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Research Article

Production of Activated Carbon from Sea Urchin Shell by Ultrasound for the Removal of Cd^{2+} and Cr (III) Heavy Metal Ions from Wastewater

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Abstract

Activation was achieved by applying the chemical activation method in the production of activated carbon from sea urchin shells, and by treating K_2CO_3 + boric acid chemicals with sea urchin shells. In order to find the optimum activated carbon production conditions, different K_2CO_3 concentrations (10, 20, 30%), different temperatures (500, 700, 900°C), different carbonization times (30, 70, 120 min), and different boric acid concentrations (4%), 6, 10) have been studied. Optimum application conditions were tried to be determined by measuring the moisture content, carbonization efficiency, iodine number, surface area, SEM, XRD, and adsorption capacity of the activated carbon samples produced by the ultrasound process. Under optimum conditions, the adsorption capacity was able to remove over 96% of cadmium and chromium metal ions in the aqueous medium. As a result of the studies, the optimum activated carbon sample was obtained at 6% boric acid, 30% potassium carbonate concentration, 900°C carbonization temperature, and 70 min carbonization time. The iodine number of the obtained activated carbon was determined as 1053.48 mg/I2 and the surface area was 851.94 m^2/g.

Keywords: Adsorption; Ultrasound; Cd^{2+}; Cr (III); Sea Urchin Shell

Introduction

Industry wastewater: These are the waters that have different contents and pollutants due to their release to nature from different types of industries. The wastewater of different types of enterprises in industries such as textile, furniture, iron-steel, copper leather, paint, paper, and automotive is different [1-2]. It constitutes an important problem in the treatment of toxic and carcinogenic industrial wastewaters, which are difficult to biodegrade due to their high solubility in water and their complex chemical structures [3,4]. In some industries, it is possible for precious metals to pass into the water and cause a loss in terms of operation. In some cases, heavy metals passing into the water can contaminate streams and groundwater. For this reason, treatment methods in wastewater may vary depending on the characteristics of the enterprise [5].

Adsorption, chemical coagulation, chemical decomposition, oxidation, membrane filtration, Fenton, ozone, and aerobic or anaerobic biological treatment methods are preferred for the economical and effective treatment of such wastewaters [6,7]. The adsorption process is the most widely used physical method for color and contaminant removal from water [8,9]. The small particle size, large surface area, and porous structure of the adsorbent are used to increase the adsorption capacity. Adsorbents such as activated carbon, aluminum oxide, fly ash, silica gel, activated silica, bentonite, resin, chitosan, olive waste (pomace), pumice, perlite, zeolite are preferred due to their low cost and efficiency in treatment [10,11]. Surface area is very important in the removal of pollutants from wastewater in the adsorption process. In addition to the advantage of having a large surface area, the widely used activated carbon is expensive and difficult to obtain adsorbent, so the use of cheap and easily available adsorbent with high adsorption capacity is recommended [12,13].

Activated carbon is a very porous carbonaceous type that has a wide range of uses and cannot be characterized by structural formula or chemical analysis. It is the small-sized micropores that give the activated carbon high adsorbing properties. Activated carbon can be found in powder form, granulated in various sizes and shapes, or in the form of pressed thin rods, depending on the purpose of use [15,16].

Among the usage areas, There are areas such as the separation/cleaning of waste materials or metals from water/solution, as well as in the food and chemistry sector. Activated carbon can be produced from various materials from charcoal with carbon content to coconut shell, from fruit kernel to nutshell. Although there is no limitation for the raw material to be used, cheap raw materials with low inorganic and high carbon content are preferred for activated carbon production. Activated carbon production is carried out in two stages. Carbonization and activation. The activation process is carried out in two ways: physical and chemical activation. In physical activation, inexpensive activated carbon with a lower surface area is produced, which is used in large-scale industrial applications. In the chemical activation method, high surface area activated carbon is obtained, which finds a more specific application area [15-17].

