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Activated Carbon Nanoparticles as Adsorbent to Remove the Cadmium Ion from Aqueous Solution: Thermodynamic Study

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ABSTRACT

Human activities such as fossil fuel burning, car exhaust, mining, agriculture, and the incineration of solid and liquid wastes all contribute to water pollution by heavy metals, therefore this water poisoning poses a threat to living beings. To minimize the pollution of the natural waters, As the adsorption process of metal in solutions, it is critical to identify effective strategies for getting rid of these toxins. This study involves the characterization and synthesis of novel activated carbon nanoparticles (AC) from natural sources (barley) and is applied in an adsorption study to remove cadmium metal. (AC) characterization using XRD, SEM and it was nanoscale in size and particle-like in shape also BET for specific surface area nitrogen adsorption isotherm nitrogen (718.01) and Average pore diameter as (16.851(Å)), from the adsorption experimental data, the results are best described by the Freundlich isotherm model, which has an adsorption removal 76.86% with exothermic process.

KEYWORDS: Activated carbon nanoparticles, barley, cadmium pollution, bio-adsorbents.

الخلاصة

تساهم الانشطة البشرية مثل حرق الوقود الاحفوري وعوادم السيارات والتعدين والزراعة وحرق النفايات الصلبة والسائلة في تلوث المياه بالمعادن الثقيلة وبالتالي التسمم المائي هذا تهديد للكائنات الحية. لتقليل ثلوث المياه الطبيعية كعملية امتصاص المعادن في المحاليل ,من الاهمية بمكان تحديد استراتيجيات فعالة للتخلص من هذه السموم ,تتضمن هذه الدراسة توصيف وتوليف جزيئات الكاربون النانوية الجديدة المنشطة من مصدر طبيعي الشعير وتطبيقها في دراسة الامتزاز لإزالة معدن الكادميوم وتم تشخيص المادة النانوية باستخدام XRAY-SEM وكان مقياس النانو في الحجم وشكل الجسيمات ايضا BET لمساحة حجم معين باستخدام غاز النتروجين ,امتزاز غاز النتروجين ٧١٨م٢/غم ومتوسط قطر المسام ١٦,٨٥١ .من البيانات التجريبية للامتصاص افضل وصف للنتائج هو نموذج فرندلش والذي يحتوي على اعلى نسبة ازالة ٧٦,٨٦٪ وهي عملية باعثة للحرارة وتلقائية.

INTRODUCTION

It is a problem that affects the environment on a global scale that toxic heavy metals, which can be found in wastewater from industries such as mining and agriculture, contaminate water. Metals are non-biodegradable and have the potential to accumulate in biological tissues, which can lead to a concentration of metals throughout the food chain [2]. This sets them apart from other harmful contaminants that are also present. Cadmium, abbreviated as Cd, is a toxic element that has a negative influence on the surrounding environment [3]. Excessive Cd intake in humans causes kidney and renal system damage, skeletal deformation (Itai-itai), cardiovascular illness[4] and high blood pressure. Anemia, tooth discoloration, loss of smell, severe gastrointestinal discomfort, muscle pain, and possibly necrotic changes in the liver and kidney are all examples of severe side effects. [5] Cadmium is also a carcinogen [6]. The process of treating water contaminated with cadmium is analogous to the process of treating effluents contaminated with a variety of other metals. To reduce the amount of heavy metal ions, present in effluents, the most common methods include chemical treatment, coagulation, lime precipitation, solvent extraction, electrolytic procedures, membrane separation, ion-exchange, and adsorption. This technique for removing trace metals from wastewater and water supplies has demonstrated its efficacy in recent years, and it has also shown to be cost-effective. Activated Carbon Adsorption on Barley Hull and Ash were discovered to be efficient adsorbents for removing cadmium from an aqueous solution [7]. Due to its low cost, efficiency, simplicity of operation conditions, variety of adsorbents and inertness to materials, adsorption technology has been highlighted as a superior alternative treatment approach compared to other treatment procedures [8, 9]. Due to its porous structure, the high surface area, availability of functional groups and high adsorption capacity, activated carbon is one of the most researched adsorbents by researchers [10]. Due to the high cost of producing activated carbon for commercial use, underutilized natural resources and agricultural waste have been identified as potentially useful feedstock substitutes for the production of activated carbon at a price that is more affordable [11]. the aim of this study included removal of cadmium polluted by activation carbon nanoparticles

MATERIALS AND METHODS

Without additional purification, all compounds were analytical grade reagents purchased from Sigma-Aldrich.

