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Biosorption of toxic heavy metals from aqueous solution by *Ulva lactuca* activated carbon

Wael M. Ibrahim ^{a,*}, Asad F. Hassan ^{b,c}, Yahia A. Azab ^d^a Botany Department, Faculty of Science, Damanshour University, Damanshour, Egypt^b Chemistry Department, Faculty of Science, Damanshour University, Damanshour, Egypt^c Institute of Organic Chemistry and Technology, University of Pardubice, Pardubice, Czech Republic^d Botany Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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ABSTRACT

Pollution with heavy metals is one of the most severe environmental problems in the world. In this study, the batch adsorption of toxic Cu^{+2} , Cr^{+3} , Cd^{+2} and Pb^{+2} ions using marine macroalgae *Ulva lactuca* (AP) and its activated carbon (AAC) were examined. The adsorption mechanism of heavy metal ions on AP and AAC was studied using various analytical techniques. The effect of several parameters such as contact time, algal dose, effect of pH, and initial concentration of metal ions on the adsorption process was estimated. The optimum adsorption was found to occur at pH 5.0, contact time 60 min, adsorbent dose 0.8 g/L, and initial concentration 60 mg/L. The maximum removal efficiency values of AP and AAC for heavy metal ions were 64.5 and 84.7 mg/g for Cu^{+2} , 62.5 and 84.6 mg/g for Cd^{+2} , 60.9 and 82 mg/g for Cr^{+3} , and 68.9 and 83.3 mg/g for Pb^{+2} . This work confirms the potential use of green macroalgae *U. lactuca* and its activated carbon for the removal of heavy metals from contaminated water.

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1. Introduction

Heavy metal pollution is a severe environmental issue and represents a threat to human beings and ecosystem [1,2]. Unlike organic contaminants, heavy metals such as chromium, cadmium, copper and lead are main pollutants of freshwater [3] due to their carcinogenic and persistent nature [4].

The main sources of these heavy metals into the ecosystem through wastewater streams are electroplating, smelting,

paint pigments, batteries, mining operations and agriculture sector [5,6]. Because of their toxic nature, most heavy metals cause several health problems like kidney damage, brain function disorders and nervous system deteriorations [7,8]. Their poisonous symptoms are insomnia, irritability, anemia, dizziness and muscles weakness [9].

A number of techniques have been developed for the adsorption of heavy metals from wastewater. These techniques include ion exchange, evaporation, chemical precipitation and membrane filtration [10,11]. Activated carbon has obviously been

* Corresponding author.

E-mail address: wms01@fayoum.edu.eg (W.M. Ibrahim).<http://dx.doi.org/10.1016/j.ejbas.2016.07.005>2314-808X/© 2016 Mansoura University. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

the greatest and widely used material for treatment of wastewater pollution. However, materials used for preparation of higher quality activated carbon cost greater [12]. Searching for low cost activated carbon resources is of great importance in the removal of heavy metals from wastewater [13–15].

Marine algae possess good metal biosorption capabilities due to the existence of active functional groups on the surface of their cell walls. The application of marine macroalgae as activated carbon materials has numerous advantages including low cost, extensive availability and high metal binding efficiency [16].

The aim of this work is to estimate the adsorption performance of *Ulva lactuca* for the removal of heavy metals from wastewater. Furthermore, this is the first study to determine the biosorption efficiency of KOH-activated carbon based on locally marine macroalga *U. lactuca* for toxic Cu^{+2} , Cd^{+2} , Cr^{+3} and Pb^{+2} ions and to identify the major parameters affecting its biosorption. In addition, Langmuir isotherm equation was employed to quantify the biosorption equilibrium.

2. Materials and methods

2.1. Preparation of adsorbents

2.1.1. Metal ion solutions

Stock solutions (1000 mg/L) of tested heavy metals were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ (analytical grade) in deionized water. The working solution was prepared by diluting stock solution to appropriate volumes.

2.1.2. Preparation of algal powder (AP)

The marine alga *U. lactuca* was collected from the Mediterranean Sea coast (Fig. 1a), Egypt, during spring season (April, 2014). The alga was washed with tap water and distilled water. The washed alga was oven dried at 60 °C for 24 h. The dried algal materials were ground using a Retsch ZM200 titanium mill. The powdered materials were used as adsorbents after sieving to obtain 0.1–0.2 mm particles.

2.1.3. Preparation of algal activated carbon (AAC)

The dried algal material was carbonized at 600 °C for 3 h in a stainless steel reactor tube (40 × 600 mm). The sample was soaked in potassium hydroxide for 48 h (potassium hydroxide: carbonized sample in ratio of 3:1). The sample was calcined at 800 °C for 3 h. The produced activated carbon was washed several times with distilled water until a neutral filtrate was obtained. The washed samples were stored for adsorption studies after drying at 110 °C [17].

