

Adsorption of Some Heavy Metals and Bacteria by Activated Charcoal Made from Date Palm Leaves

Al-Turki A. I., A. H. El-Nadi, K. N. Al-Redhaiman, H. M. Abdel Magid and M.

Salad Department of Soil and Water, College of Agriculture and Veterinary Medicine, King Saud University, Al-Qassim, P.O. Box 1482, Saudi Arabia

ABSTRACT

The Adsorption of heavy metals, Mn, Zn, Cu, and Cr and three types of bacteria (*Enterobacter aerogenes*, *Escherichia coli*, and *Rhizobium meliloti*) on the surface of activated charcoal made from date palm leaves was investigated. Results obtained indicated that metal ions were adsorbed to charcoal to a considerable extent amounting to 71.4% for Zn^{2+} , 71.5% for Mn^{2+} , 72% for Cr^{3+} and 94% for Cu^{2+} . The nature of this type of adsorption is suggested to be of the physical type, since formation of new compound was not observed. The adsorption of bacteria to charcoal surface was found to be much more pronounced, reaching 71% for *E. aerogenes*, 94% for *E. Coli* and 98% for *R. meliloti*. It is suggested that the nature of interaction between bacteria cells and charcoal surface is of chemisorption type as evidenced by the increase in electrical conductivity (EC) and the marked decrease in the pH of the bacterial suspension. Our results suggest that charcoal, made from date palms, may be considered as a useful tool for purification of drinking water.

INTRODUCTION

Changes in the nature or intensity of molecular forces is a phenomenon that relates to a number of physical processes of which adsorption is the most important. Adsorption falls into two main categories namely, physical adsorption and chemisorption (Alexander and Kitchener, 1953). The physical type involves the operation of weak polar interactions termed as Van der Waal forces in which no chemical bond is formed between adsorbent and adsorbate. On the other hand, chemisorption involves chemical interactions in which a chemical bond, in a new two dimensional chemical compound, is consequently formed. Since adsorption occurs at the surface of the interface between adsorbent and adsorbate, the inherent properties such as size and chemical nature of both adsorbent and adsorbate are of utmost importance in the adsorption process.

The adsorptive ability of a number of varied adsorbents has been investigated by a number of authors (Bradford, 1975; Allen et al., 1971). Ray et al. (1981) studied the adsorption of metallic ions to algal cell walls at pH 4.5 and found that the strength of adsorption falls in the order $Cu^{2+} > Sr^{2+} > Zn^{2+} > Mg^{2+} > Na^+$ suggesting a trend from probable covalent to ionic bonding. Charcoal has been employed in a number of adsorption processes. For instance, in medicine (Westall, 1987), in purification of drinking water and removal of resin byproducts in organic synthesis (El-Nadi et al., 2001). The adsorptive potential of an adsorbent has been described by

a number of relations mainly mathematical (Langmuir, 1916; Brunauer and Teller, 1938; Harkin and Jura 1944). Activated charcoal made from date palm leaves was recently studied in this respect and its remarkable adsorptive potential was demonstrated (El-Nadi et al., 2001).

In this study the adsorption of metal ions namely, Cu^{2+} , Cr^{+3} , Mn^{2+} , and Zn^{+2} , and three different types of bacteria, namely *E. coli*, *E. aerogenes* and *R. meliloti* on the surface of activated charcoal was investigated with the ultimate goal of practical application of the obtained results in the field of purification of drinking water and other related processes.

MATERIALS AND METHODS

Preparation of Charcoal:

Charcoal was prepared from leaves of date palm (*Sci*) grown in central Saudi Arabia (Al-Qassim Region) according to the procedure described by El-Nadi et al. (2001).