Synthesis activated carbon nanoparticles (AC)

The (barley) was bought at a local market, rinsed completely with distilled water, dried for 6 hours in sun, then oven dried at 105 °C to remove residual moisture content. The seed was carbonized in a muffle furnace (Vecstar Ltd England), which allows for a limited flow of air. Carbonization took 30 minutes at 350 °C. The carbonized material was then collected and allowed to cool at room temperature in a desiccator. The carbonized was chemically activated according to the procedure [12] then product placed in a 500 cm^3 beaker containing 0.3 M (HCl). The contents of the beaker were well mixed before being heated on a magnetic stirrerwith until a paste forms. The paste was placed in an evaporating dish and put in a furnace at at 500 ˚C for 30 minutes. This black powder left to cool down temperature overnight.It was then neutralized with KOH and rinsed numerous times with deionized water until the pH was stable at 6 then dried in the oven at 105 ˚C.

Preparation of Standard Solutions

In a 500 mL standard flask, 0.925 g of analytical grade Cd $(NO_3)_2.4H_2O$ was dissolved in distilled water to make a stock solution containing 500 mg/L of the metal. Distilled water was used to create this lasting impression. For future usage, this stock was utilized to prepare standard solutions of varying concentrations.

RESULTS AND DISCUSSION

X-ray diffraction studies

Activated carbon XRD patterns are presented in Figure 1 between 17 and 25˚, a wide peak appears, In the absence of any other x-ray traceable substances, the absence of additional peaks confirms this further proof that the acid has been eliminated from our sample [13, 14].

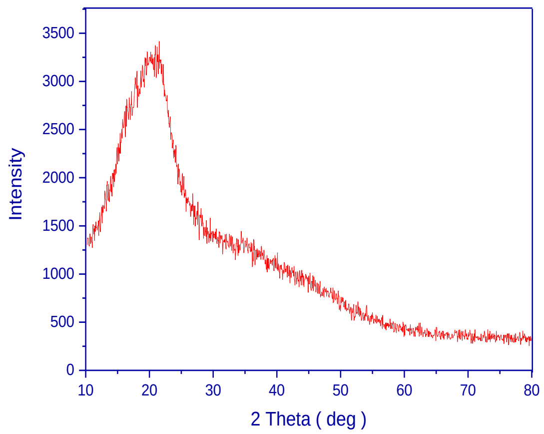

Figure 1. XRD pattern of activated carbon.

SEM of nanoparticles

SEM microscopic images of activated carbon revealed two types of surfaces: smooth surfaces with long straight edges, and others in the form of clumps of particles that represent the most part of the surface. It was found that the Nano scale limits of this material were in the 50 nm range as can see in Figure 2.

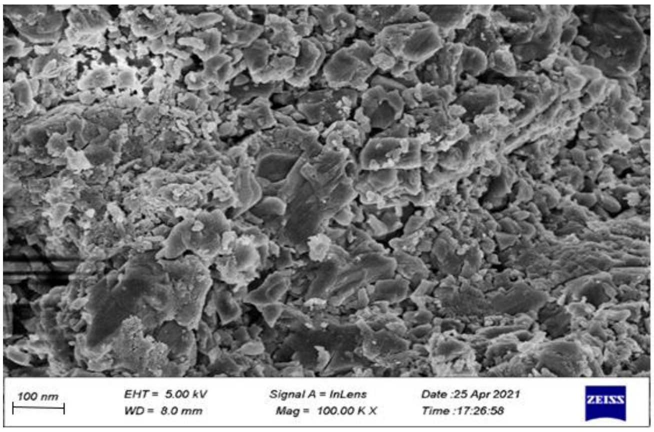

Figure 2. SEM image of activated carbon Nanoparticles.

Adsorption study

The effects of pore shape, pH, time and amount of deorbited on cadmium adsorption on (activated carbon nanoparticles) were examined in this work**.**

N_2 adsorption–desorption isotherms

In order to measure surface area, the AUTOSORB-1 (Quanta Chrome Instruments, Talban Lab) automatic gas adsorption analyzer is employed using adsorption-desorption isotherms at 77 °C. A 0.0601-gram sample was utilized for each assay. According to the Bruner, Emmett, and Teller (BET) method [15], the specific surface area of (AC) was computed. The Dubinin-Radushkevich (DR) equation[16] was used to calculate the microspore volume. The nitrogen pore volume was obtained from the maximum relative pressure (P/P_o=0.99) [17]. Nitrogen isotherms of activated carbon nanoparticles (AC) are illustrated in Figure 3 shows that the isotherms for adsorption and desorption have characteristics similar to those of type (III) isotherms in accordance with (IUPAC) classification. Upon reaching saturation pressure, the adsorption isotherm meets with the line P/P_o=1 and the platform appears horizontal or almost so. Adsorption rate was higher at low relative pressures (P/P_o=0.54), and adsorptive capacity grew rapidly with increasing relative pressures, reaching a saturation level of more than 80% at $P/P_o \leq 0.65$.

