

RESEARCH ARTICLE



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BATCH ADSORPTION STUDIES OF ACTIVATED CARBONS IN THE REMOVAL OF CADMIUM (II) ION FROM INDUSTRIAL WASTE WATER

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ABSTRACT

The general purpose of the research was to evaluate the adsorption capacity of activated carbon on heavy metal cadmium (II) ion from Industrial waste. The adsorptive capacity of the activated carbon obtained from the sugarcane bagasse (SCBC) was studied by carrying out liquid phase adsorption tests with a stirring time of 60 min. The activated carbon was obtained through a chemical activation process of the precursor with 2N HNO₃ and a temperature of 500°C. The adsorbent characterization consisted of a physicochemical analysis (bulk density, % ash and % humidity) according to ISI & ASTM standards, as well as the determination of the specific surface area following the iodine index technique method. Commercial Activated carbon sample (CACS) was used as the reference standard. The specific surface areas for SCBC and CACS were 594.9 mg I₂ adsorbed / g carbon, and 478.22 mg I₂ adsorbed / g carbon, respectively. The total cadmium (II) ion content in the Industrial effluent was analyzed, observing that the activated carbon had higher efficiencies in the removal of this metal ion compared to CACS. Key words: cadmium (II) ion adsorption, activated carbon, isotherms, Industrial effluents.

I.INTRODUCTION

The biggest global challenge today is the supply of drinking water. Uncontaminated water is a basic requirement for all living organisms. However, even with more than 71% of the Earth's surface covered by water, less than 1% of it is drinkable, according to international standards, due to various types of contamination [1]. Industrial processes that use high water demands contribute to the contamination of water bodies, since at the end of the processes, they present high levels of organic compounds and heavy metals, which are not always removed in the effluent treatment systems [2].

Industrial activity has contributed greatly to a significant increase in the concentration of metal ions in water, representing an important source of contamination of aquatic bodies, especially when we

consider that such ions can be disseminated via the food chain.

Of the 2.9 million tons of hazardous industrial waste generated annually in India, only 850 thousand tons receive adequate treatment, as estimated by the Brazilian Association of Special Waste Treatment, Recovery and Disposal Companies. The remaining 72% is improperly deposited in landfills or discarded in waterways without any type of treatment [3].

Excessive heavy metals can cause many diseases and serious physiological problems, since they are accumulative in the human body. Residues containing cadmium, chromium, manganese and nickel have a high level of contamination power and easily reach groundwater or even reservoirs and rivers, which are the city's water supply sources. Contact with the skin can cause allergic dermatitis

and, more rarely, cause skin ulcerations forming scars, perforations of the nasal septum, cancer, affective disorders, neuromuscular irritation, headache, nausea and fainting. There are also suspicions that they may affect the immune system of human beings [4-5].

The presence of heavy metals in ecosystems is a serious problem to the environment due to the high risk associated with human health, even in very low concentrations, because, unlike some organic substances, heavy metals are not metabolically degradable, being accumulated in tissues of living beings, causing serious metabolic problems or even death. Different methods are applied for the removal of heavy metals present in wastewater such as flotation, membrane filtration, chemical precipitation and adsorption [6]. Among them, adsorption stands out for its simplicity, versatility, ease of operation and effectiveness [7]. Thus, in this study the use of agro-industrial residue based carbon for the removal of cadmium (II) ions present in aqueous solution was evaluated.

The growing international demand for activated carbons, mainly associated with its use in solving environmental problems, has led to research on the use of various agro-industrial wastes as potential precursors for its production. This type of low cost and abundant availability lignocellulosic materials, such as: fruit peel or seeds, wood sawdust, sugarcane bagasse, are subjected to different activation strategies for conversion to activated carbons [8]. The objective of this work is to evaluate the adsorption capacity of activated carbon on total cadmium (II) ion from Industrial waste, through chemical activation with Nitric acid.

Experimental part

Materials and methods

The industrial wastewater was taken from the industry located in the Industrial estate, Vijayawada municipality during 2013 to 2014. In this investigation, eight samples of Industrial wastewater were analyzed, resulting from a biological treatment through an aerobic process using activated sludge in a sequential charge reactor (SBR) fed with a mixture of the Industrial effluent from the processes of fur and dyed. Said samples were analyzed in the research laboratory of the Department of Sanitary

and Environmental Engineering (DISA), Faculty of Engineering. University of Zulia.

Adsorbents

Sugar Cane bagasse was selected as a sample, which was collected from the waste generated by extracting the sugarcane juice from a station located Bhimadolu, West Godavari District, in the state of Andhra Pradesh.

