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MISWAK (SALVADORA PERSICA ROOTS): DISCOVERY OF A NEW BIOMATERIAL FOR REMOVING HEAVY METALS FROM WATER IN SAUDI ARABIA

MISWAK (KORENINE SALVADORA PERSICA): ODKRITJE NOVEGA BIOMATERIALA ZA ODSTRANJEVANJE TEŽKIH KOVIN IZ VODE V SAUDSKI ARABIJI

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The aim of this study was to evaluate Miswak (Salvadora Persica Roots Powder, SPRP) as a natural bio-adsorbent from Saudi Arabia for water treatment. The adsorption capacity of the SPRP increased with an increasing concentration of heavy-metal ions and the temperature of the experimental solution. The maximum adsorption capacity of the SPRP was 18.2 mg g^{-1} and 20.79 mg g^{-1} for lead at 25 °C and 45 °C, respectively. Of the two isotherm models (Langmuir and Freundlich), the Langmuir model fitted the experimental data well at 45 °C, while the Freundlich model correlated well with the experimental data at 25 °C.

Keywords: Miswak (Salvadora Persica Roots), Miswak powder, lead, Langmuir, Freundlich ishotherm model, contaminated water, adsorption capacity

Namen te študije je bila ocean Miswaka (prah iz korenin Salvadora Persica, SPRP) kot naravnega bioadsorbenta iz Saudske arabije, za obdelavo vode. Zmogljivost absorpcije SPRP se povečuje z naraščanjem koncentracije ionov težkih kovin in temperature eksperimentalnih raztopin. Maksimalna zmogljivost absorpcije svinca s SPRP je bila 18,2 mg g^{-1} in 20,79 mg g^{-1} pri 25 °C oziroma pri 45 °C. Med dvema izotermnima modeloma (Langmuir in Freundlich), se je Langmuir model dobro skladal z eksperimentalnimi podatki pri 45 °C, medtem ko je bila korelacija Freundlich modela z eksperimentalnim podatki dobra pri 25 °C.

Ključne besede: Miswak (korenine Salvadora Persica), Miswak prah, svinec, Langmuir, Freundlichov izometrični model, kontaminirana voda, zmogljivost absorpcije

1 INTRODUCTION

Lead (Pb) is one of the toxic metals present in different types of waters as a pollutant. It is a potential source of human health hazards such as heart failure, thyroid and liver damage when its concentration in water is above the permissible limits for various uses. Currently, many conventional water-treatment techniques such as membrane processes, chemical precipitation, ion-exchange processes and adsorption are used for the removal of heavy metals such as lead. Existing technologies for heavy metals' removal from waters and wastewaters are often ineffective, expensive, time consuming and unavailable in developing countries. Therefore, the use of Miswak (SPRP) as a low-cost adsorbent seems a viable approach for removing the lead ions from waters and or wastewater through an adsorption process.

Among the different water-treatment techniques, the adsorption of heavy metal by miswak (SPRP) is considered as cheap and cost effective compared to more expensive process such as ion exchange. Many natural local materials such as clay, charcoal, solid waste from water-treatment plants and different agricultural wastes (biomaterials) are available for wastewater purification. Saudi Arabia is one of the largest producers of Miswak stick (roots of Sulvadora persica tree) in the world and this is mainly used for cleaning teeth instead of using chemically produced tooth pastes.

Many industries use aqueous solutions of heavy metals such as lead for manufacturing batteries. Unfortunately, the removal of heavy metals such as Pb, Zn, Co and Cr from aqueous solutions is both difficult and expensive. Previously, different types of adsorbents, such as activated carbon, activated sludge, various types of natural clays, carbon aerogels, coirpith carbon, natural zeolites and date-pits powder were used for water treatment. Similarly, heavy-metal removal was achieved by expensive ion-exchange resins (U.S. Patent No. 4,133,755). These investigators used various adsorbents, mainly a dithiocarbamate bond-containing low-molecular-weight compound, amorphous silica and activated carbon powder, granulated with a vinyl acetate polymer binder and clay as a thixotropic excipient for removing heavy metals. However, Cody (U.S. Patent No. 5,667,694) used granulated materials for treating mercury-contaminated wastewater for removing heavy metals such as lead and the radioactive contaminants from contaminated aqueous systems including aqueous soil systems. They used organically modified smectite clay or organoclay to treat these systems. This product removes heavy-metal ions by flotation and air sparging (U.S. Patent No. 5,256,615). According to this patent, a granular inorganic ion exchanger was obtained by firing at 400 °C or above, a granular molded product of a mixture of a metal alkoxide such as $Si(OMe)_4$ or hydrolyzate, a clay mineral such as sepiolite and an inorganic ion exchanger such as antimony pentoxide having mechanical strength and heat resistance without losing its inherent ion exchangeability (World Patent Publication No. WO 00/72958). M. Minamisawa et al.[1] investigated the adsorption of Cd(II) and Pb(II) at pH 2–6.7 on different biomaterials and inorganic adsorbents. They also stated that biomaterials prepared from plant materials are promising for the development of novel and low-cost adsorbents. Also, bio-adsorbents proved to be potential remediation materials for the removal of heavy metals and organic materials.[2] Rice husk (RH), fly ash and similar other low-cost (agricultural by-product) bio-adsorbents were used for the removal of various heavy metals and metalloids (such as Pb, Cd, Zn, Ni and As) from both groundwater and surface water.[3] In another study, agricultural waste-based biosorbents (AWBs) showed equal or even greater adsorption capacities compared to conventional adsorbents for removing heavy metals from contaminated waters.[4] Recently, a wide range of low-cost modified adsorbents including activated carbon, natural source adsorbents (clay, bentonite, zeolite, etc.), biosorbents (black gram husk, sugar-beet pectin gels, citrus peels, banana and orange peels, carrot residues, cassava waste, algae, algal, marine green macroalgae, etc.), and byproduct adsorbents (sawdust, lignin, rice husk, rice husk ash, coal fly ash, Snail Shells, Melanoides tuberculata Muller etc.) were examined for the removal of some heavy metals from water.[5,6] The reported the highest adsorption capacities for Zn^{2+} were 168 mg g^{-1} on powdered waste sludge, 128.8 mg g^{-1} dried marine green macroalgae, 73.2 mg g^{-1} lignin, 55.82 mg g^{-1} cassava waste, and 52.91 mg g^{-1} bentonite. Some investigators utilized Portulaca oleracea plant biomass (dried leaves and stem) and dried leaves of water hyacinth along with the effect of pH, contact time and adsorpent dose on biosorption and removing some heavy metals such as Cd, Pb, Zn and Cr from the aqueous solutions and wastewaters.[7] They reported a maximum removal of Pb at pH of 5 with 120 min of contact time and 3 g of adsorbent dose.

