

Adsorptive Properties of a Desert Salsola Vermiculate Species from Synthetic Aqueous Solutions

Benaouda Bestani¹, Baghdad Benstaali^{2*}, Nouredine Benderdouche¹, Mustapha Belhakem¹

¹Faculté des Sciences et Sciences de l'Ingénieur, Université de Mostaganem, B.P.188, 27000 Mostaganem, Algeria.

²University of Bahrain, Faculty of Engineering, Department of chemical engineering, P.O. Box 32038, Kingdom of Bahrain.

*Corresponding author: bbenstaali@eng.uob.bh

خواص الإمتزاز لسالسولا الصحراوية من محلول مائي محضر

بن عودة بستاني , بغداد بستاني, نورالدين بندردوشي, مصطفى بلحاكم
جامعة مستاجانم, كلية العلوم, ص. ب. 188, مستاجانم 27000, الجزائر
جامعة البحرين, كلية الهندسة, قسم الهندسة الكيميائية, ص. ب. 32038, مملكة البحرين

يعد التلوث من المشاكل البيئية الرئيسية والتوجه الحديث لإزالة السموم من السوائل هو عن طريق استغلال الكتلة الحية المتوفرة. أوضحت النتائج الأولية لدراسة الإمتزاز [التجمع السطحي] أن لنبات السويد الصحراوي فائدة مقدرة في نزع التلوث من المياه الراجعة مقارنة بالممتدة الحيوية الأخرى. وقد عولج نبات السويد بالبخار و تنشيط حامض الفسفوريك للحصول على الكربون الم وقد اتبعت أنماط لا نجمير في تجارب الإمتزاز لحمض الخليك و أيونات النيكل واتضح من الدراسة أن لل هيدروجيني تأثير في عملية الإمتزاز فقد كان معدل الإمتزاز أيونات النحاس والنيكل عند رقم هيدروجين يتراوح بين (3,4-3,9) فضلاً عن ذلك أظهرت تجارب تحديد حرارة الإمتزاز بثوابت لانجمير أن لحمض الخليك إمتزاز فيزيائي.

Key words: Pollution, Adsorptive properties, Activation, Desert plant

ABSTRACT

Pollution is becoming a major environmental problem and the current trend is to use available biomass to remove toxic substances from aqueous solutions. The preliminary adsorption results on a natural Salsola Vermiculata desert plant showed that it is compared well with other biosorbents and might be proved to be useful for wastewater decontamination. Steam and phosphoric acid activations were applied to this plant in order to obtain activated carbon. The batch adsorption experiments followed Langmuir models for acetic acid and nickel ions adsorption. pH influence on the adsorption process showed that copper and nickel ions were best adsorbed in the pH range between 5 and 6 whereas for acetic acid this was achieved in the 3.4-3.9 range. The heat of adsorption determination from Langmuir constants for the acetic acid showed physical adsorption.