2.2. Characterization methods

2.2.1. Scanning electron microscopy (SEM)

Scanning electron micrographs of AP and AAC were obtained using Quanta 250 FEG (USA). The sample was dried at 110 °C for 4 h then coated by thin layer of gold for charge dissipation.

2.2.2. Thermal gravimetric analysis (TGA)

TGAs were achieved for AP and AAC by differential thermal analyzer (Shimadzu DTA-50, Japan) up to 800 °C.

2.2.3. Textural characterization

Total pore volume (mL/g), total surface area (m^2/g) and pore radius (\AA) were performed via nitrogen adsorption at -196 °C for AP and AAC using Quantachrome gas sorption analyzer (NOVA2000, USA).

2.2.4. FTIR spectroscopy

Fourier transform infrared spectra (FTIR) were recorded for AP and AAC on a Mattson 5000 FTIR spectrometer (UK).

2.3. Adsorption procedure

2.3.1. Effect of pH

During the study of pH effect, the parameters of initial metal concentration, algal dosage, and shaking time were fixed at 10 mg/L, 0.1 g and 120 min, respectively. Effects of pH were tested at pH value 2, 3, 4, 5, 6, 7 and 8.

2.3.2. Effect of biomass dosage

This experiment was achieved to verify the effect of biomass weight on the sorption process. Different weights of biomass (0.2, 0.4, 0.6, 0.8 and 1.0 g/L) were mixed and shaken with a solution of 10 mg/L at pH 5 for 120 min.

2.3.3. Effect of contact time

Constant weights of AP and AAC (0.4g) were added to 10 mg/L heavy metal solution. Contact times were fixed at $t = 5, 10, 20, 60$ and 120 min. The solutions were filtered after each contact time and analyzed by atomic absorption spectrophotometer.

2.3.4. Effect of initial heavy metal ions concentration

In order to assess the effect of initial metal concentration on the adsorption, different metal concentrations of 5, 10, 20, 30, 40, 50, 60, 70 and 80 mg/L were examined at constant parameters; pH 5 with 0.6 g/L of biosorbent for 60 min.

2.3.5. Metal removal efficiency

Biosorption capacity (q_e), the amount of metal adsorbed per gram of biosorbent, can be calculated in mg/g as follows:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where C_0 is the initial metal ions concentration (mg/L), C_e is the equilibrium concentration of metal ions (mg/L), V is the volume of solution (L) and m is the mass of biosorbent (g). Percentage of metal removal can also be displayed by the percentage of metal removal as follows:

$$\text{Metal removal (\%)} = 100(C_0 - C_e)/C_0 \quad (2)$$

3. Results and discussion

3.1. Characterization of solid adsorbents

3.1.1. Scanning electron microscopy (SEM)

Surface morphologies for AP and AAC are shown in Fig. 1. It displays asymmetrical size cavities and the wide distribution of pore size may be due to the drastic effect of KOH at 800 °C