Adsorption of heavy metals

Solutions of copper sulfate [CuSO_4] manganese nitrate [$\text{Mn}(\text{NO}_3)_2$], zinc nitrate [$\text{Zn}(\text{NO}_3)_2$] and chromium nitrate [$\text{Cr}_2(\text{NO}_3)_2$] ions were made to reach the final concentration of 5ppm. All cations used in this work are of analytical grade. Charcoal (3g, 2mm mesh size) was added to equal volumes (100 ml) of each solution of the cations and shaken mechanically for 15 min, filtered, using Wattman filter paper No.40. The filtrate obtained was used for the determination of the remainder cations in solution, using inductively coupled plasma (ICP) model GBC SC Equipment Pty, Ltd., England. Triplicate determinations were carried out. Percentage adsorption of metal ions was calculated from the concentration differences of each ion before and after the adsorption process.

Adsorption of bacterial cells

Preparation of bacterial cells: *Escherichia coli*, *E. aerogenes*, and *R. meliloti* were obtained from the Soil Microbiology laboratory of Department of Water and Soil, at the College of Agriculture and veterinary medicine in Al-Qassim. *E. coli* and *E. aerogenes* were prepared by growing cultures overnight at 35°C in lactose broth (EC medium, Difco, Detroit, MI, USA) and *R. Meliloti* was prepared by growing cultures for 48 hr in yeast mannitol broth (YMB) at 30°C. Cells of each microorganism were harvested by centrifugation at 5000 rpm for 15 min and washed in physiological saline solution (0.15 M Na Cl). The washed cells were resuspended in 50 ml of sterile phosphate buffer (Fisher, Cincinnati, OH, USA). The resuspended cells were brought to a final volume of 100 ml by adding deionized water. Bacterial cell concentrations in the suspension were determined by standard

plate method using four replicates (Zuberer, 1994).

Charcoal (10 g), 2mm mesh size, were mixed with 100 ml of each microbial suspension and shaken using a reciprocating shaker for 20 min. Charcoal was immediately removed from each suspension and 10 ml of each suspension was serially diluted by 10-fold steps into deionized water. Culture tubes containing a defined substrate medium (MacConkey-Bouillon, E. Merck Darmstadt, Germany) for *E. coli* and *E. aerogenes*, and YMB for *R. meliloti* were inoculated from each bacterial suspension after dilution. Most probable number as described by Woome (1994) was determined after incubation at 35°C for 48 hr for coliform (*E. coli* and *E. aerogenes*) and at 30°C for 3 days for *R. meliloti*.

Measurements of pH and EC

The pH and EC of bacterial cell suspension were measured before and after addition of charcoal. The pH was determined using the Jenway pH-meter model 3310 and EC was determined using the Jenway EC-meter model 4340.

RESULTS AND DISCUSSION

The adsorption of the heavy metals (Mn, Zn, Cu, and Cr) and three types of bacteria (*E. coli*, *E. aerogenes*, and *R. meliloti*) on the surface of activated charcoal, made from date palm leaves, was investigated. Table (1) shows that the strength of adsorption to charcoal surface was almost identical for Cr^{3+} , Mn^{2+} and Zn^{2+} ranging from 71.4 to 72% and was much higher for Cu^{2+} corresponding to 94.3%. Ray et al, (1981) studied the adsorption of some heavy metals including Cu^{2+} , Zn^{2+} , Mg^{2+} and Na^+ on algal cells and found that the largest value of adsorption was for Cu^{2+} .

Results may indicate that adsorption of these metals to charcoal surface belongs to the physical type since no new compounds were isolated i.e. no chemical bond is formed. The differences in values of adsorption determined for these metals are possibly attributed to the differences in affinity of these metal ions toward charcoal. Since the values of ionic radii of these metal ions are approximately identical (Table 1), they do not play significant role in determining the degree of adsorption.

