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Research Paper

Desorption and Reutilization Studies of Copper and Lead Lons by Activated Carbons Prepared from Ulva Fasciata sp

Chemistry

KEYWORDS : Green algae; Carbon; Adsorbent dose; Desorption; Reutilization

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ABSTRACT

The aim of this present work is to study the desorption and reutilization studies of copper and lead ions from aqueous solutions onto activated carbons prepared from of marine green algae Ulva fasciata sp. (CCUC, SSUC and SCUC) and commercially activated carbon (CAC). Adsorption of Cu (II) and Pb (II) was investigated with the variation in the parameters of pH, contact time and the adsorbent dose. Also the activated carbons were applied in the industrial waste water for studying the adsorption efficiency of copper and lead ions.

1. INTRODUCTION

Water is an universal solvent. It shapes the earth's surface and moderates the climate[1]. Industrialization in many regions has increased the discharge of industrial wastes, especially those containing heavy metals, into natural water bodies or on land. Heavy metals such as copper, lead, chromium, etc., are hazardous to the environment. Their presence in the aquatic ecosystem poses human health risks and causes harmful effects to living organisms in water and also to the consumers of them [2]. Copper and lead are widely used in various important industrial applications. Copper at excessive concentration is toxic to living organism of humans and other creatures, especially fish [3]. Lead, one of the three most toxic heavy metals, has long-term potential negative impacts on anemia, encephalopathy, hepatitis and nephritic syndrome [4]. The removal of these toxic heavy metals from wastewaters is of great interest and importance in the field of water pollution control, since metals are persistent and have potential to be bio-accumulated by a range of organisms [5].

The removal of such a heavy metal from contaminated water bodies has been attempted by several scientists employing a wide variety of techniques including chemical precipitation, ion-exchange, electro flotation, membrane filtration, reverse osmosis, etc [6]. These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational costs [7]. The most promising alternative method for the removal of metal ions is the adsorption. Although commercial activated carbon with high surface area, micro porous character and high adsorption capacity, has made its potential adsorbent for the removal of heavy metals from industrial wastewater, it is expensive, has relatively high operation costs. Thus, there is a growing demand to find low-cost and efficient, locally available adsorbent [8].

The biological materials that have been investigated for heavy metal uptake include fungi [9], bacteria [10], yeast [11], and macro algae [12]. Seaweeds have a high bonding affinity with heavy metals Since their cell walls have different functional groups (such as carboxyl, hydroxyl, phosphate or amine) that can bind to metal ions , they are much more efficient than active carbon and natural zeolites and, depending on the pH, these groups are either protonated or deprotonated [13]. The objective of this work is to study the adsorption, desorption and reutilization studies of copper and lead ions from aqueous solutions onto activated carbons prepared from of marine green algae Ulva fasciata and compared with commercially activated carbon.

2. MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

Adsorbent

The green marine algae Ulva fasciata sp. in the present study were collected from the coastal area of Kanyakumari district, Tamil Nadu, India. The collected algae were washed with tap water and further by deionized water several times to remove impurities. The washed algae were then completely dried. Then the dried algae Ulva fasciata were pretreated with Calcium Chloride, Sodium Sulphate and Sodium Cabonate salts respectively. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400ºC powdered well and finally thermally activated at 800ºC for 10 minutes [14]. The carbons are further known as Calcium Chloride treated Ulva fasciata Carbon (CCUC), Sodium Sulphate Treated Ulva fasciata Carbon (SSUC) and Sodium Carbonate treated Ulva fasciata Carbon (SCUC).

2.2. PREPARATION OF METAL ION SOLUTIONS

Stock solutions of copper and lead concentration 1000 mg/L were separately prepared by dissolving analytical grade CuSO4.5H2O and Pb $(NO_3)_2$ in deionized water. The range of concentration of the prepared metal solutions varied between 10 to 80 mg/L and they were prepared by diluting the Copper and Lead stock solutions with deionized water.

