon than biochar prepared at the lower temperature of 400°C.

Thermal analysis characterises a substance when subjected to a controlled temperature program. Figure 4 shows the thermal behaviour of the SW, SWC300 and SWC400. The SW starts to decompose steeply after 190°C, with ca. 50%. The decomposition becomes slower after 280°C. On the other hand, the biochar forms are relative stable. The mass loss of SWC300 starts from around 225°C until 245°C, with 21%. At the second step, up to 355°C, the highest mass loss is observed, with 76%. SWC400 shows similar but related behaviour to SW and two-step decomposition is observed from 245°C to 325°C and above. The mass is lost at the first step, with around 55%. The mass loss starts with water loss at lower temperatures (<200°C). However, the

biggest mass loss of a biomass generally occurs between 150°C and 800°C, in the context of the probable release of CO_2, CO, and CH_4, which is able to take place due to the main decomposition reactions of the major biomass constituents; hemicellulose, cellulose and lignin, as well as aldehydes, ketones, acids, etc. (García et al., 2013). Sebio-Puñal et al. (2012) stated that CO_2 is produced by the degradation of both hemicellulose and cellulose, but CO comes mainly from cellulose and lignin decomposition at the higher temperature of 450°C. Uzun et al. (2010) determined the thermal degradation behaviour of tea waste up to 1200°C. They indicated that mass loss gives the first peak at ~100°C. The second and highest weight loss starts at ~190°C and finishes around 350°C which is probably responsible for the degradation of holocellulose and partially of lignin. Although the TGA temperature was set up to high temperature of 1200°C, it was observed no obvious mass loss above this temperature.

Figure 4   TGA analyses of SW, SWC300 and SWC 400

The SEM pictures of SW, SWC300 and SWC-400 are given in Figure 5. The amorphous and heterogeneous structure of tea waste and biochar samples can be seen. By converting SW to SWCs, the jagged surface becomes less jagged and even more flat at 300°C. Increasing the temperature from 300°C to 400°C causes the particles to break up which can lead larger internal cavities at higher temperature.

The XRF results are given in Table 2. As it is seen in Table 2, the mineral composition is around 17% in SW.

Figure 5   SEM pictures of SW, SWC300 and SWC 400
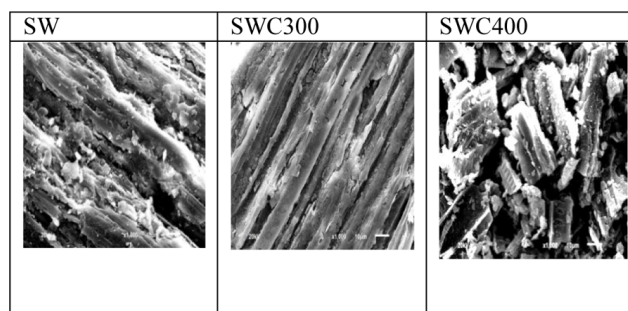
3.2 Adsorption experiments

In this work, the Ni ion removal potential of tea waste and its biochar forms from water were investigated. At the beginning, the working pH was selected as 4. However, adding SWCs to water solutions increases the initial pH values effectively. Starting with the solution at 5.0 pH value, the pH was sharply increased to 7.9 with SWC400 in a very short time. It was found that the pH change is around 10% when the initial pH is 2. Since the Ni ions get precipitated due to the formation of hydroxide at pHs >5.0, the pH of the solutions was maintained constant at 2 for all experiments. The pH adjustments were performed with 0.1 M HNO_3 and 0.1 M NaOH solutions.

Table 2 ED-XRF results of SW

Compound	Concentration
MgO	926 ppm
Al_2O_3	1.15%
SiO_2	0.71%
P_2O_5	0.81%
SO_3	0.88%
Cl	0.22%
K_2O	8.23%
CaO	3.23%
TiO_2	484 ppm
Cr_2O_3	258 ppm
MnO	1.01%
Fe_2O_3	0.48%
NiO	160 ppm
CuO	189 ppm
ZnO	265 ppm
As_2O_3	6 ppm
SeO_2	–
Br	35 ppm
Rb	230 ppm
SrO	145 ppm
Y_2O_3	–
ZrO_2	11 ppm
Sb_2O_3	–
BaO	60 ppm
HfO_2	54 ppm
HgO	–
PbO	30 ppm

Although several previous studies have reported the effective adsorption of organic and inorganic contaminants by various biochar (Ahmad et al., 2014; Rajapaksha et al., 2014; Mohan et al., 2014; Elaigwu et al., 2014; Han et al., 2013), no effective adsorption was observed for tea waste biochar in this study. Adsorption experiments were performed by SWC300 and SWC400 at pH 2 and with 107.5 ppm initial Ni concentration. However, the adsorption performances were worse than 5 mg/g.

The properties of biochar strongly depend on the feedstock type and the production conditions. Parameters such as pH, particle size, ion type, surface area and surface textures can also play an important part in the adsorption process.