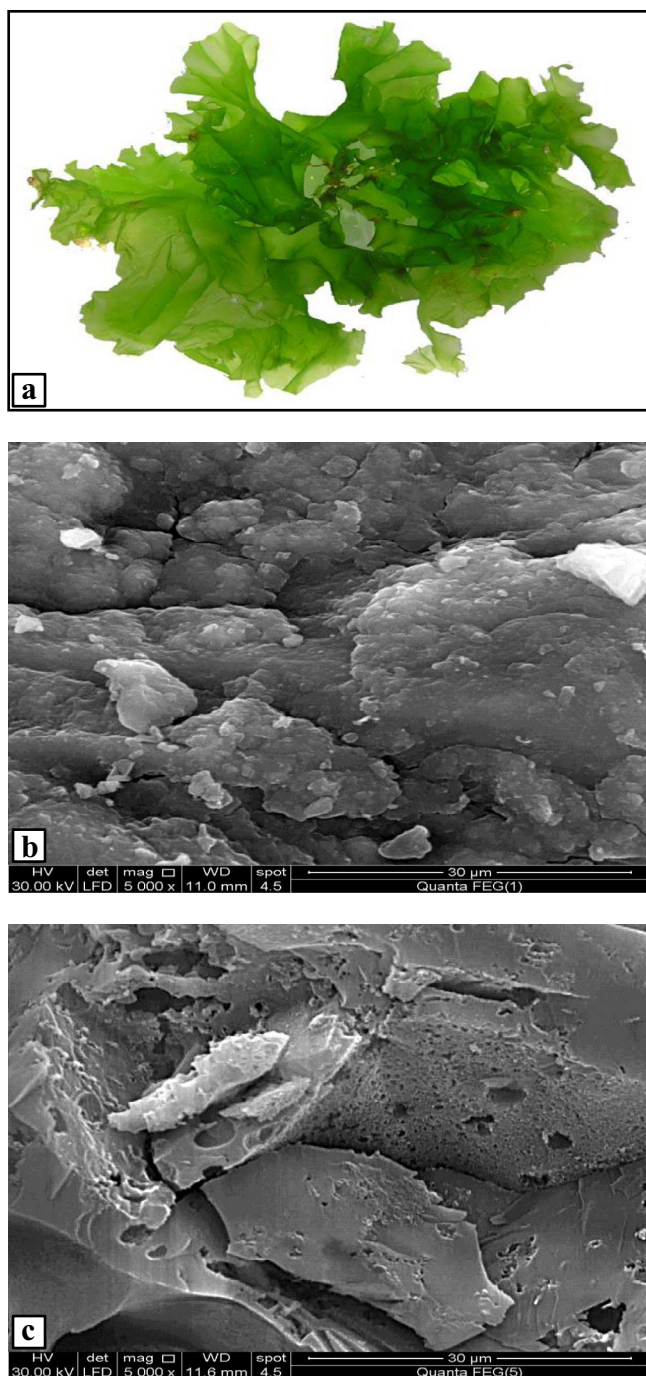


Fig. 1 – Collected marine alga *Ulva lactuca* (a), SEM of dried powder (b) and SEM of KOH-activated carbon (c).

on AP surface during activation. SEM image for AP exhibits the absence of pores which reflects the small surface area for AP.

3.1.2. Thermogravimetric analysis

Fig. 2 shows thermogravimetric analysis (TGA) for AP and AAC samples. It indicates that: (i) At lower temperatures (up to 110 °C) for AP as a raw material, the mass loss ($\approx 3.6\%$) is due to moisture removal. The loss of AP weight at higher temperatures (245–410 °C) may be due to the decomposition of algal organic compounds into condensable gas (methanol and acetic acid)

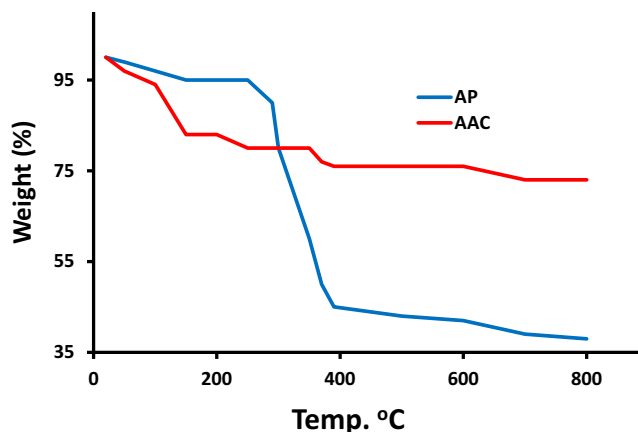
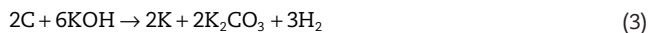


Fig. 2 – Thermogravimetric analysis of algal powder (AP) and its activated carbon (AAC).

and incondensable gas (CO_2 , CH_4 , H_2O , H_2) [18,19]. The temperature curve over 700 °C showed weight constant at this stage, indicating residual carbon atoms with the ash content of AP. (ii) TGA curve for AAC exhibits high thermal stability compared to AP because it was carbonized at higher temperature. (iii) Weight loss at 110 °C due to moisture (7.9%) is higher compared with AP (3.6%), indicating the presence of more surface hydrophilic function groups on AAC and its higher surface area accepted by activation [20].

3.1.3. Nitrogen adsorption parameters

Adsorption capacity for algal adsorbent materials is affected directly by surface area and porosity. Table 1 lists the obtained data using nitrogen adsorption isotherm at -196°C [21,22]. Upon inspection of Table 1, it was found that the (i) surface area of AAC ($345.4\text{ m}^2/\text{g}$) is about 1.8 times more than the surface area of AP ($193.9\text{ m}^2/\text{g}$), which is related to the influence of KOH as activating agent in the creation of internal surface area due to the formed micropores and the (ii) total pore volume for AAC (0.320 mL/g) is about 2.2 times more than that calculated for AP due to the effect of activating agent (KOH), which can create new pores based on the following equation:



Equation (3) indicates the production of potassium element, which can mix into the algal powder surface and support the development of high porosity [23].

3.1.4. Surface function groups

Adsorption capacity of solid adsorbents not only depends on surface area but also on chemical surface function groups.

Table 1 – Surface area, pore volume and pore radius of *Ulva lactuca* powder (AP) and its activated carbon (AAC).