Table (2) indicates that charcoal reduced the number of bacteria in the suspension by 71%, 94%, and 98% for *E. aerogenes*, *E. coli*, and *R. meliloti*, respectively. The decrease in pH of the bacterial cell suspension (Table 3) clearly indicates proton (H^+) exchange at the interface between bacterial cells and charcoal particles resulting in H^+ release to the medium and consequently the pH value shifted to the acid zone. Table 3 shows also that the electrical conductivity (EC) of the bacterial suspension has increased indicating that the

ionic strength of the bacterial suspension has also increased due to liberation of charged entities at the surface. Thus, adsorption of the bacterial cells to charcoal surface is more likely to be of chemisorption type since charged entities are involved as indicated by decrease in pH value and increase in EC.

It may, therefore, be concluded that charcoal made from date palm leaves could be employed in varied adsorption processes, one of utmost importance is the purification of drinking water.

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Table 1. Adsorption of heavy metals on the surface of charcoal made from date palm leaves

	Heavy metals			
	Zn ⁺²	Mn ⁺²	Cr ⁺³	Cu ⁺²
Adsorption (%) †	71.4 ±0.02	71.5 ±0.015	72.0 ±0.02	94.3 ±0.21
Ionic radius ‡	0.7	0.80	0.69	0.7

† % Adsorption values were averages of triplicate

‡ Ionic radii (Pauling, 1960)

Table 2. Effect of charcoal on microbial populations measured in the suspension

Treatment	MPN index (cells/ml) X 10 ⁴		
	<i>E. coli</i>	<i>E. aerogenes</i>	<i>R. meliloti</i>
Untreated	2.4	1.5	110
Treated with charcoal	0.15	0.43	21
% Reduction	94	71	98

Table 3. pH and EC levels in bacterial suspension before (A) and after (B) treatment with charcoal

Microbial suspension of:	pH			EC (dS/m)		
	A	B	% Decrease	A	B	% Increase
<i>E. coli</i>	7.2	4.8	67	1.5	6.5	433
<i>E. aerogenes</i>	7.2	4.9	68	1.2	6.2	517
<i>R. meliloti</i>	7.0	4.7	67	1.4	4.0	286

المخلص العربي

امتزاز بعض المعادن الثقيلة والبكتريا على سطح الفحم المنشط المصنع من
جريد النخيل

احمد التركي, عبدالرحمن النادي, خالد الرضيمن, هجو عبدالماجد, محمد صلاح
قسم التربة والمياه-كلية الزراعة والطب البيطري-جامعة الملك سعود- القصيم- المملكة العربية
السعودية ص. ب. ١٤٨٢

في هذه البحث تم دراسة امتزاز أربعة من المعادن الثقيلة هي (Mn, Zn, Cu, Cr) و ثلاثة أنواع من البكتريا هي (*Entrobacter aerogenes*, *Escherichia coli*, *Rhizobium meliloti*) على سطح الفحم المنشط والمصنع من جريد النخيل. أشارت النتائج إلى أن امتزاز أيونات المعادن على سطح الفحم تراوح من ٧١,٤% في Zn^{+2} إلى ٧١,٥% في Mn^{2+} , إلى ٧٢% في Cr^{3+} , وإلى ٩٤% في Cu^{2+} . تقترح النتائج أن الامتزاز في هذه الحالة هو من النوع الفيزيائي, حيث لم يلاحظ تكوين مركبات جديدة بعد إضافة أيونات المعادن إلى الفحم المنشط. هذا, وقد تراوح امتزاز البكتريا على سطح الفحم من ٧٠% في *E. aerogenes*, إلى ٩٤% في *E. coli* وإلى ٩٨% في *R. meliloti*. لقد صاحب امتزاز البكتريا على سطح الفحم ارتفاع كبير في التوصيل الكهربائي وانخفاض ظاهر في قيمة الأس الهيدروجيني لمعلق البكتريا, الأمر الذي يشير إلى أن الامتزاز في هذه الحالة هو من النوع الكيميائي. تدل نتائج هذه الدراسة على أن الفحم المصنع من جريد النخيل قد يكون مناسباً لاستخدامه في تنقية مياه الشرب.