Table 1 summarizes the BET surface area, total pore volume, pore volumes and average pore diameter of activated carbon.

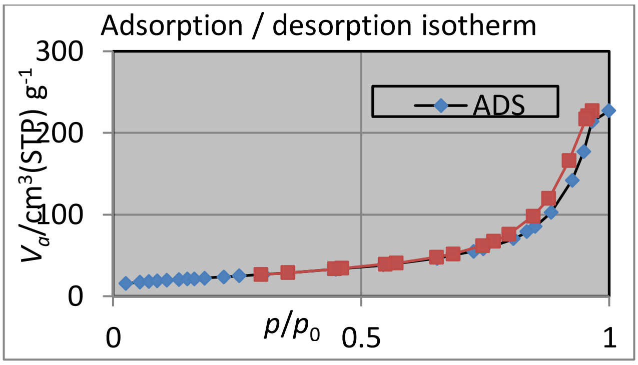

Figure 3. Adsorption–desorption isotherm.

Table 1. summary of the BET associated parameters plot.

Sample	BET surface area (m^2/g)	Total pore Volume (cm^3/g)	Microspore volume (cm^3/g)	Average pore diameter (Å)
Activated carbon	718.011	0.3455	0.305	16.851

Effect of PH

The pH of a solution affects the adoption of heavy metal ions by adsorbents Figure 4. The pH range for this investigation was 2-10. With increasing pH, cadmium-adsorption on barley ash increases, reaching its maximum value when the pH of the solution is 9. On the other hand, the adsorption of the metal on the adsorbent depends on the adsorbent surface and species distribution of the metal. At acid pH=2 activated carbon sorption was about 24.2 percent at 60 min When the pH was elevated by two units, the absorption increased to around 91.2 percent. There could be two probable explanations for the remarkable increase in adsorption efficiency. To begin with, at low pH, protons and metal ions compete for adsorption sites on the adsorbent surface. Examining the end pH of solutions with low beginning pH values is one technique to validate this. For each hydrolysable metal ion, there was also a critical pH range (usually 2 units wide) where metal absorption efficiency went from very low level to a maximum value3.The adsorption edge is the term used to describe this pH value. As a result of the production of soluble hydroxyl complexes, a decrease in absorption was seen above pH=9 [18].

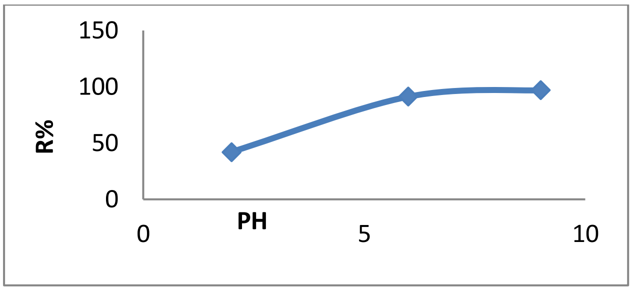

Figure 4. Effect of pH on the removal of cadmium by activated carbon nanoparticles (adsorbent dosage = 5 g L^{-1}, cadmium concentration = 30 mg L^{-1}).

Effect the concentration with equilibrium capacity

Figure 5 demonstrated that the amount of cadmium adsorb increases with increasing starting concentration, implying that cadmium removal is dependent on metal concentration. Cadmium may easily identify accessible adsorption sites at low concentrations since the active adsorption sites are very high, but at higher concentrations, the available adsorption sites decrease with time.

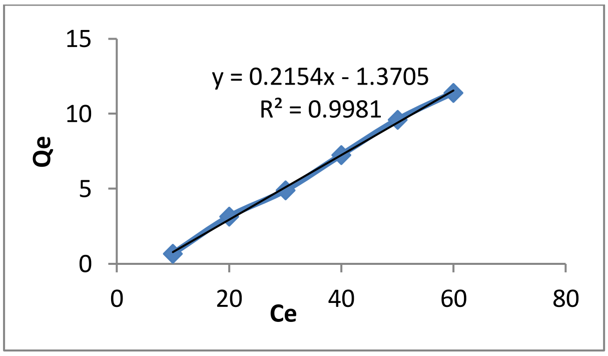

Figure 5. Effect of initial different concentration on removal of cadmium at equilibrium.