Adsorbents	Surface area (m^2/g)	Pore volume (mL/g)	Pore radius (\AA)	R^2
AP	193.90	0.108	11.13	0.997
AAC	345.40	0.320	18.50	0.999

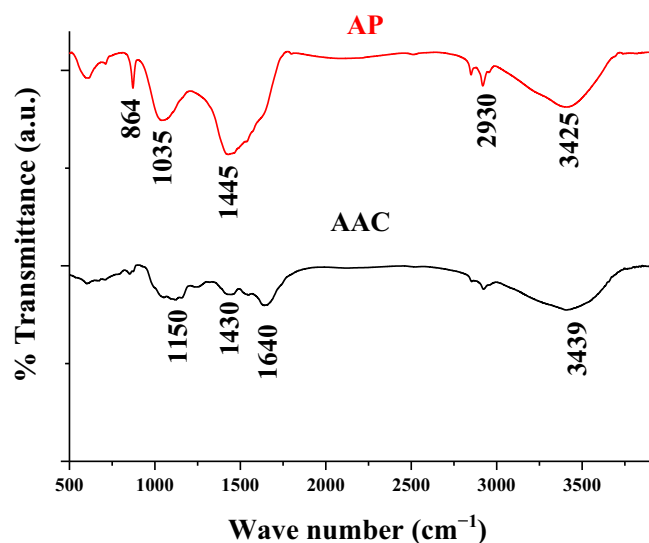


Fig. 3 – FTIR for *Ulva* powder (AP) and its activated carbon (AAC).

Infrared is considered as the most useful technique to characterize the surface functions of activated carbons [24]. Fig. 3 shows FTIR for AP and AAC. The broad bands at 3439 cm^{-1} and

3425 cm^{-1} exhibited by AP and AAC, respectively, are due to O—H of phenolic groups. In case of AP, the band located at around 1100 cm^{-1} is attributed to sulfate group, while the band at 3300–3500 cm^{-1} is due to amine N—H stretching and the band around 2500–3000 cm^{-1} is due to carboxylic acid O—H stretching. In case of AAC, the band located at around 1640 cm^{-1} could be attributed to C=C stretching for unsaturated aliphatic structures [25]. The band located at 1610–1386 cm^{-1} is attributed to C=O (ketone, aldehyde and carboxyl). The band located at 2930 cm^{-1} which is observed with AAC denotes the attendance of methylene group [26]. Band at 864 cm^{-1} was ascribed to alkenes vibrations [27]. From the latter, it is observed that AAC due to activation with KOH is rich with C—O surface function groups compared with the original AP.

3.2. Adsorption of heavy metals

3.2.1. Effect of pH

The algal biomasses contain different groups of amino, hydroxyl, carboxyl and sulfate on the cell wall, which are affected by changes in the solution pH [28]. The influence of solution pH on the metal ions adsorption capacity was examined at various pH values (2.0 to 8.0) as displayed in Fig. 4. The maximum adsorption of Cd^{+2} was obtained at pH 4.5, while Cr^{+3} and Cu^{+2} exhibited the maximum adsorption capacity at pH