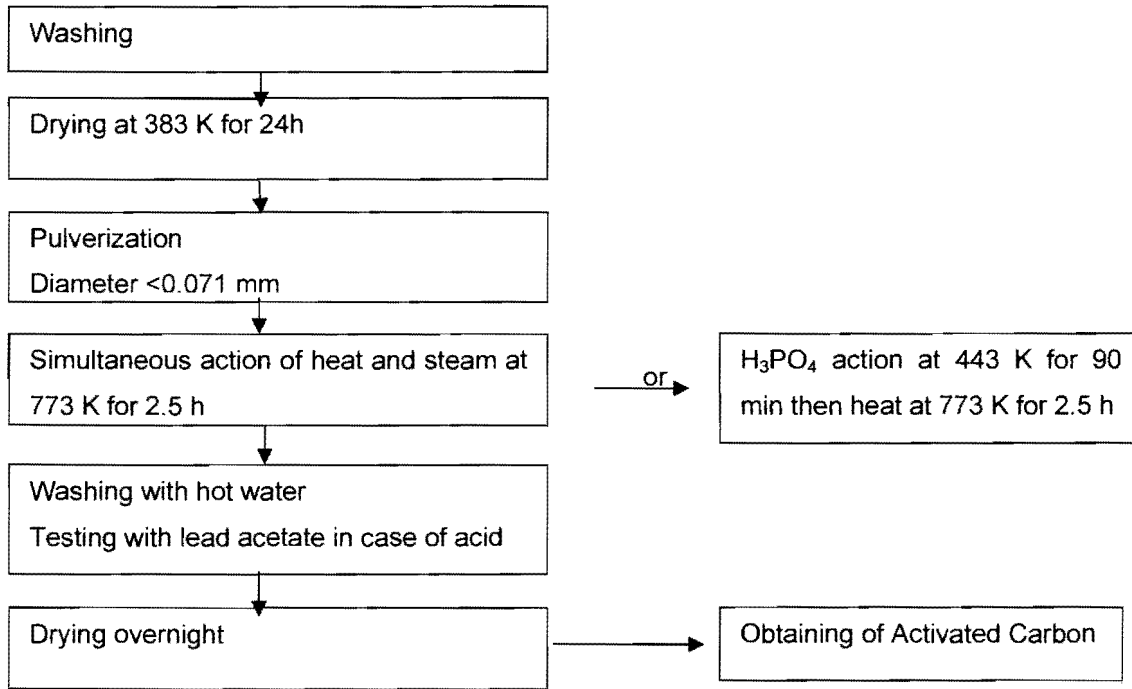
1 Introduction

Conventional methods for water purification although well developed proved to be less efficient and more costly with newly imposed environmental regulation rules. The need to use other adsorbents as alternatives to the standard activated carbons is due to the rising production cost of the latter [1]. Many organic substances, such as tealeaves, tree barks, ground coffee and others have been studied for this purpose [2-8]. Copper and nickel are toxic heavy metals that promote oxidation and cancer [9- 10]. Acetic acid a well-known organic substance is extensively used in the study of activated carbons. Adsorption capacities obtained with activated carbons attained values of 112 mg g^{-1} for AKOM carbons with specific surface area of $117 \text{ m}^2 \text{ g}^{-1}$ [11] and up to 480 mg g^{-1} for ZM-1 and ZM-2 Vinylon activated carbons (China) with specific surface area of $1300 \text{ m}^2 \text{ g}^{-1}$. Copper (II) ion adsorption capacities onto adsorbents such as chitosan attained values of 288 mg g^{-1} [12]. Nickel (II) ion adsorption has also been studied on various adsorbents but their adsorption capacities towards this element were generally low [13]. Attention was focused in this study on the adsorption properties of a natural Salsola Vermiculata desert plant species found in southwest Algeria.

2 Material and Methods

The leaves of the Saharan plant were subjected to the following methods of activation in order to increase their surface area and enhance their adsorption potential. Scheme 1 shows the activation processes that were carried out on the plant leaves. The physical activation used in this study was a one-step process in the absence of oxygen in which the simultaneous action of steam and heat at 773 K for 2.5 hours serves to remove volatile matter and enlarge the total surface area and porosity. On the other hand, the applied chemical activation which is used here involved a two step-process: impregnating the leaves with diluted phosphoric acid at 443 K for 90 minutes, and then heating the plant at 773 K for 2.5 hours. Phosphoric acid acts as a dehydrating and stabilising agent of the porous structure and has the advantage of being easy to extraction. Solutions of the relevant substances of cupric sulphate, nickel (II) sulphate, sodium thiosulphate, potassium iodide and iodine (Merck, Germany) of known concentrations were prepared according to standard procedure. Sodium thiosulphate titrations by using a 1% starch end-point indicator were performed for the estimation of copper (II) ion solutions [13]. Acetic acid was titrated by sodium hydroxide with phenolphthalein as an indicator. Nickel (II) ion solutions were prepared by adding 3 ml of 0.5 M HCl solution, 2 ml of 2.5% dimethylglyoxime in 0.1 M NaOH solution, 1 ml of 10 M NaOH solution, and 0.3 ml of 10% ammonium persulphate solution to the nickel analyte. Visible spectrophotometric measurements were performed on the nickel (II) ion solutions at 480 nm using a UV-VIS 120-01 Shimadzu spectrophotometer. All measurements were repeated twice.