Methods

Development of activated carbon

50g of sugarcane bagasse was weighed, the precursors were brought to the stove for one hour, placed in a glass container and added a solution of Nitric acid (2N) for the sugarcane bagasse precursor and 1N (HNO₃) for the CACS. This mixture was then left to react for one hour in the desiccator. Subsequently, a smooth consistency paste was obtained, which was charred in an electrically heated muffle at a temperature of 500°C for one hour under an extraction hood.

After that time, the carbons obtained were washed with enough hot water (between 70 ° C and 80 ° C), and with an alkaline solution of 0.02N sodium hydroxide (NaOH), until adjusting their pH between (6.5 to 7.0).

Characterization of activated carbon and load tests.

The determination of some physicochemical properties, such as bulk density, ash content, moisture content and surface area were made under ASTM standards. The granular activated carbons were sieved to obtain a suitable particle distribution. For this, the powder made up of particles greater than sieve No. 70 and smaller than sieve No. 80 was taken, thus the particle diameter was between (0.212 and 0.180) mm. The prepared activated carbons received the following nomenclature: sugarcane bagasse activated carbon (SCBC), compared to a commercial carbon sample (CACS).

Adsorption process by charge test

Liquid phase adsorption studies were performed at a temperature of 25 ° C with constant agitation of 50 rpm, using a batch-type electric stirrer (Burrell Scientific). A 100 mL quantity of the Industrial waste water sample that came from a biological treatment in a reactor by sequential charge, with about 0.1 g of the activated carbon sample, was placed in a 250 mL flask.

The stirring period was 1 hour. The activated carbon was then removed from the solution by vacuum filtration, using Whatman No. 12.5 cm filter paper. The filtrates were subsequently analyzed.

The results obtained from the adsorption process were adjusted to the Freundlich equation:

$$\log q = \frac{1}{n} \log C_e + \log K_f \dots \text{Eq (1)}$$

Where q is the amount of adsorbed adsorbate (mg / g), K_f is the Freundlich constant indicating the adsorption capacity (L / g), C_e is the equilibrium concentration of the liquid phase (mg / L) and n is the constant of heterogeneity of energy sites. The Freundlich isotherm can be graphed from equation 2, where the slope of the line is equal to $1 / n$ and the intercept is the value of K_f .

In the same way they were adjusted to the Langmuir model.

$$\frac{1}{Q} = \frac{1}{bK_e C_e} + \frac{1}{b} \dots \text{Eq (2)}$$

where q is the amount of adsorbed adsorbate (mg / g), K_e is the Langmuir equilibrium constant (L / mg), b is the monolayer adsorption capacity constant (mg / g) and C_e is the concentration in the equilibrium of the liquid phase (mg / L). Langmuir's isotherm can be graphed from equation 3 where the slope of the line equals $1 / b K_e C_e$ and the intercept equals b .

Results and Discussion

Adsorbent characterization and physicochemical properties

The yield obtained for activated carbon from sugarcane bagasse was 34.4%, while for carob carbon it had a value of 27.2%. These values are lower than those reported by other researchers, who reported

37.0% for SCBC [9], under similar conditions. The particle distribution of the different types of treated activated carbons is shown in Figure 1.

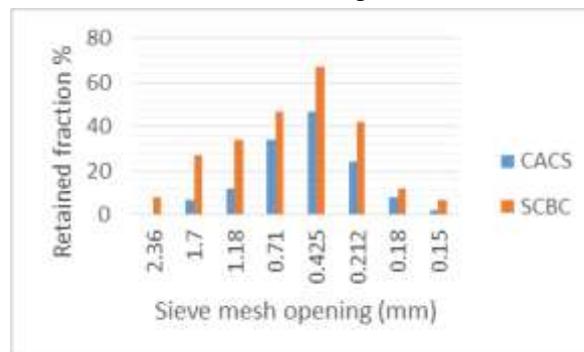


Figure 1. Particle size distribution of SCBC and CACS.

In Figure 1, the formation of a fairly symmetrical wave or bell can be observed, while for the CACS the particle diameter is between 0.71 and 0.43 mm, constituting 76.60% of the total particles. For the SCBC, the particle diameter ranged between 1.18 and 0.710 mm, forming 67.00% of particles as a whole.

The analysis of the physicochemical characteristics of the activated carbons is shown in Table 1. It is observed that the ash content for the activated carbons is high, but the SCBC has lower ash content than the CACS, the increase in ash is due to the increase in the amount of inorganic or mineral compounds, formed by the addition of the activating agent (HNO_3) and by the increase in temperature of the heat treatment [14].

Table 1: Physicochemical characteristics of activated carbons

Adsorbent	Apparent density (g / mL) Avg±SD	Ashes (%) Avg± SD	Moisture (%) Avg± SD	DPPefectivo/mm
CACS	0.63 ± 0.04	8.72 ± 0.47	10.00 ± 0.00	0.76
SCBC	0.22 ± 0.005	2.7 ± 0.005	4.40 ± 1.00	0.93

For its part, the SCBC showed a much lower humidity value than that reported for the precursor from which it comes (9.4%) [10], this is due to the activation process to which it was exposed, where the molecules generally of water are evaporated. The mechanical strength of activated carbons can be determined by the bulk density.