The ultrasound process (US) has recently come to the fore in order to increase the activity of the adsorbent surface [17-19]. The ultrasound process, which works according to the cavitation principle, provides the adsorbent surface activation thanks to the. OH radicals and the pyrolysis effect, which are formed as a result of the explosion of the bubbles formed in the water under high temperature and pressure, and as a result, the adsorption process is given continuity [18,20]. A large surface area is obtained by activating the particle surface more with the effect of ultrasound, the radical production of the cavitation bubble formed in the water, and the mechanical force. The diffusion of adsorbed molecules through the pore is provided faster by the mechanical force effect originating from ultrasound [21,22]. It has been demonstrated by the studies that the activated carbon surface becomes active with the ultrasound process [23]. Ultrasound technology was used in order to increase the adsorption capacity of activated carbon with surface activation, and 80% removal efficiency was achieved when activated carbon was used unmodified for Cr (VI) purification, while 88% removal efficiency was obtained with activated carbon modified by ultrasonic treatment [21].

Heavy metals, cadmium (Cd), copper (Cu), cobalt (Co), lead (Pb), mercury (Hg), iron (Fe), chrome (Cr), and nickel (Ni). Wastewaters containing cadmium and chromium metal, which are released into the aqueous environment in molten form from industries, can cause cancer in the environment and human health [22,24].

In this study, sea urchin shells found as waste in nature were used. After the foreign wastes on the sea urchin shells were cleaned with plenty of water, they were divided into small pieces in a roller crusher and sieved in a vibrating sieve system to determine the grain sizes. Powder samples with a grain size of 0.5 mm were used in the activation and carbonization processes and in all stages of adsorption. In the study, by using an ultrasonic bath with a frequency of 20 kHz, the surface area of the activated carbon was increased by the mechanical force effect and the diameter range was reduced, thereby increasing the removal and diffusion rate. The effects of adsorbent dose, adsorption time, pH, temperature, and initial dye concentration parameters were investigated by using activated carbon, $Cd^{2+,}$ and Cr (III) heavy metal ions in adsorption experiments. BET, XRD, and SEM analyzes were performed for activated carbon obtained from natural and sea urchin shells. As a result of the interaction of activated carbon adsorbent with ultrasound, adsorption was evaluated with kinetic and isotherm models.

Materials and Methods

Preparation and activation of sea urchin shells

Sea urchin shells procured from İzmir (March 2022 Sea urchin shells were obtained from Dikili district) province were washed with distilled water and cleared of foreign matter, and then crushed in a roller crusher. It was sieved in a vibrating sieve system to determine the grain sizes. 0.5 mm grain size samples were used to be activated and used in carbonization processes.

For the activation process, sea urchin shells with 0.5 mm grain size were mixed in 10%, 20%, and 30% potassium carbonate solutions in an ultrasonic bath for 6 hours and dried. According to the literature results, the samples were subjected to a carbonization process in a nitrogen gas atmosphere at 900°C and for 70 minutes in a tube furnace. The potassium carbonate + boric acid activation process was performed using these parameters (Table 1).

K_2CO_3 concentration (%)	H_3BO_3 concentration (%)	Carbonization	
		Temperature (°C)	Time (min)
30	4	900	30
	6		
	10		
30	4	900	70
	6		
	10		
30	4	900	120

Table 1: Potassium carbonate + boric acid test parameters.

After drying, the samples activated with potassium carbonate were mixed in 4%, 6%, and 10% boric acid solutions in an ultrasonic bath at 90°C for 4 hours. The dried samples were subjected to carbonization in the tube furnace (Figure 1).

Characteristic properties of activated carbon sample

Moisture determination of the activated carbon sample was determined by placing it in an oven at 105 ± 5°C and keeping it for 24 hours. The iodine number (IS) determination is a measure of the adsorption capacity of the adsorbent. The determination of the iodine number is one of the important tests used to determine the adsorption capacity of solid adsorbents, especially activated carbon samples, and gives information about the surface area of activated carbons due to its ability to adsorb small molecules and an indicator of porosity. In the study, the iodine number (IS) of the activated carbon samples obtained under different conditions was determined.