2.3. BATCH ADSORPTION STUDIES

2.3.1. Adsorption Studies

Batch adsorption equilibrium experiments were conducted for the adsorption of Copper and Lead on activated carbons of green algae Ulva fasciata and commercially activated carbon as a function of initial pH, adsorbent dose and contact time by adding 0.2 g of dried carbon to 100 mL of Cu (II) and Pb (II) solutions with 20 mL concentrations in 250 mL stoppered reagent bottles at a constant shaking speed (250 rpm). All the experiments were carried out at room temperature (28 ± 2ºC). For studying the influence of pH on the adsorption of Cu (II) and Pb (II), the experiments were conducted at various initial metal solution pH values of 1-10. The pH of each solution was adjusted to different values with either NaOH or HCl. The concentrations of Copper and Lead metal ions in solution before and after adsorption were determined using atomic adsorption spectrophotometer. The amount of adsorption at equilibrium (q_e) (mg/g) and the percentage adsorption (%) were computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{X} \qquad (1)$$

Percentage adsorption $= \frac{(C_0 - C_e)}{C_0}$ X100 (2)

Where C_0 and C_e are represented the initial and equilibrium concentrations (mg/l), V is the volume of solution and X the weight of adsorbent (g).

2.3.2. Desorption and Reutilization

Studies The desorption and reuse studies can give a clear idea about the mechanism of adsorption along with the stability of the adsorbent for further use. Therefore, attempts were made to desorb Cu (II) and Pb (II) from the loaded carbon adsorbents (CCUC, SSUC, SCUC and CAC). After adsorption experiments, the carbon adsorbents (CCUC, SSUC, SCUC and CAC) were collected by filtration and washed with de-ionized water for three times, to remove residual Cu (II) and Pb (II) on the surface. Hence, experiments were conducted with water, acidic, alkaline and EDTA solutions to desorb Cu (II) and Pb (II) ions by adding 0.20 g carbon adsorbent to 50 ml desorbent solution (water, acid, alkali and EDTA). Desorption of metal ions from adsorbent was carried out on a rotatory shaker (250 rpm) for 18 h, then the filtrates were analysed to determine the concentration of Cu (II) and Pb (II) after desorption. Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in desorption medium, as the following equation.

$$\text{Desorptio ratio} = \frac{\text{Amt.desorbed}}{\text{Amt.adsorbed}} \text{x}100$$

In order to determine the reusability of the adsorbents, consecutive adsorption–desorption cycles were repeated 5 times by using the same immobilized carbon adsorbents with effective adsorbent. After each cycle of adsorption–desorption, immobilized activated carbons were washed with buffer solution and reconditioned for adsorption in the succeeding cycle. It is an important feature to use Ulva fasciata activated carbon to remove Cu (II) and Pb (II) in continuous systems in industrial processes

3. RESULTS AND DISCUSSION

3.1. Adsorption studies

In order to find out optimum pH, contact time and adsorbent dose the batch adsorption experiments were carried out as follows:

3.1.1. Effect of pH

The effect of hydrogen ion concentration was examined from solutions at different pH levels covering a range of 1.0–10.0 with 100 mL of Cu (II) and Pb (II) concentration 20 mg/L containing 0.2g activated carbon. The optimum pH values are shown in Table-1.

3.1.2. Effect of contact time

The optimum contact time on the adsorption efficiency of Cu (II) and Pb (II) on activated carbons of Ulva fasciata and CAC is shown in Table- 2. The experiments were carried out using 100 mL of Cu (II) concentration 20 mg/L containing 0.2g activated carbon at pH 5 for activated carbons of Ulva fasciata (CCUC, SCUC and SSUC) and pH 6 for CAC. A set of solutions containing these carbons were equilibrated for varying periods ranging from 30 to 300 minutes at an agitation speed 250 rpm. The same experiments were carried out using 100 mL of Pb (II) concentration 20 mg/L containing 0.2g activated carbon at pH 4 for activated carbons of Ulva fasciata and CAC.

3.1.3. Effect of adsorbent dose

The dependence of Copper and Lead adsorption on the amount of carbon adsorbent was studied by varying the adsorbent amount from 0.05g to 0.4 g at optimum pH for CCUC, SCUC, SSUC and CAC. The experiments were carried out using 100 mL of Cu (II) and Pb (II) concentration 20 mg/L, contact time (2h) and agitation speed (250rpm).