Iodine adsorption

The iodine adsorption was performed with the purpose of establishing the capacity of the activated carbons prepared by chemical activation to adsorb small diameter nonpolar molecules. Generally, iodine values can be directly related to the adsorptive capacity of activated carbons [11]. The adsorbed iodine values are presented in Table 2.

Table 2: Adsorptive capacity of the carbons by the iodine index technique

Adsorbent	mg I ₂ adsorption/g carbon
CACS	478.22
SCBC	594.9

The highest value of the iodine index reached in the activated carbons obtained in the carbonization at 500 ° C was with the SCBC with 594.9 mg I₂ adsorbed / g carbon.

The lowest iodine adsorption was for CACS with an amount of adsorbed I₂ of 478.22 mg I₂ adsorbed / g carbon. In Figure 2, the Cadmium ion concentration decay curve is observed.

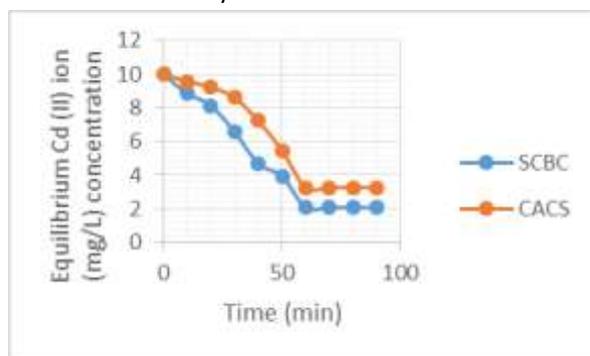


Figure 2. Cadmium ion concentration decay curve. Initial conditions: 0.1 g of activated carbon prepared at 500 ° C and commercial, 100 mL of solution at C₀ = 10 mg / L and T = 25 ° C.

In Figure 2, the decay curve of Cadmium ion concentration with respect to time is observed at a given temperature. The results obtained indicated that there is a certain affinity of the adsorbate towards the adsorption sites present on the surface of the activated carbon. It was found that at the indicated conditions, the balance of solid-liquid adsorption by the prepared activated carbon (SCBC) and commercial activated carbon occurs around 60 min approximately.

This is observed graphically as the residual amount of the metal decreases as the contact time between the metal in solution and the surface of the carbon elapses. However, according to SCBC and CACS, they saturate the metal causing the adsorption rate to decrease, reaching the Cadmium ion adsorption equilibrium, that is, until the reduced concentration becomes constant.

Table 3 shows the results of the total Cadmium ion concentrations in the Industrial wastewater, as well as the amount of adsorbate adsorbed. The amount of solute adsorbed on the activated carbons (SCBC and CACS), was calculated according to the following equation:

$$q = \left(\frac{C_o - C_e}{m} \right) \times V$$

Table 3: Concentration and adsorbed amount of Cadmium (II) ion

C _o (mg/L)	C _e CACS (mg/L)	C _e SCBC (mg/L)	q (CACS)	q (SCBC)
Avg ± SD	Avg ± SD	Avg ±SD	mg Cd/g	mg Cd/g
1.64 ± 0.01	0.71 ± 0.12	0.46 ± 0.17	0.93	1.17
2.70 ± 0.02	0.90 ± 0.01	0.68 ± 0.17	1.8	2.01
3.70 ± 0.17	1.11 ± 0.06	0.99 ± 0.01	2.58	2.7
4.05 ± 0.03	1.2 ± 0.06	1.14 ± 0.08	2.85	2.9
4.29 ± 0.01	1.33 ± 0.05	1.28 ± 0.06	2.95	3
5.01 ± 0.04	1.62 ± 0.05	1.55 ± 0.03	3.38	3.45
5.76 ± 0.01	1.82 ± 0.03	1.76 ± 0.03	3.94	3.99
6.80 ± 0.02	1.95 ± 0.15	1.89 ± 0.06	4.84	4.9

Where q is the amount of adsorbed adsorbate (mg / g), C_o is the initial concentration of the solution (mg / L), C_e is the equilibrium concentration of the liquid phase (mg / L), m is the weight of the adsorbent (g) and V is the volume of the solution.

The C_o of the metal was on an average of 4.24 ± 0.03 mg of Cadmium ion / L, with the application of

the CACS, SCBC carbon, an average C_e of 1.33 ± 0.06 mg / L was obtained ; 1.21 ± 0.07 mg / L and 1.59 ± 0.06 mg / L respectively. The value of (q) increases with the increase in the initial Cadmium ion concentration as shown in Table 3. This theoretical behavior agrees with the experimental results obtained by other researchers [3]; these authors

observed that the removal capacity (q) of the carbons increased with increasing initial Cd(II) concentration.