Time effect on the adsorption process

For activated carbon, cadmium absorption increased with contact time and became virtually constant after 120 minutes as seen in Figure 6. The fact that the most cadmium is connected to the adsorbent during the first one hour of adsorption suggests that the sorption process is very rapid.

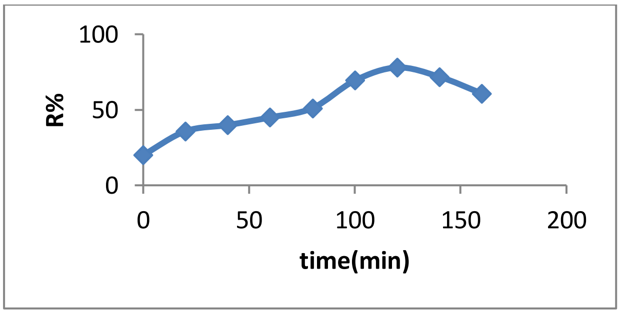

Figure 6. Effect of contact time on the removal of cadmium by activated carbon nanoparticles.

Adsorption isothermal

Experimental isotherms are important for defining adsorption capacity, which aids in determining the feasibility of this procedure for a given application, selecting the most suited adsorbent, and estimating adsorbent dosage requirements. Furthermore, in the analysis and design of sorption systems, the isotherm plays a significant role in predictive modeling. As shown in Figure 7, the Langmuir and Freundlich isotherms are the most widely employed to describe sorption data from solution Figure 7, Langmuir and Freundlich equations were used to calculate cadmium adsorption onto barley ash. Then, as reported in, isotherm studies were performed.

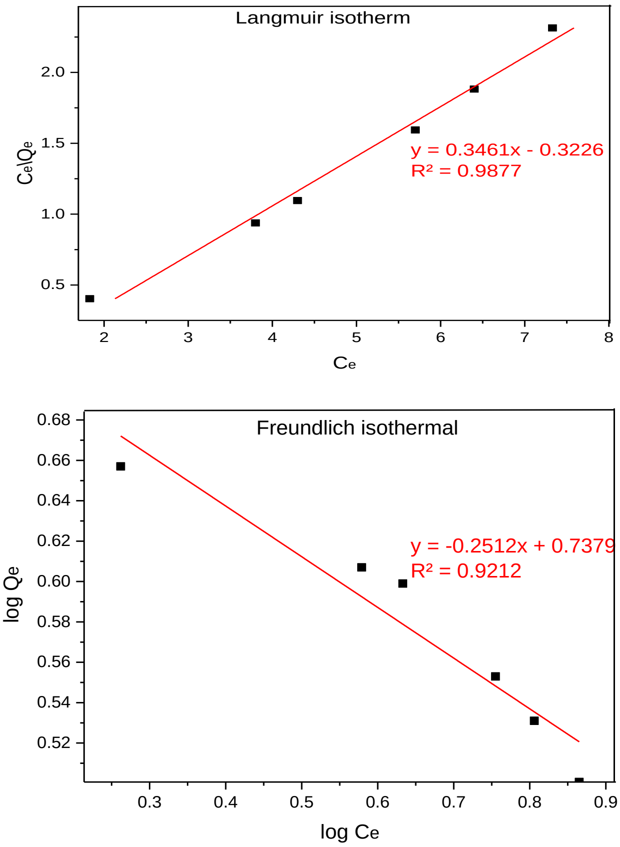

Figure 7. Langmuir and Freundlich models.

Table 2. summarizes the associated parameters of the Langmuir and Frendlich models.

Langmuir		
equation	$\frac{C_e}{Q_e} = \frac{1}{a} + \frac{b}{a} C_e$	
Parameters		
a $(\frac{mg}{g})$	**b** $(\frac{L}{mg})$	$\mathbf{R^2}$
3.0998	1.0768	0.9877
Freundlich		
equation	$\log (Q_e) = \log(k_f) + \left(\frac{1}{n}\right) log\ (C_e)$	
Parameters		
K $(\frac{L}{g})$	**N**	$\mathbf{R^2}$
5.1	-3.89	0.9212

$Q_e =$ quantity of adsorption $\frac{mq}{g}$,

$C_e =$ solution's equilibrium concentration $\frac{mg}{L}$,

a, b, K and $n =$ constant.