Table- 1. Different parameters and optimum values of Cu (II) and Pb (II) ions

Adsorbent	Optimum pH		Optimum Contact time		Optimum dose	
	Copper	Lead	Copper	Lead	Copper	Lead
CCUC	5	4	1h	1h	0.15g	0.15g
SSUC	5	4	1h	1h	0.15g	0.15g
SCUC	5	4	1h	1h	0.15g	0.15g
CAC	6	4	2h	2h	0.20g	0.20g

3.2. DESORPTION STUDIES

3.2.1. Desorption of Cu (II) ions

Desorption study is most importance when the activated carbon preparation is costly, as it is possible to decrease the adsorption process cost and also dependency of the process on a continuous supply of adsorbent. After desorption, the adsorbent should be close to its original form, and should not lose its adsorption ability. The desorption of the adsorbed Cu (II) ions from the tested activated carbons were studied in a batch system. The desorption studies of Cu (II) ions adsorbed onto the activated carbons were performed with 0.25N HCl.

From the table -2 it is well known that the desorption efficiency of CCUC reached from 55.61% to 76.23% SSUC reached from 66.72% to 90.53% SCUC reached from 62.93% to 85.17% and CAC reached from 37.45% to 60.35% when the concentration of HCl increased from 0.01 to 0.25 N, indicating that higher concentration of HCl was more efficient in releasing Cu(II) ions. The negligible desorption of Cu (II) with de-ionized water indicated the predominance of the chemical bonding and ion-exchange between the adsorbate and adsorbent. This implied that physical adsorption played insignificant role in Cu (II) adsorption on the activated carbons. The desorption of Cu (II) in the acidic solution suggested that either chemisorption or ion exchange are the possible mechanisms of Cu (II) adsorption. The higher percentage of desorption indicated the bond between the adsorbate and adsorbent molecules were weak. From the above discussion, it can be concluded that ion exchange mechanism played a significant role in the sorption process.

Table - 2. Desorption of Cu (II) with various desorbents.

Desorbent	Desorption % of Cu(II)			
	CCUC	SSUC	SCUC	CAC
De-ionized water	1.56	2.71	2.26	1.17
0.01N HCl	55.61	66.72	62.93	37.45
0.10 N HCl	75.82	89.38	83.65	58.73
0.25 N HCl	76.23	90.53	85.17	60.35
0.01N NaOH	47.18	61.20	57.35	29.65
0.10N NaOH	64.17	77.36	71.25	44.94
0.25N NaOH	64.95	78.26	72.41	45.19
0.01N EDTA	50.27	63.45	59.80	35.07
0.10N EDTA	58.51	73.16	70.31	48.36
0.25N EDTA	59.70	74.58	70.85	50.26

3.2.2. Desorption of Pb (II) ions

The effect of various desorbents on the desorption of Pb (II) ion was investigated. A successful desorption process requires the proper selection of the desorbent, which strongly depends on the type of adsorbent and the mechanism of adsorption [15]. The selected desorbents must be effective, harmless for the adsorbent, non-polluting and cheap. In this study, 0.25 N HCl solution was selected as an effective desorbent to desorb Pb (II) ions from the Pb (II) -loaded activated carbons. In acidic conditions, Pb (II) ions are displaced by protons from the binding sites. The desorption efficiency of CCUC reached from 60.14to 80.29% SSUC reached from 70.25to 92.23% SCUC reached from 66.40% to 87.35% and CAC reached from 41.55% to 60.87% when the concentration of HCl increased from 0.01 to 0.25 N, indicating that higher concentration of HCl was more efficient in releasing Pb(II) ions. However a complete desorption of Pb(II) ions could not be obtained even with 0. 0.25 N HCl, which might be due to Pb(II) ions becoming trapped in the intrapores, therefore difficult to release [16].

Table - 3. Desorption of Pb (II) with various desorbents

Desorbent	Desorption % of Pb(II)			
	CCUC	SSUC	SCUC	CAC
De-ionized water	1.89	3.12	2.63	1.38

0.01N HCl	60.14	70.25	66.40	41.55
0.10 N HCl	78.82	91.43	85.67	60.31
0.25N HCl	80.29	92.23	87.35	60.87
0.01N NaOH	51.39	65.40	60.51	34.60
0.10N NaOH	67.18	80.72	76.05	52.83
0.25N NaOH	68.40	82.08	76.94	53.55
0.01N EDTA	53.20	66.07	62.24	40.15
0.10N EDTA	63.16	79.53	73.08	55.85
0.25N EDTA	64.32	80.27	73.86	56.71

The negligible desorption of Pb(II) with de-ionized water indicated the predominance of the chemical bonding and ion-exchange between the adsorbate and adsorbent. This implied that physical adsorption played insignificant role in Pb(II) adsorption on the activated carbons. The desorption of Pb(II) in the acidic solution suggested that either chemisorption or ion exchange are the possible mechanisms of metal adsorption. The higher percentage of desorption indicated the bond between the adsorbate and adsorbent molecules were weak. From the above discussion, it can be concluded that ion exchange mechanism played a significant role in the sorption process.