From the values in Table 3, (q_e) vs (C_e) was plotted to determine the Cadmium ion adsorption isotherms. In Figure 3, the total Cadmium ion adsorption isotherms by activated carbons are shown.

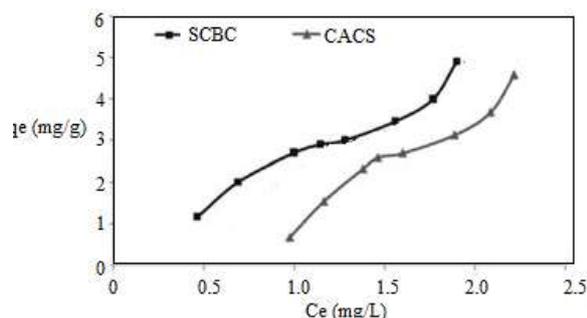


Figure 3. Cd(II) ion adsorption isotherms using 0.1 g of activated carbon, temperature of 25 ° C, 1 hour contact, stirring 50 rpm.

All the isotherms showed the type H shape, according to the Giles classification [15]. This type of isotherm (H) is considered a special case of type L isotherms and is indicative of a high affinity between solute and adsorbent. For low concentrations, the mass of solute in the solution is completely and instantly adsorbed. The initial part of the curve that describes this isotherm is initially vertical since the solute of the solution is completely adsorbed. In this case, the mass of solute adsorbed by the solid matrix is very large, a high concentration of solute is usually needed in the solution that is in contact with the porous medium in order to saturate the adsorption sites. In some cases complex formation and solute

precipitation may occur in the form of other minerals [13].

Figures 4 (a) and 4 (b) show the fit of the results obtained in the adsorption process to the Freundlich and Langmuir models. In Figure 4 (a) there is greater linearity and less dispersion of the experimental data in relation to Figure 4 (b) for all the samples. This fact can be interpreted as a greater applicability of the Freundlich model in relation to the Langmuir model, which translates into an optimal fit of the Freundlich model to the data obtained experimentally.

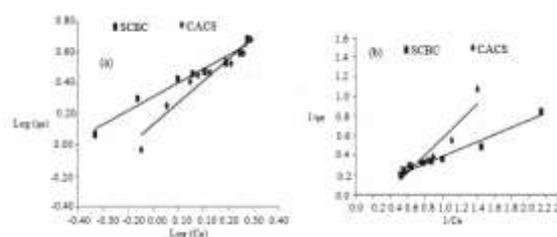


Figure 4. Correlation of adsorption isotherm data for Cd(II) ion (A) Freundlich adjustment. (B) Langmuir adjustment.

The Freundlich isotherms allow us to estimate that the equilibrium capacity could increase proportionally with the increase in the concentration in the liquid phase [13].

Values such as slope and intercept of the equation of the lines obtained from the linear fits of the Cadmium ion adsorption isotherms and that are related to the mathematical models of Freundlich and Langmuir are shown in Table 4, separately for each type of adsorbent.

Table 4: Freundlich and Langmuir isotherm constants from Cd(II) ion experimental data

Adsorbent	Freundlich			Langmuir		
	$K_f, L/g$	n	r	$K, L/mg$	$b, mg/g$	r
SCBC	2.53	1.11	0.98	0.06	40	0.98
CACS	1.88	0.7	0.96	0.33	3.47	0.94

The results obtained for the Langmuir adjustment show, according to the values of (K) and (b), that the degree of Cadmium ion adsorption on the carbons is not very high, which implies that the number of moles of solute to form a monolayer on the surface of the adsorbent it is low. On the other hand, according to the Freundlich model, the K_f

values show that the Cadmium ion adsorption capacity is relatively low, however the adsorption on the SCBC was above that reported for commercial activated carbon (CACS).

The values of correlation coefficients r obtained for the Freundlich adjustment showed a more linear trend than those obtained for the

Langmuir adjustment, as a consequence this model correlates satisfactorily with the isotherm data obtained experimentally. For its part, the value of n for the SCBC was greater than unity, this shows a favorable multilayer adsorption for the metal under study and indicates the affinity of the adsorbate with activated carbon [15].

Conclusions

Applying the mean comparison test, the activated carbons had statistically different physico-chemical characteristics, obtaining higher moisture and ash% than the CACS, followed by the SCBC respectively. The highest iodine index reached was obtained on SCBC with 594.9 mg I₂ adsorbed / g carbon, followed by CACS with 478.22 mg I₂ adsorbed / g carbon respectively.

The treatment system proved to be effective for the removal of total Cadmium ion present in the waste water under study, having removals of 71.44% with SCBC, followed by CACS with an average removal of 67.45%.

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