Thermodynamic Study

Several thermodynamic parameters were calculated to assess adsorption capability and spontaneity. Various parameters for adsorption were estimated using the van't Hoff equations seen at Equation 1 [19] as shown in Figure 8, including free energy change, enthalpy changes, and so on. The values of ΔG, ΔH and ΔS are shown in Table 3. Since ΔG was negative, the adsorption process was spontaneous and practicable; the positive value of ΔH (J/mol) indicated that the adsorption was endothermic; and the increasing randomness and disorder of the adsorbent surface after adsorption was indicated by a positive value of ΔS seen at Equation 2.

$$\log x_m = \frac{-\Delta H}{2.303R} + \frac{\Delta S}{R} \quad (1)$$

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Table 3. Summarizes the thermodynamic parameters.

1/t	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/mol)
0.0033	-2279.3	12396.3	49.247
0.0032	-2771.8		
0.0031	-3264.2		
0.0030	-3756.7		

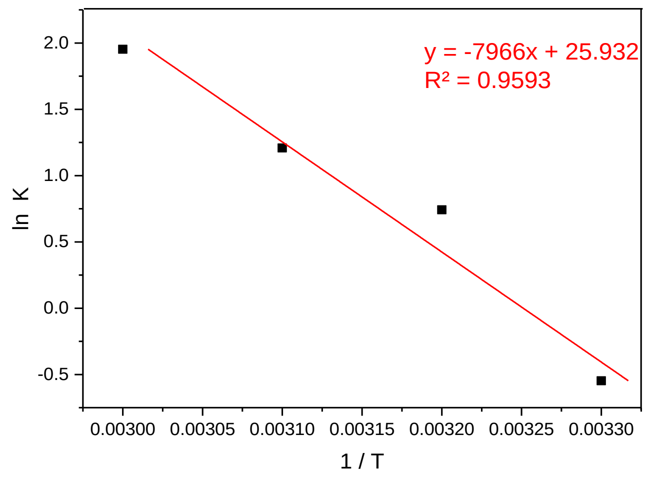

Figure 8. The relation between $\ln k$ and $^1/_T$ for the adsorption of cadmium.

CONCLUSIONS

This study used a low-cost bio adsorbent made from seed and activated with KOH to successfully remove cadmium. During the nano experiments, a high removal viz. was observed. At 55 °C and pH=9, it was feasible to get 76.86 percent. The Freundlich model is a decent fit for the data, but due to the value of ΔH = 12396.3 (J/mol), the Freundlich model behaved better than the Langmuir isotherm based on the values of the regression coefficients. The process' equilibrium was modeled using Langmuir's model, and Frendlich constants were calculated. Thermodynamic experiments on cadmium removal by nanotechnology were undertaken in order to calculate the thermodynamic parameters ΔG, ΔH and ΔS.

Disclosure and Conflict of Interest: The authors declare that they have no conflicts of interest.

REFERENCES

[1] N. Sharma, K. K. Sodhi, and M. Kumar, "Heavy metal pollution: Insights into chromium eco-toxicity and recent advancement in its remediation," Environ. Nanotechnology, Monit. Manag., vol. 15, p. 100388, 2021. https://doi.org/10.1016/j.enmm.2020.100388

[2] M. L. Sall, A. K. D. Diaw, and D. Gningue-Sall, "Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review," Environ. Sci. Pollut. Res., vol. 27, no. 24, pp. 29927-29942, 2020. https://doi.org/10.1007/s11356-020-09354-3

[3] S. Saini and G. Dhania, Cadmium as an Environmental Pollutant: Ecotoxicological Effects, Health Hazards,

and Bioremediation Approaches for Its Detoxification from Contaminated Sites. 2020. https://doi.org/10.1007/978-981-13-3426-9_15

[4] Y. C. Sharma, "Thermodynamics of removal of cadmium by adsorption on an indigenous clay," Chem. Eng. J., vol. 145, no. 1, pp. 64-68, 2008. https://doi.org/10.1016/j.cej.2008.03.006

[5] G. Genchi, M. S. Sinicropi, and G. Lauria, "The effects of cadmium toxicity," Int. J. Environ. Res. Public Health, vol. 17, no. 11, pp. 1-24, 2020. https://doi.org/10.3390/ijerph17113782

[6] A. Maleki, A. H. Mahvi, and M. A. Zazouli, "Aqueous cadmium removal by adsorption on barley hull and barley hull ash," Asian J. Chem., vol. 23, no. 3, pp. 1373-1376, 2011.