The adsorption of acetic acid, copper (II) and nickel (II) ions was studied using a batch wise process at a fixed temperature of 298 K. The starting solutions of the relevant substances were titrated beforehand with the corresponding analytical reagents. For the sorption studies, 25 ml volume of the relevant sample solution was mixed with 0.1g of the powdered plant or wood carbon. The resulting suspension was then agitated magnetically for 90 min at a constant speed of 250 rpm. After the adsorption process had occurred, the solutions were centrifuged at 4000 rpm and the supernatants were analysed.



Scheme 1. Activation processes carried out on the Salsola Vermiculata plant leaves

3 Result and discussion

Table 1 shows the preliminary results for the adsorption of acetic acid, nickel and copper ions obtained with the natural desert plant in comparison with various biosorbents

found in recent literature. The maximum adsorption capacities corresponding to complete monolayer coverage were obtained either from:

- Langmuir isotherms represented by $\frac{x}{m} = \frac{KbC_{eq}}{1 + KC_{eq}}$ through the computation of the

constant b where x/m (mg g^{-1}) is the mass of substance adsorbed (adsorbate) per unit mass of adsorbent, C_{eq} (mg l^{-1}) is the concentration of adsorbate in solution at equilibrium, K (l mg^{-1}) is the Langmuir constant [15]. The determination of b allows the active specific surface area of the adsorbent to be calculated, provided a surface site covered per molecule is known. The

Langmuir constant K can be expressed by $K = K_{\infty} \exp\left(\frac{Q}{RT}\right)$ where Q is the heat of adsorption,

K_{∞} the Langmuir constant at infinite temperature, R the universal gas constant and T the absolute temperature [16].

- or the maximum value of amount adsorbed from Freundlich empirical isotherms represented by $\frac{x}{m} = K_f C_{eq}^{\frac{1}{n}}$ where K_f and n are constants related to adsorption capacity and intensity [17].

It can be observed from Table 1 that the adsorption potential of the inactivated Salsola Vermiculata plant was interesting since it compared rather well with the majority of adsorbents cited.

Table 1: Adsorption capacity of various adsorbents in comparison with the Saharan plant.

Adsorbent	Adsorbate	Maximum adsorption capacity (mg g ⁻¹)	Reference
Palm oil fibres	Copper ions	2.0	[18]
Aspergibes orysae	Copper ions	6.9	[19]
Sago waste	Copper ions	12.4	[6]
Sphagnum peat	Copper ions	16.4	[20]
Anaerobic sludge	Copper ions	49.0	[21]
Natural Salsola Vermiculata plant (leaves)	Copper ions	65.0	This study
Chitosan	Copper ions	288.0	[12]
Akom carbons	Acetic acid	112.7	[11]
Natural Salsola Vermiculata plant (leaves)	Acetic acid	53.5	This study
Cherry stones	Nickel	122	[13]
Activated carbon (apricot stones)	Nickel	92	[13]
Activated carbons (grape seeds)	Nickel	41	[13]
Creosote (leaves)	Nickel	5.9	[22]
Natural Salsola Vermiculata plant (leaves)	Nickel	18	This study

3. a. Effect of pH on the adsorption of acetic acid, copper and nickel ions

Figure 1 depicts the results obtained for the adsorption of acetic acid, copper and nickel ions onto steam-activated plant as a function of initial pH of solution.

The pH values for maximum adsorption for acetic acid ranged from 3.94 to 3.41. It can be seen that high values for the adsorbed concentration were obtained with this activation process. Similarly, Figure 2 shows the adsorption results obtained with the chemical activation system. Although somewhat lower, the adsorption results were similarly high in comparison with those for the inactivated plant.

It should be noted that both steam and chemical activation processes improved significantly the adsorption capacity for acetic acid up to 476 mg g⁻¹.