3.3. Reutilization studies

3.3. 1. Reutilization of the activated carbons after desorption of Cu (II) by 0.25N HCl

In order to show the reutilization of the activated carbon adsorbents, adsorption–desorption cycle of Cu (II) ions was repeated 5 times by using same preparations. The high recovery percentage of Cu (II) by 0.25N HCl allows the reuse of adsorbent and the values are shown in Table- 4. The adsorption capacities did not change too much during the repeated adsorption–desorption operations. These results showed that activated carbons could be repeatedly used in Cu (II) adsorption studies without detectable losses in their initial adsorption capacities.

Table - 4. Removal efficiencies of Cu (II) by 0.25N HCl regenerated adsorbents

Cycle No	CCUC (%)	SSUC (%)	SCUC (%)	CAC (%)
1	85.23	95.28	93.13	70.59
2	77.15	89.50	86.45	51.65
3	72.76	81.28	75.31	42.86
4	67.56	75.28	67.26	31.73
5	58.36	70.75	62.59	28.51

Five successive cycles of sorption and desorption of Cu (II) were carried out in the batch system to evaluate the reusability of activated carbons of Ulva fasciata. Metal adsorption by the carbon adsorbent decreased slightly after each successive cycle could be noticed from Table 4. In all the cycles, more than 75% of Cu (II) was recovered back by using 0.25N HCl as the desorbing agent. If we take into account the loss of adsorbent carbon (10–15%) at the end of the fifth cycle, it is apparent that the metal adsorbing ability of the adsorbent carbon did not considerably diminish during repeated adsorption-desorption cycles.

3.3.2. Reutilization of the activated carbons after desorption of Pb (II) by 0.25N HCl

In order to evaluate the reutilization of the activated carbons, the adsorption–desorption cycles were repeated five times by using same preparations. In these tests, desorption of Pb (II) ions from the activated carbons of Ulva fasciata and CAC was performed with 0.25N HCl solution. The activated carbons were separated by filtration, washed several times with deionized water until the pH of the wash solution was 4.0, because the use of 0.25N HCl solution as an eluent deposits H_3O^+ ions on the activated carbon surface. Excessive amounts of H_3O^+ ions can reduce the metal adsorption capacity of the adorbent, and washing the carbon with deionized water is, thus necessary to remove H_3O^+ ions [17].

Table - 5. Removal efficiencies of Pb (II) by HCl regenerated adsorbents

Cycle No	CCUC (%)	SSUC (%)	SCUC (%)	CAC (%)
1	91.84	97.65	95.48	75.42
2	82.45	90.63	87.27	61.58
3	76.31	85.84	82.60	46.43
4	65.72	79.57	76.67	35.57
5	60.29	76.82	73.58	30.16

The results are illustrated in Table-5. After the first cycle, the adsorption capacity decreased, and for all consecutive cycles, as the number of cycle increased, the amount of newly adsorbed Pb(II) decreased. The reasons of this situation can be explained as: (i) although HCl has a high capacity to desorb metals, several studies show that it decreases metal sorption ability of adsorbent in successive cycles because it damages metal binding sites and hydrolyzes polysaccharides on the surface of activated carbons of Ulva fasciata and CAC [18]. (ii) after each adsorption process, the number of already occupied sites increases leaving little space for further sorption and (iii) some of activated carbon may be lost during the adsorption–desorption process. It can be concluded that the activated carbons of Ulva fasciata can be used at least 5 times effectively with repeated regeneration.