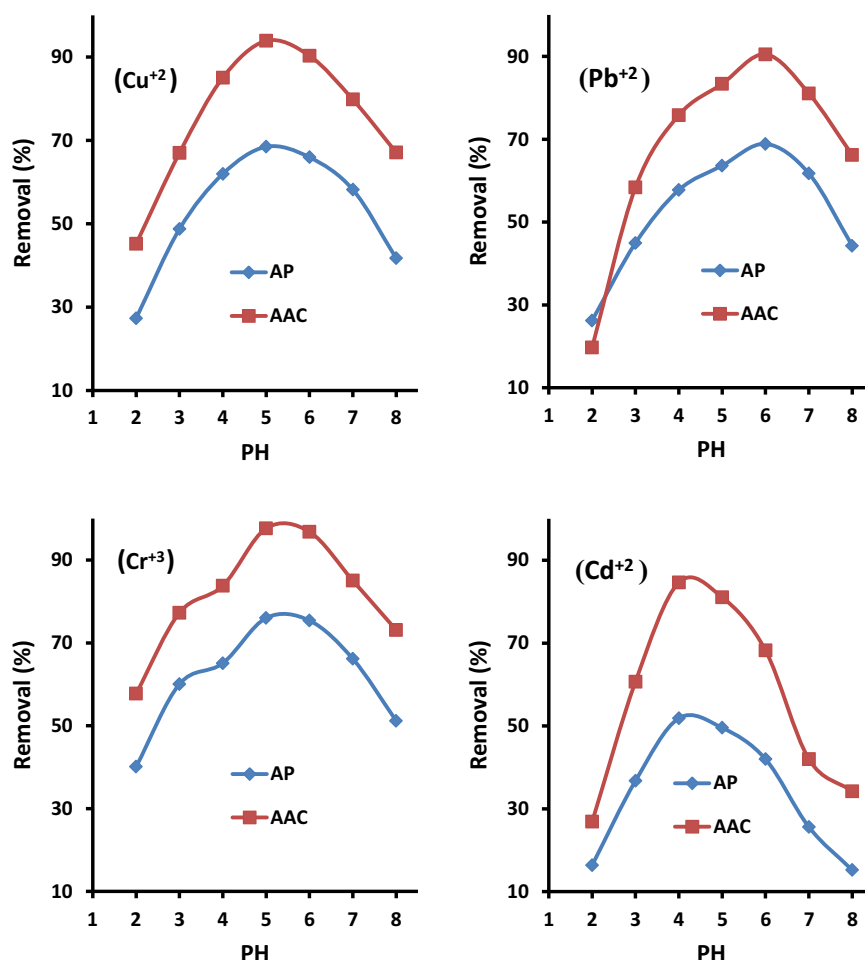


Fig. 4 – Effect of pH on heavy metal biosorption efficiency by *Ulva* powder (AP) and its activated carbon (AAC).

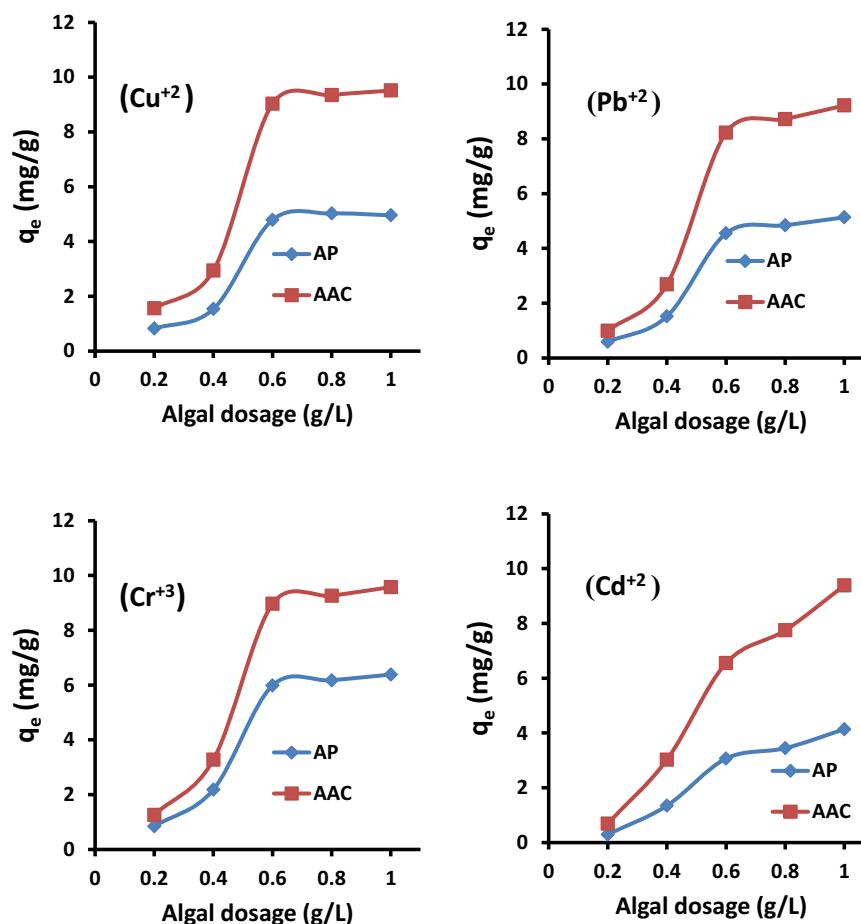


Fig. 5 – Effect of algal dosage on heavy metal biosorption efficiency by *Ulva* powder (AP) and its activated carbon (AAC).

5. In case of Pb^{+2} the removal efficiency was reached to a maximum at pH 6.

At pH value ranging from 2.0 to 4.0, the poor biosorption of metal ions may be due to the competition with H_3O^+ ions on active sites for both AP and AAC. At higher solution pH (5.0–6.0), the electrostatic repulsions between the surface of adsorbents and the positively charged metal ions are depressed, which increase the % of metal removal [27,29,30]. The decrease in the adsorption capacity at pH values (6.0–8.0) could be related to the repulsion between the negative charge of anionic species in solution and negative surface charge of the sorbents [31–33].

3.2.2. Effect of adsorbent dosage

In this work, various quantities of AP and AAC (0.2–1.0 g/L) were contacted with a fixed solution pH 6.0 and initial metal concentration at 10 mg/L. The amount of metal adsorption q_e (mg/g) against the algal dosage (g/L) is revealed in Fig. 5. For adsorption of metal ions onto AAC, increase adsorbent dosage from 0.2 to 0.8 g/L is accompanied by an increase in q_e (mg/g) from 1.3 to 9.2, 1.5 to 9.3, 1.0 to 8.7 and 0.7 to 7.6 mg/g for Cr^{+3} , Cu^{+2} , Pb^{+2} and Cd^{+2} , which is comparable to an increase in adsorption percentage by 520, 770, 607 and 985%, respectively. The same trend was observed in case of AP but with lower adsorption percentage due to the higher biosorption efficiency of AAC compared to AP.