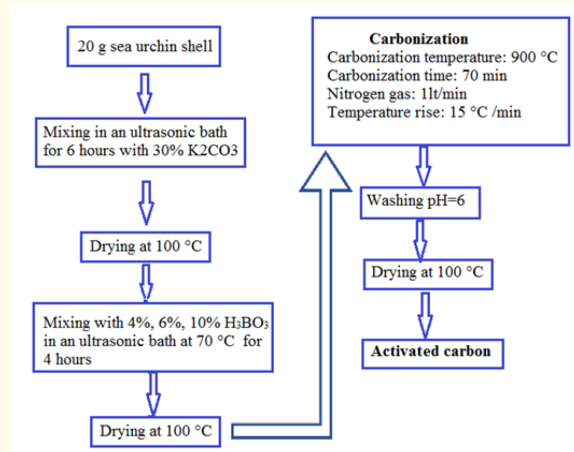

Figure 1: Flow chart of carbonization with potassium carbonate + boric acid.

The specific surface area of the activated carbon samples was determined by using the N2-BET method, the images of the pores were carried out by scanning electron microscopy (SEM), the pore size, distribution, and surface area measurements in powder or bulk samples, and the data used in the mass density determination were made with a mercury porosimetry device. Ball Pan hardness analysis was carried out according to the ASTM D3802-79 standard. In order to evaluate the adsorption capacity of activated carbons, the adsorption capacities were measured in the UV device. A 20 kHz fixed frequency ultrasonic bath device was used to increase the adsorption capacity.

Adsorption experiment

Adsorption experiments were carried out in two stages. It was used for the purification of Cd^{+2} and Cr (III) after it was modified by an ultrasonic bath process (20 kHz) and different adsorbent dose (3,6,9g), adsorption time (10-300 min), pH (2-10) Experimental studies were carried out considering the temperature (15-50°C) and initial wastewater concentration (20-100 mg/L) conditions. The pH of the solution was adjusted using 0.2 N HCl and the chemical NaOH. Modified sea urchin powder adsorbent was added to the solution prepared in 100 mL volume and a homogeneous mixture was obtained with the help of an ultrasonic bath device. After the samples were centrifuged at 4000 rpm/min for 10 minutes, they were measured at a wavelength of 525 nm using a UV-VIS spectrophotometer [25].

Adsorption isotherms

The experimental results obtained are defined by the Langmuir and Freundlich isotherms, which are important in determining the adsorption efficiency. Langmuir and Freundlich adsorption isotherms were applied to the results obtained for different wastewater concentrations (20-100 mg/L) considering optimum conditions. The adsorption capacity of Cd^{2+} and Cr (III) from wastewater, qe (mg/g), is given in equation 1. Langmuir isotherm is the adsorption in which the molecules adsorbed on the surface do not interact with each other, the adsorbent surface has the same adsorption activity, and the adsorption of the molecule is attached to the adsorbent surface occurs in a single layer [26]. Equation 2 of the Langmuir isotherm is given.

Here; qe: The amount of substance adsorbed in the unit mass of the adsorbent (mg/g); X: Mass of adsorbed substance (mg), m: Mass of adsorbent (g); C0: Initial concentration of adsorbed substance (mg/L); Ce: Concentration of the adsorbed substance remaining in solution (mg/L); V: volume of solution (L); W: Weight of the adsorbent (g); ‘qmax: Maximum adsorption capacity of the adsorbent (mg/g); b: It is used to express the Langmuir constant (L/mg).