3.4.1. Industrial wastewater adsorption experiment for Cu (II)

Actual industrial wastewater was used to evaluate the practicality of the Ulva fasciata activated carbons and CAC. The wastewater was collected from copper plating industry. The initial pH of industrial wastewater was 4.35 and the initial concentration of Cu (II) was 26.56 mg/L. The waste water was adjusted to pH 5.0 in the cases of CCUC, SSUC, SCUC and pH 6.0 for CAC by using 0.1N HCl. The effect of varying adsorbent dose on the removal of Cu (II) from industrial wastewater was carried out under optimum pH and contact time and the mixtures were shaken for 12 h. Figure 1 represents the removal of Cu (II) as a function of adsorbent dose for an initial Cu (II) Concentration of 26.56 mg/L. After adsorption the Cu (II) ions detected were below the wastewater discharge standard in World Health Organization. From this study we come to know, the Ulva fasciata activated carbons were effective for the removal of Cu (II) ions from industrial wastewater. It has been observed that maximum removal of 77.53% of Cu (II) could be achieved with an adsorbent dose of 0.4g/100mL by CCUC, 85.88 % with an adsorbent dose of 0.35g/100mL by CCUC, 82.37 % with an adsorbent dose of 0.35g/100mL by CCUC and 64.55% with a sorbent dose of 0.7g/100mL by CCUC respectively.

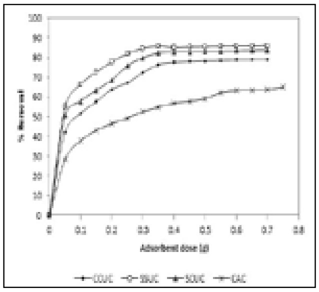

Fig.1 Effect of adsorbent dose*(Ulva fasciata* activated carbons and CAC) on the Cu (II) removal from industrial waste water

3.4.2. Industrial wastewater adsorption experiment for Pb (II)

To say about the activated carbons are effective adsorbents, when they remove the maximum possible impurities from the industrial wastewater. In order to determine the performance of Ulva fasciata activated carbons and CAC, they were employed for the removal of Pb (II) from industrial Lead battery wastewater.

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S.NO	Parameter	Concentration(mg/L)
1.	Lead(II)	82.45
2.	Chlorides	12.82
3.	Calcium	18.54
4.	Sulphates	1.27

The industrial wastewater contains high concentration of lead (II) ions to an amount of 82.45 mg/L and pH was 9.25, it was then diluted to 4 times to have the Pb (II) concentration at around 20 mg/L, before adsorption studies were carried out with Ulva fasciata activated carbons and CAC. The diluted waste water was adjusted to pH 5.0 in the cases of CCUC, SSUC, SCUC and pH 6.0 for CAC by using 0.1N HCl. The effect of varying adsorbent dose on the removal of Pb (II) was carried out under optimum pH and contact time, then the mixtures were shaken for 12 h. Figure.2 represents the removal of Pb (II) as a function of adsorbent dose for an initial Pb (II) Concentration of 20.61 mg/L.

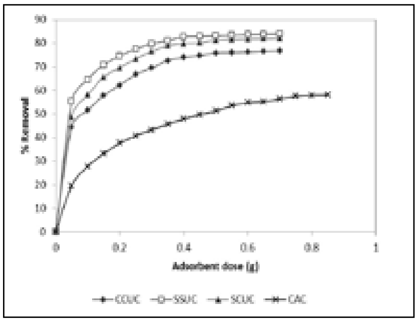

Fig.2 Effect of adsorbent dose *(Ulva fasciata* **activated carbons and CAC) on the Pb (II) removal from industrial waste water**

It has been observed that maximum removal of 75.81% of Pb (II) could be achieved with an adsorbent dose of 0.5g/100mL by CCUC , 82.89 % with an adsorbent dose of 0.45g/100mL by CCUC, 80.17 % with an adsorbent dose of 0.45g/100mL by CCUC and 57.45% with an adsorbent dose of 0.75g/100mL by CAC respectively. This shows that SSUC is more efficient adsorbent than CCUC, SCUC and CAC in the removal of Pb (II) from wastewater.

4. CONCLUSIONS

The aim of this present work is to study the adsorption, desorption and reutilization studies of copper and lead ions from aqueous solutions onto activated carbons prepared from of marine green algae Ulva fasciata (CCUC, SSUC and SCUC) and commercially activated carbon (CAC). Adsorption of Cu (II) and Pb (II) ions was investigated with the variation in the parameters of pH, contact time and the adsorbent dose. Also the activated carbons were applied in the polluted water for studying the adsorption efficiency of copper and lead ions.

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