The maximum metal adsorption at a higher adsorbent dosage (0.8 g/L) may be due to the higher active sites for AP and AAC which enhance the metal ions uptake [13,34]. With increasing adsorbent load than 0.8 g/L, the quantity of most heavy metal ions adsorbed on the adsorbent q_e (mg/g) is more or less constant. High adsorbent amounts are known to cause agglomeration and a consequent reduction in intercellular distance, leading to the protection of binding sites from metal ions [35].

3.2.3. Effects of contact time and adsorption kinetics

Contact time is the most important factor affecting the efficiency of biosorption. Fig. 6 shows the adsorption of Cu^{+2} , Pb^{+2} , Cr^{+3} and Cd^{+2} ions by *U. lactuca* powder (AP) and its activated carbon (AAC) with different contact times (5–120 min). The adsorption efficiency increases with rise in contact time up to 60 min, after which it is more or less constant. However, the majority of adsorption onto adsorbents was achieved after the first 60 min in case of AP and AAC. Therefore, the optimum contact time was selected as 60 min for further experiments. The higher biosorption at the initial contact time could be related to the driving force of heavy metal ions into the surfaces of AP and AAC and the abundance of active sites on the adsorbent [36,37]. The slow removal capacity with the subsequent time may be due to the diffusion of heavy metal ions into the

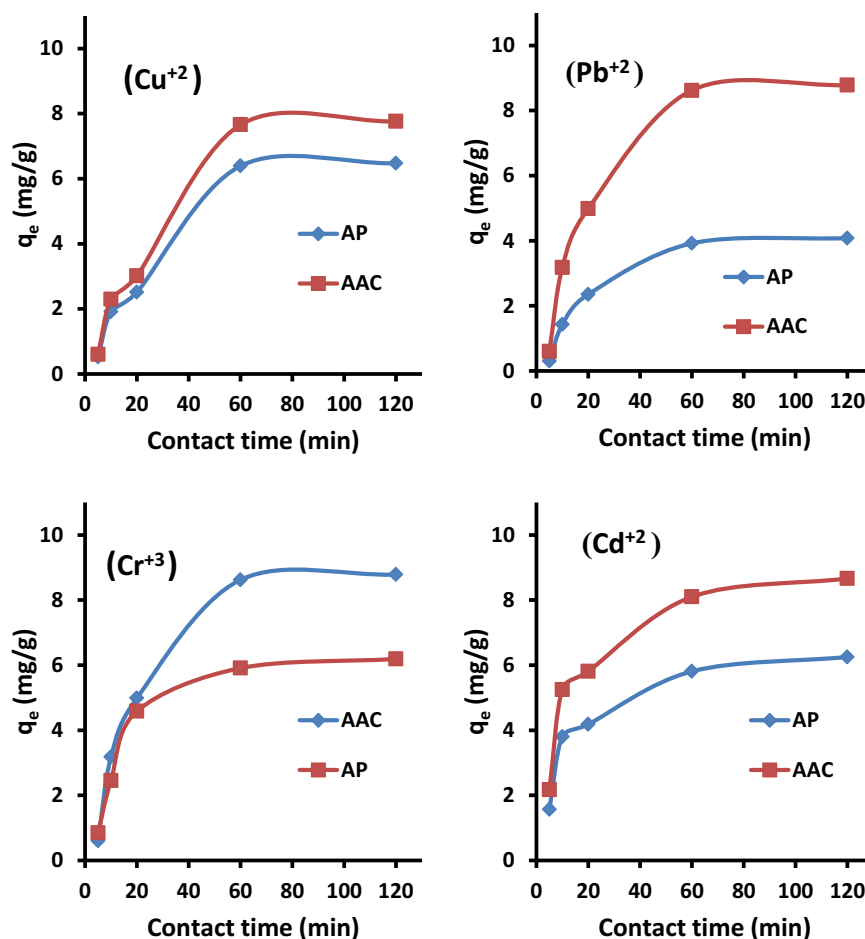


Fig. 6 – Effect of contact time on heavy metal biosorption efficiency by *Ulva* powder (AP) and its activated carbon (AAC).

surface of AP and AAC and fewer remaining binding sites [38].

3.2.4. Effect of metal ion concentration on adsorption

Initial metal ion concentration strongly influences the metal uptake in the adsorption of metal ions. The results in Fig. 7 showed that the biosorption of different metal ions increased at the beginning and reached the maximum of 87.5% and 100% at 60 mg/L for AP and AAC, respectively. After that, with increasing metal concentration, the adsorption capacity remained unchanged. This behavior was attributed to the fact that all active sites on the surface of algal materials were vacant, resulting in high metal adsorption at the beginning. Thereafter, with increasing metal concentration, the removal of metal was decreased due to a few binding sites that were available on the surface of AP and AAC.