Results and Discussion

Ash and moisture analysis in activated carbon

The low ash content of the sea urchin shell changes with at least a 1% carbonization process. In general, an increase in the ash content was observed in the activated carbon samples obtained by increasing the carbonization temperature (Table 2). This is due to the separation of volatile substances from the mass during heat treatment and the increase of non-volatile mineral matter in the remaining product [27]. The fluctuations in the values given in table 2 also coincide with the iodine number values. As the degree of heat treatment applied to the material increases, the pore value also increases, so the material is affected by the ambient humidity for a short time after the treatment. In terms of usage areas, it is desired to contain a maximum of 3% ash and a maximum of 8% moisture [28].

Iodine number and bet analysis of activated carbons

It has been stated that the iodine number values of the activated carbons according to their effects, as a result of the activation of boric acid with 6% boric acid after the activated carbon samples and 30% potassium carbonate concentrations, depending on the BET surface area [29]. The iodine number was 1053.48 mg/g and the surface area was 851.94 m2/g. It has been stated in different studies that the iodine number is parallel to the surface area [30,31]. It has been observed that the use of boric acid following potassium carbonate increases the surface area of activated carbons.

K_2O_3 Concentration (%)	Time (min)	Ash content (%)	Moisture rate (%)
10	30	1.63	4.47
	70	2.03	5.37
	120	2.72	8.86
20	30	4.93	6.59
	70	6.12	5.03
	120	9.56	5.48
30	30	1.87	4.85
	70	2.11	4.25
	120	10.29	5.42

Table 2: Ash and moisture analysis results of activated carbon samples.

SEM analysis

While no significant porosity was observed on the surfaces of the activated carbon samples prepared by the chemical activation method, the presence of pores was detected when their internal structures were examined. The images showed that the porosity was not macro-dimensional but developed significantly in the interior rather than the outer surface. The resulting structure shows the presence of meso and micropores rather than macropores. The surface of the untreated hazelnut shell has a polished, smooth, and shiny appearance, but when viewed from the cracked part, a dull, fibrous structure is observed (Figure 2). Therefore, the images of both surfaces were examined in the SEM study of the activated carbon samples [32].

XRD Result

XRD images of raw sea urchin powder and activated carbon structures with 30% K_2O_3 + 6% boric acid added are given in figure 3. First, the XRD analysis of the structure containing raw sea urchin powder is shown in figure 3. As observed in the analyses, characteristic peaks were observed at 2θ = 19.4°, 54.7°, 69.62°, 86.8°, and

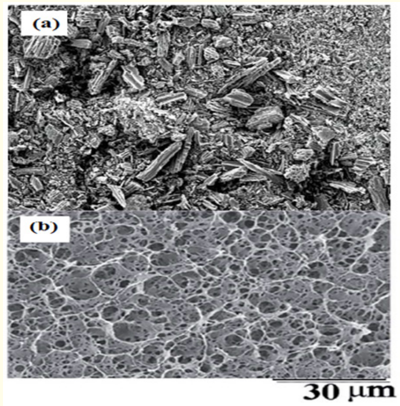

Figure 2: (a) Raw sea urchin powder; (b) SEM images of activated carbon with 30% K2O3 + 6% boric acid

104.2° angles. In addition, the characteristic peak values formed at the angles of 2 theta = 51.6°, 59.2°, 62.3°, 86.6, 104.4°, 112.5°, 113.2°, 114.8°, 115.1°, 117.3° in the structure to the activated carbon with the addition of 30% K_2O_3 + 6% boric acid. is seen. In the XRD spectrum given in figure 3, the change in peak intensities can be seen with the intensity of the peaks increasing and decreasing proportionally with the change in the amount of activated carbon with 30% K_2O_3 + 6% boric acid and raw sea urchin powder.