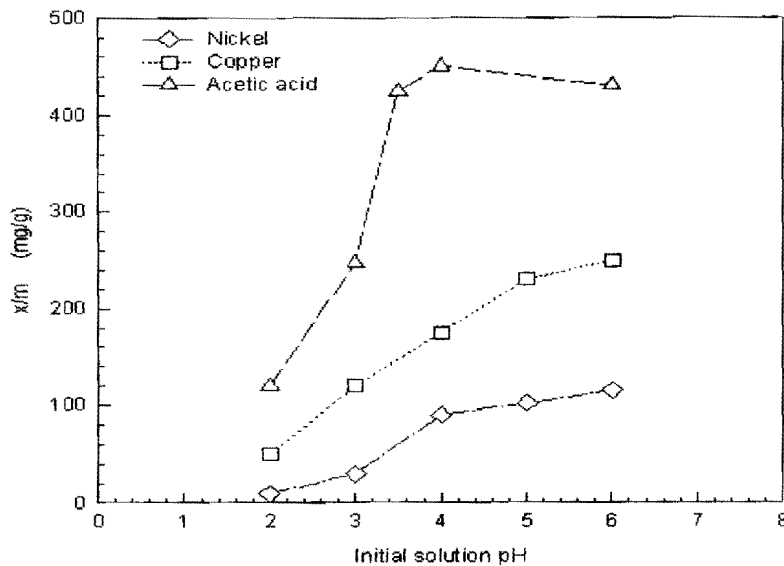


Figure 1: Effect of pH on the adsorption of acetic acid, copper and nickel ions onto the steam-activated plant

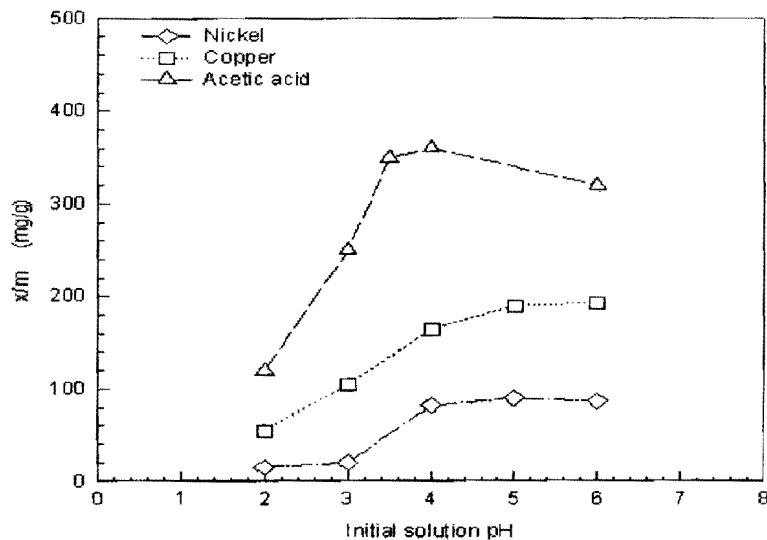


Figure 2: Effect of pH on the adsorption of acetic acid, copper and nickel ions onto the chemically activated plant

For copper adsorption, Freundlich fitted plots of the data for the steam and chemically activated substances presented in Figure 3 show linear behaviour, with correlation coefficients of 0.97 for both types of adsorbent. The corresponding equations of the Freundlich-fitted linear plots are reported in Table 2. The steam-activated adsorbent gave values of 0.83 and 1.37 for $1/n$ and K_f constants whereas these quantities were equal to 0.80 and 1.29, respectively, for the chemically activated system. Hence, the values of the adsorption intensity ($1/n$) for these two systems are close within experimental errors. This suggests that the forces between the adsorbed copper (II) ions and the treated plant surface were of equal strength. This kind of behaviour has also been observed with other adsorbents for which corresponding $1/n$ values of 0.18 [3] and 0.98 [12] were obtained. The K_f value for the steam-activated plant was slightly higher than that for the chemically activated plant; suggesting a slightly better affinity between the adsorbed copper (II) ions and the chemically activated surface.