The Langmuir adsorption model is the most applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm was used to characterize the relation between C_e/q_e and C_e (mg/L) according to the following equation.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where C_e (mg/L) is the equilibrium concentration, b (L/mg) is Langmuir constant, q_e (mg/g) is the amount of algal material, and q_m (mg/g) represents the maximum adsorption capacity. A plot of C_e/q_e against C_e (Fig. 8) gives a straight line with slope $1/q_m$ and intercept $1/bq_m$. From the Langmuir equation, the constants are calculated in Table 2. Upon inspection of Table 2 the (i) q_m for AAC adsorbent is greater than AP, which is related to the presence of microporosity on the surface of AAC as

Table 2 – Langmuir constants for adsorption of heavy metal ions onto algal powder (AP) and its activated carbon (AAC).

	q_e (mg/g)	b (L/mg)	R^2
AP			
Cu^{+2}	64.51	0.0629	0.958
Cd^{+2}	62.5	0.0330	0.897
Cr^{+3}	60.91	0.0394	0.887
Pb^{+2}	68.92	0.0364	0.926
AAC			
Cu^{+2}	84.77	0.0513	0.959
Cd^{+2}	84.61	0.0523	0.967
Cr^{+3}	81.97	0.0539	0.966
Pb^{+2}	83.34	0.0535	0.968

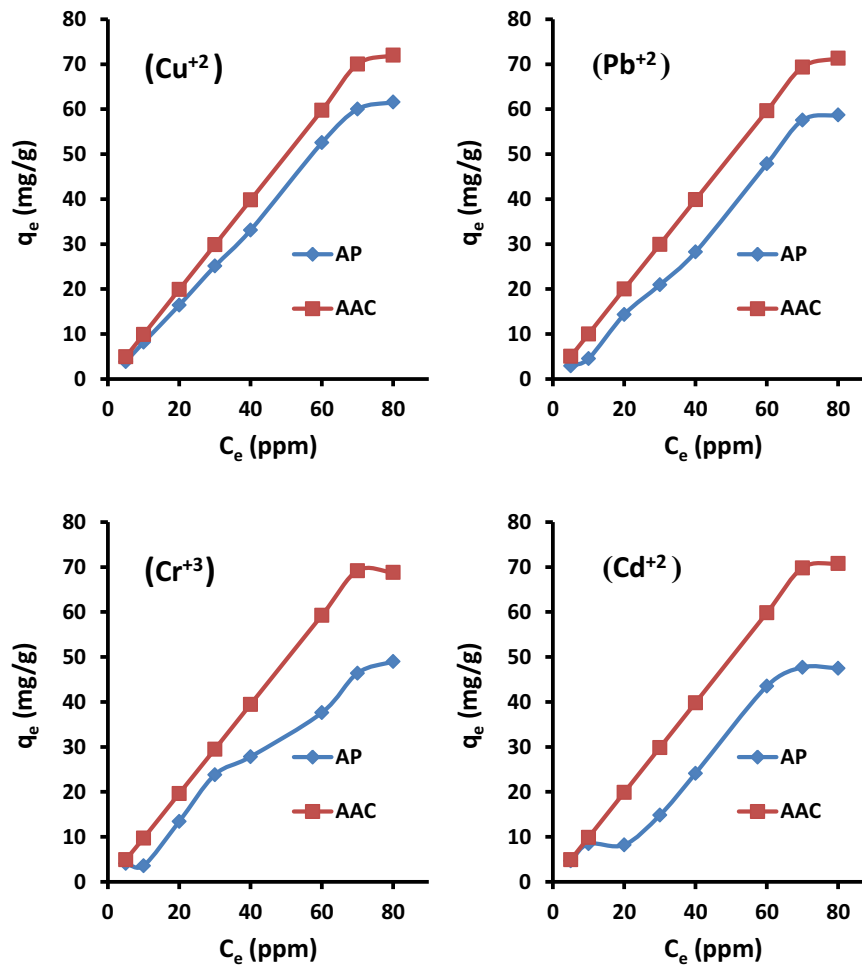


Fig. 7 – Effect of metal ion concentration on heavy metal biosorption efficiency by *Ulva* powder (AP) and its activated carbon (AAC).

indicated by SEM image; and the (ii) correlation coefficient (R^2) of AAC ranged from 0.959 to 0.968, indicating the applicability of Langmuir equation. When the q_m values for KOH-activated carbon based *U. lactuca* are compared with previous work (Table 3), the higher efficiency of KOH-activated carbon to remove about 4.2 times for Cd^{2+} , 3.8 times for Pb^{2+} , 4.5 times for Cu^{2+} and 27.1 times for Cr^{3+} are indicated. This comparison demonstrated that activated carbon of macroalga *U. lactuca*

is a potential biosorbent for different heavy metals because of its high maximum adsorption capacity.