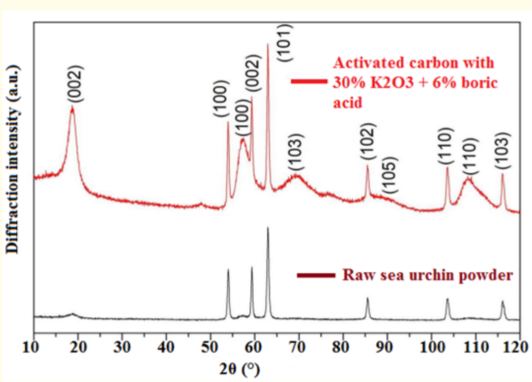

Figure 3:XRD spectrum of raw sea urchin powder and activated carbon with 30% K_2O_3 + 6% boric acid

Adsorption results

When the data obtained from the adsorption studies are examined, it is seen that the removal rate of the Cd_{2+} sample also decreased slightly due to the increase in Cr (III) ion removal. When the activated carbons produced are examined, it is seen that it is higher than the possible commercially supplied activated carbon with a higher surface area. Here, it can be said that the high surface area and boric acid have a positive effect on the removal of both heavy metals (Figure 4) [33].

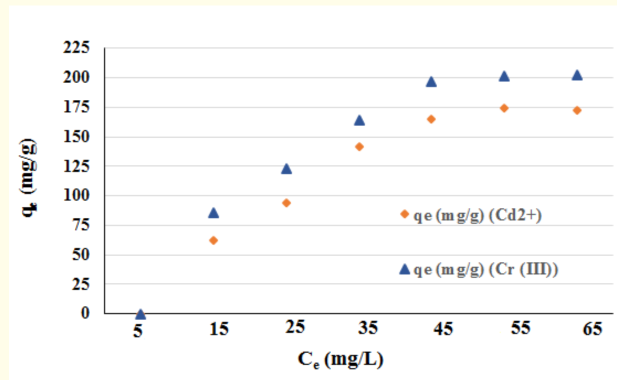

Figure 4: Adsorption capacities of activated carbon sample.

When the amount of adsorbed substance (qe) (mg/g) per unit mass of the adsorbent is taken into account, since it has a large surface area to the activated carbon with 30% K_2O_3 + 6% boric acid, the adsorbed Cd^{2+}, and Cr (III) metal increases with the increase in the dose amount. amounts are decreasing. Since the surface area of the activated carbon increases with the effect of ultrasound mechanical force and the diameter range decreases, it has been determined that the color removal is much faster and the time is halved [34-41].

Conclusion

By using natural sea urchin and activated carbon with 30% K_2O_3 + 6% boric acid addition, Cd^{2+} and Cr (III) removal was achieved by increasing the surface area with ultrasound technology without the addition of a chemical, and an improvement in adsorption capacity was achieved. As the adsorbent dose increased at acidic pH, the adsorption capacity increased. The surface area of the activated carbon adsorbent increased with the effect of ultrasonic mechanical force and the diameter range was reduced. Thus, Cd^{2+} and Cr (III) removal was obtained in a lower dose and in a short time when modified sea urchin was used. As an alternative, successful results have been obtained with the application of ultrasound applied to increase the surface activity and adsorption potential of activated carbon. It was determined that the adsorption of Cd^{2+} and Cr (III) increased with the increase in temperature and the adsorption of activated carbon obtained from sea urchins was an endothermic reaction. As a result, it was determined that the surface area was increased by the mechanical effect of ultrasound, and the heavy metal adsorption capacity was increased with surface-activated sea urchins. It is seen that the results obtained will be an important reference for scientific studies to improve the adsorbent surface efficiency with ultrasound. The adsorption-desorption cycle was carried out by repeating the ultrasound method 7 times. It has been observed to have a high level of recovery performance even after the 7th cycle. It is seen from the results that activated carbon can be studied as an environmentally friendly, inexpensive, and effective method because it is effective in removing Cd^{2+} and Cr (III) heavy metal ions in wastewater. As a result of the studies carried out; It has been determined that sea urchin shell is a potential raw material source that can be used in the production of activated carbon.

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