On the other hand, SW is adsorptive for Ni ion from water solutions. Figures 6 and 7 show the results of adsorption experiments. The adsorption equilibrates in a very short time for lower concentrations. After 100 min, all the experiments had gone to equilibrium (Figure 6). The slopes seen Figure 7 could be because of dynamic adsorption-desorption hysteresis of water soluble compounds of SW since it was used without any pre-treatment such as washing (Malkoc and Nuhoglu, 2005). It is determined that the water solubility of SW is 2.35 % and 2.25%, when the pH is not adjusted and at pH 2, respectively.

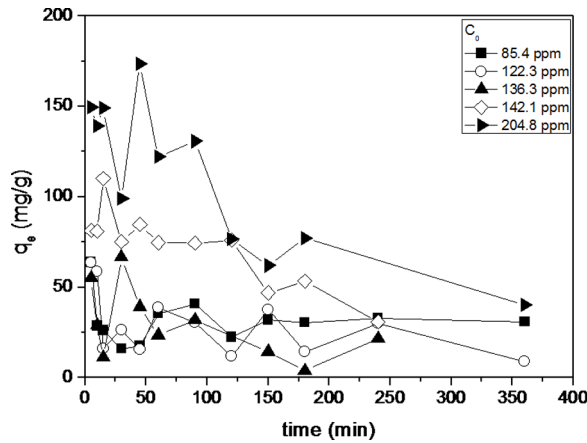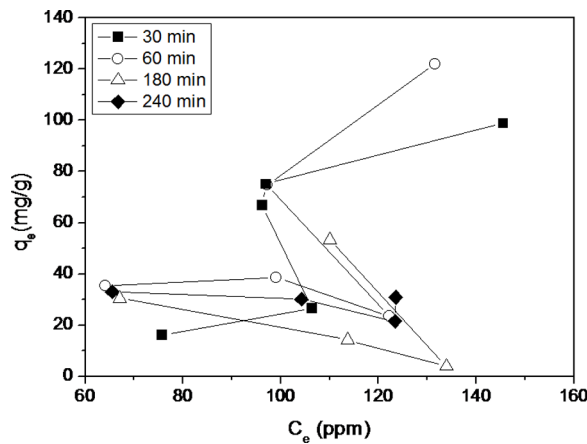**Figure 6**   Adsorption of Ni(II) by SW at various C_0

**Figure 7**   Adsorption of Ni(II) by SW at various times

The sorption system performance at equilibrium is reflected in the sorption isotherm. Wan et al. (2014) showed that Langmuir and Freundlich isotherms could describe the sorption behaviour of tea wastes satisfactorily. However, these isotherms do not comply with the adsorption results obtained in this study. Yang and Xing (2010) discussed the adsorption of carbon particles. It is reported that the 'Polanyi' isotherm has been recognised as the most suitable theory for dealing with adsorption on heterogeneous surfaces.

The adsorption potential (ε) is given in equation (2):

$$\varepsilon = -RT \ln \frac{C_e}{C_s},$$ (2)

where R is the universal gas constant, T is the absolute temperature, C_s and C_e is the water solubility and the equilibrium solution of adsorbate, respectively. The magnitude of ε for SW is between 500 J/mol and 4000 J/mol and decreases with increasing Ni concentration and time (Figure 8). Although it seems that the points are regular on the same line, the values of the adsorption potentials fluctuate.

Figure 8 Adsorption potential of SW at pH 2 at various C_0
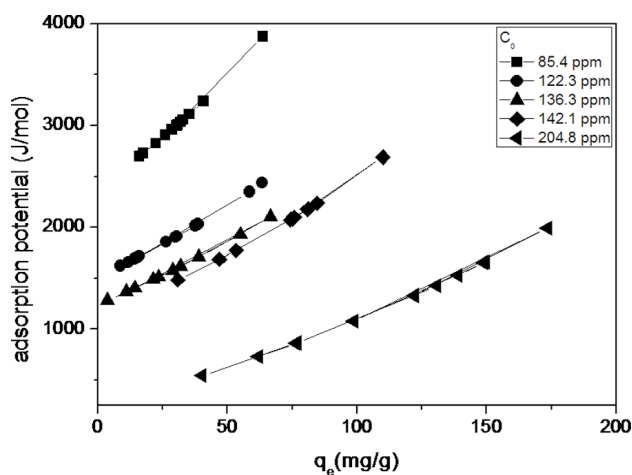
4 Conclusions

In this study, biochar was produced from industrial tea waste at 300°C and 400°C, characterised in detail and biochar's heavy metal adsorption potential to Ni(II) ions was determined. The detailed characterisations help to explain adsorption characteristics of biomass and its biochar form. When the adsorption is considered as porosity of the material, the adsorption capacity decreases since the pyrolysis results decreasing of the surface area related with porosity. On the other hand, the solubility of some organics of tea waste causes a hysteresis behaviour. Carbonisation reveals more OH groups which can cause the increasing pH value. It seems that increasing intensity of surface functionalities does not affect the adsorption more. However, jagged surface is more effective for tea waste structure. Biochar samples feature mesoporous structures and more

cellulosic characteristics. It can be concluded that tea waste without any pre-treatment and its biochar forms are not sufficient adsorbents for Ni ion removal.

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