4. Conclusion

U. lactuca powder (AP) and its KOH-activated carbon (AAC) were prepared and characterized for sorption of Cd^{2+} , Cu^{2+} , Cr^{3+} and

Table 3 – Comparison of adsorption capacity of *Ulva lactuca* for heavy metal ions with different biomasses and other activated carbon.

Biosorbent	Adsorption capacity (mg/g)				Reference
	Cd^{2+}	Pb^{2+}	Cr^{3+}	Cu^{2+}	
<i>Pinus sylvestris</i>	19.1	22.2	–	–	[39]
Coconut shell	7.19	–	–	–	[40]
Oak wood	–	–	3.03	–	[41]
<i>Phaseolus</i> hulls activated carbon	15.7	21.8	–	19.5	[42]
Grape lex activated carbon	58.2	–	–	–	[43]
Bamboo activated carbon	0.19	0.67	0.32	0.58	[44]
Commercial activated carbon	25.1	–	–	–	[45]
Granular activated carbon	–	–	0.99	–	[46]
<i>Ulva lactuca</i> (AP)	62.5	68.9	60.9	64.5	Present study
<i>Ulva lactuca</i> (AAC)	84.6	83.3	81.9	84.7	Present study

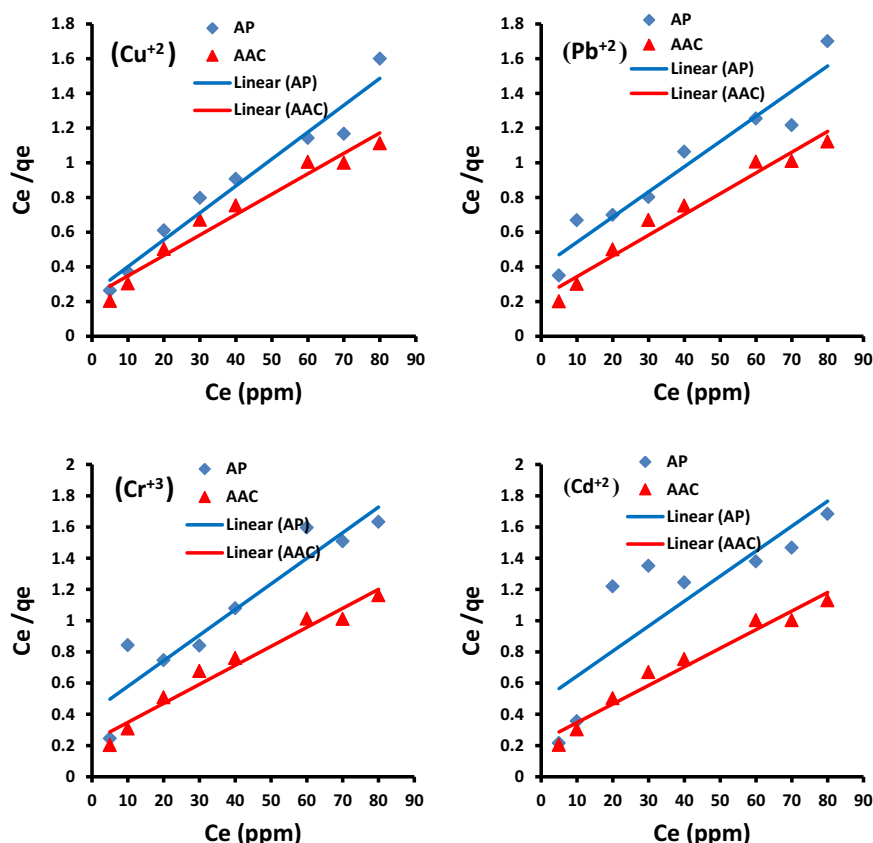


Fig. 8 – Langmuir adsorption isotherm of heavy metal on *Ulva* powder (AP) and its activated carbon (AAC).

Pb^{2+} ions. SEM and nitrogen adsorption indicated the presence of porosity on KOH-activated carbon more than its precursor powder. TGA exhibited thermal instability in the case of *U. lactuca* when compared with KOH-activated carbon and the presence of chemical function groups on both adsorbents was illustrated by FTIR. The optimum adsorption condition was found to occur at around pH 5.0, contact time 60 min, adsorbent dose 0.8 g/L, and initial concentration 60 mg/L. KOH-activated carbon was found to be more efficient than algal powder in removing heavy metal. Finally, it was concluded that KOH-activated carbon based *U. lactuca* can be used as an effective technology for removal of metal ions from contaminated environment.

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