Figure 3: Freundlich adsorption isotherms of nickel (II) adsorption onto physically and chemically activated plant

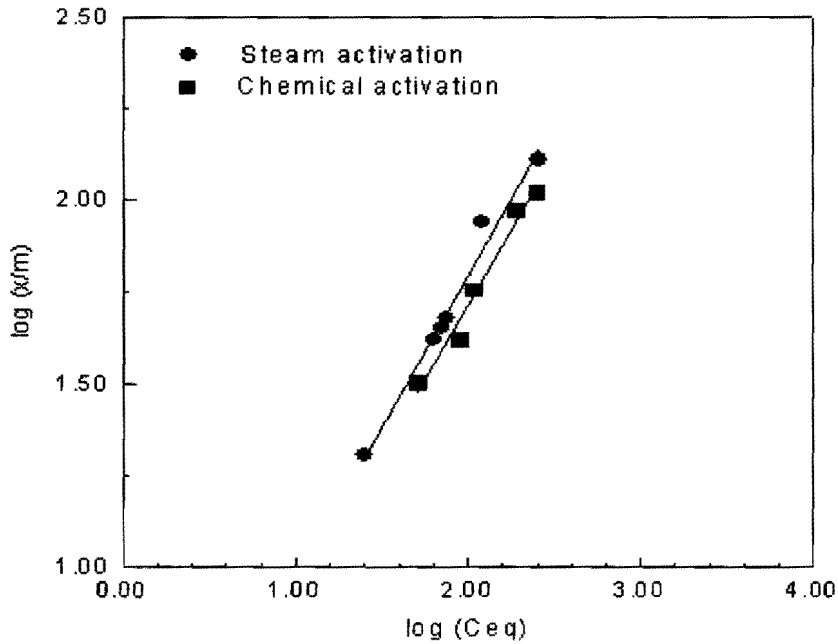


Table 2: Freundlich equations and constants for Copper (II) adsorption onto Salsola Plant.

System	Freundlich Equation	K_f	$1/n$	R^2
Steam activated	$\log (x/m) = 0.137 + 0.829 \log C_{eq}$	1.37	0.83	0.99
Chemically activated	$\log (x/m) = 0.109 + 0.803 \log C_{eq}$	1.29	0.80	0.97

As for the nickel adsorption, Table 3 shows the results obtained from Langmuir fitting to the data obtained for the steam and chemical activation systems. It can be observed that the model describes well the adsorptive properties of the plant; In addition, the nickel ions uptake was also significantly improved (up to 144 mg.g⁻¹).

Table 3: Langmuir constants for Nickel (II) Ion Adsorption onto the Salsola Vermiculata plant.

System	Langmuir equation	K (l mg ⁻¹)	b (mg g ⁻¹)	R^2
Steam activated	$C_{eq}/(x/m) = 1.58 + 0.0069C_{eq}$	0.004	144.93	0.99
Chemically activated	$C_{eq}/(x/m) = 0.7 + 0.029C_{eq}$	0.041	34.48	0.93

3. b. Determination of the heat of adsorption

The heat of adsorption Q can be determined using Langmuir constants from the equation $\ln K = \frac{Q}{RT} + \ln K_{\infty}$ by deducing Q and K_{∞} from the slope and intercept of $\ln K$ versus $1/T$ at different temperatures 298, 303 and 313 K. It is an indication of the extent of the interaction between the adsorbate and the adsorbent. Table 4 reports these values for the inactivated, steam and chemically activated systems as obtained from acetic acid results. The plots for these systems were linear with slopes that gave activation energies of 15.36 and 13.40 kJ mol⁻¹ for the steam and chemically activated plant, respectively. A value of 5.4 kJ mol⁻¹ was obtained for the natural plant. Matching values of Langmuir constants at infinite temperature were 1.0 10⁻⁴ and 5.7 10⁻⁵ l mg⁻¹ for the activated plants while 9.1 10⁻⁴ l mg⁻¹ was deduced for the inactivated one. These values suggest physisorption processes.

Table 4: Langmuir constant versus temperature for the different systems of the Salsola Vermiculata plant for the adsorption of acetic acid.