[7] A. Maleki, R. Rezaee, and R. Ebrahimi, "Fluoride adsorption from aqueous systems using barley husk and barley husk ash," in Proceedings of the 30th Conference of the. International Society for Fluoride Research, which will be held, 2012, pp. 5-8.

[8] N. A. A. Aboud, B. E. Jasim, and A. M. Rheima, "Methylene orange dye removal in aqueous solution using synthesized cdo-mno2 nanocomposite: Kinetic and thermodynamic studies," Chalcogenide Lett., vol. 18, no. 5, pp. 237-243, 2021. https://doi.org/10.15251/CL.2021.185.237

[9] N. A. A. Aboud, B. E. Jasim, and A. M. Rheima, "Adsorption study of phosphate ions pollution in aqueous solutions using microwave synthesized magnesium oxide nanoparticles," vol. 16, no. 3, pp. 801-807, 2021. https://doi.org/10.15251/DJNB.2021.163.801

[10] M. A. Hadj Ammar, B. Benhaoua, and K. Salhi, "Performance Study and Advantages of a Novel Activated Carbon Adsorption Cycle Run by Sunlight," Arab. J. Sci. Eng., vol. 46, no. 6, pp. 5933-5944, 2021. https://doi.org/10.1007/s13369-020-05090-5

[11] T. C. Egbosiuba, A. S. Abdulkareem, and A. S. Kovo, "Ultrasonic enhanced adsorption of methylene blue onto the optimized surface area of activated carbon: Adsorption isotherm, kinetics and thermodynamics," Chem. Eng. Res. Des., vol. 153, pp. 315-336, 2020. https://doi.org/10.1016/j.cherd.2019.10.016

[12] P. M. Sanka, M. J. Rwiza, and K. M. Mtei, "Removal of Selected Heavy Metal Ions from Industrial Wastewater Using Rice and Corn Husk Biochar," Water. Air. Soil Pollut., vol. 231, no. 5, 2020. https://doi.org/10.1007/s11270-020-04624-9

[13] P. Kalyani and A. Anitha, "Refuse derived energy - tea derived boric acid activated carbon as an electrode material for electrochemical capacitors," Port. Electrochim. Acta, vol. 31, no. 3, pp. 165-174, 2013. https://doi.org/10.4152/pea.201303165

[14] Q. Jiang, M. Z. Qu, and G. M. Zhou, "A study of activated carbon nanotubes as electrochemical super capacitors electrode materials," Mater. Lett., vol. 57, no. 4, pp. 988-991, 2002. https://doi.org/10.1016/S0167-577X(02)00911-4

[15] D. Propolsky, E. Romanovskaia, W. Kwapinski, and V. Romanovski, "Modified activated carbon for deironing of underground water," Environ. Res., vol. 182, p. 108996, 2020. https://doi.org/10.1016/j.envres.2019.108996

[16] M. Kwiatkowski, J. Serafin, A. M. Booth, and B. Michalkiewicz, "Computer analysis of the effect of activation temperature on the microporous structure development of activated carbon derived from common polypody," Materials (Basel)., vol. 14, no. 11, 2021. https://doi.org/10.3390/ma14112951

[17] D. Ngakan, K. Putra, T. Gde, T. Nindhia, and I. W. Surata, "ScienceDirect Textural characteristics of activated carbons derived from tabah bamboo manufactured by using H 3 PO 4 chemical activation," Mater. Today Proc., vol. 22, pp. 148-155, 2020. https://doi.org/10.1016/j.matpr.2019.08.030

[18] M. Hasanzadeh, A. Simchi, and H. Shahriyari Far, "Nanoporous composites of activated carbon-metal organic frameworks for organic dye adsorption: Synthesis, adsorption mechanism and kinetics studies," J. Ind. Eng. Chem., vol. 81, pp. 405-414, 2020. https://doi.org/10.1016/j.jiec.2019.09.031

[19] E. C. Lima, A. A. Gomes, and H. N. Tran, "Comparison of the nonlinear and linear forms of the van't Hoff equation for calculation of adsorption thermodynamic parameters (ΔS° and ΔH°)," J. Mol. Liq., vol. 311, p. 113315, 2020. https://doi.org/10.1016/j.molliq.2020.113315

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