Temperature (K)	K (l mg ⁻¹)		
	Inactivated plant	Steam activated	Chemically activated
298	0.008	0.051	0.013
303	0.0078	0.045	0.012
313	0.0072	0.038	0.010

4 Conclusion

This investigation showed that the low-cost natural desert plant is a good adsorbent for acetic acid, nickel (II) and copper (II) ions when tested with synthetic aqueous solutions. Both the physical and chemical activation resulted in an increased adsorption potential towards these substances. For the data obtained from the acetic acid system, a maximum uptake (476 mg g⁻¹) was obtained for the pH range of 3.4 – 3.9. The chemically and physically activated plant exhibited an enhanced adsorption capacity towards the copper (II) ion system in the pH range 5.1 – 6.4. Copper (II) ion adsorption on the steam and chemically activated materials were best described by Freundlich isotherms, with $1/n$ and K_f values of about 0.80 and 1.3, respectively. The same pH range (5 – 6) contributed to a maximum nickel uptake of 144 mg g⁻¹. The values of the heat of adsorption at various temperatures showed that the adsorption process and the adsorbent-adsorbate interaction were physical phenomena for the acetic acid system.

REFERENCES

- [1] Quek, S.Y., Wase, D.A.J. and Forster, C.F., (1998), *Water S.*, **3**, 24.
- [2] Yan, G. and Viraraghavan T., (2000), *Water S.*, **1**, 26.
- [3] Marshall, W.E. and Champagne, E.T., (1995), *J. Environ. Sci. Health. A* **30**, 241.
- [4] Vazquez, G., Antorrena, G., Gonzalez, J. and Doval, M.D., (1994), *Bioresource Technol.* **48**, 251.

- [5] De Vasconcelos Teles, L.A., Beca-Gonzales, C.G., (1992), *Eur. Water Pollut. Control.* **2**, 13.
- [6] Ruff, B., Anabalon, P., Maturana, H., Aguilera, C., Freer, J. and Baeza, J., (1992), *Proc. Brazil. Symp. Chem. Lignins Wood Compon.* 157.
- [7] Tee, T.W. and Khan, R.M., (1988), *Environ. Technol. Lett.* **9**, 1223.
- [8] Randall, J.M., Reuter, F.W. and Waiss, A.C., (1975), *J. Appl. Polym. Sci.* **19**, 1563
- [9] Schmuhl, R., Krieg, H.M. and Keizer, K., (2001), *Water SA* **1**, 27.
- [10] Hazardous Substance Fact Sheet, New Jersey Department of Health, CAS number 7440-02-0.
- [11] Avom, J., Ketcha, M., Matip, M.R.I. and Germain, P., (2001), *Algerian J. Sci. Technol.* **2**, 2.
- [12] McKay, G., Blair, H.S. and Findon, A., (1989), *Indian J. Chem.* **28A**, 356.
- [13] Petrov, N., Budinova, T, Razvigorova, M. and Minkova, V., "Preparation of Activated Carbons from Cherry Stones, Apricot Stones and Grape Seeds for Removal of Metal Ions from Water", (2003), *Rep. Inst. Org. Chem., Bulgarian Academy of Sciences*, 46.
- [14] Alexeev, V., (1980), *Analyse quantitative*, 3rd Ed., Editions MIR, Moscow, USSR, 431.
- [15] Cooney, D.O., (1999), *Adsorption Design for Wastewater Treatment*, Lewis Publishers, Boca Raton, FL., USA, 27.
- [16] Do, D.D., (1998), *Equilibria and Kinetics*, Imperial College Press, London, 77.
- [17] Benderdouche, N., Bestani, B., Benstaali, B., and Derriche Z., (2003), *Adsorp. Sci. and Technol.* **21**, 739.
- [18] Low, K.S., Lee, C.K., and LEE, (1993), *Bioresour. Technol*, KP. **44**, 109
- [19] Huang, J.P., Huang, C.P. and Morehart, Al. (1991), In: Vernet JP (Ed.), *Heavy metals in the environment*, Elsevier, Amsterdam, London, New York and Tokyo, 329.
- [20] Ho, Y.S., Wase, D.A.J., and Forster, C.F., (1994), *Process Saf. Environ. Prot.* **17**, 185.
- [21] Gould, M.S., and Genettelli, E., (1978), *J. Water Res.* **12**, 505
- [22] Gardea-Torresdey, J.L., Hernandez, A., Tiemann, K.J., Bibb, J. and Rodriguez, O., (1998), *J. Hazard. Subst. Res.* **1**, 3.