A review on the use of Sulvadora persica roots powder (SPRP) as a bioadsorbent for the removal of heavy metals from waters did not refer to any study relating to this material. However, in the water- or wastewater-treatment sector dealing with polluted groundwater, waste effluents from industrial, domestic, agriculture, potable drinking water in the markets and health facilities, it is imperative to remove highly toxic heavy metals from the available water and waste effluents for its safe reuse in agriculture and other purposes. In Saudi Arabia, Miswak (roots of Sulvadora persica tree) is abundant and is a cost effective biomaterial. Therefore, a study on the use of Miswak powder as an adsorbent for removing heavy metals may determine it as an appropriate biomaterial substitute for commercial activated-carbon and other adsorbents. The main aim of this study was to explore the possibility of using Miswak (SPRP) as a new natural biomaterial and low-cost adsorbent for removing toxic heavy metals such as lead from waters and wastewaters.

2 MATERIALS AND METHODS

2.1 Materials

The adsorbate is a lead-ion solution prepared from lead (II) nitrate purified LR and supplied by VWR International SAS 201.

Salvadora persica is a tree naturally growing in Jazan, Saudi Arabia from which the miswak (root portion of tree) was prepared and is commonly known as Arak tree. The miswak samples were collected, dried, crushed and milled to a particle size less than 125 mesh (particles sized between about 0.125 mm to 0.25 mm). Then, the powder was used as an adsorbent for removing heavy metals from waters and wastewater. The inherent ion-exchange capacity of this powder is in the pH range between 3 and 5. For example, the miswak powder contains many functional groups such as carboxylic groups as found by FT-IR analysis (**Table 1**). As the pH of the solution affects the charge on the functional groups, therefore the functional groups such as carboxylate are protonated at low pH values.[8] The surface area and pore characteristics of miswak powder as an adsorbent are given in **Table 2**. The chemical analysis of miswak powder was carried by XRF and presented in **Table 3**.

Table 1: Some of the main functional groups in Saudi miswak powder
Tabela 1: Nekaj glavnih funkcionalnih skupin v savdskem miswak prahu

Observed band (cm^{-1})	Functional group
3488- 3100	O-H
	N-H
2800-2900	C-H
1600-1740	C=O
	Carbonyl
1000-1200	C-O

Table 2: Surface area and pore characteristics of Saudi miswak powder
Tabela 2: Površina in značilnosti por v savdskem miswak prahu

Element	Miswak stick powder
BET surface area (m^2 g^{-1})	0.6933
Pore volume (p/po=0.97) (cm^3 g^{-1})	0.001788
Average pore width (nm)	10.3144

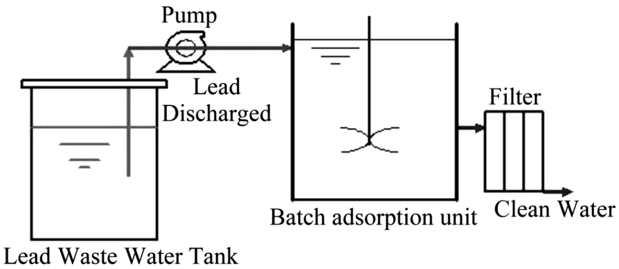

Figure 1: Experimental setup for heavy-metal adsorption
Slika 1: Eksperimentalni sestav za adsorpcijo težke kovine

Table 3: Chemical analysis of Saudi miswak powder by XRF
Tabela 3: XRF kemijska analiza savdskega miswak prahu

Element	Composition (%)
S	23.0752
Cl	11.195
K	10.02
Ca	55
Fe	0.492
Zn	0.108
Br	0.0998

The experimental set up showing the adsorption system including a batch adsorption unit for removing heavy metals from contaminated wastewater is presented in **Figure 1**.

2.2 Equilibrium experiments

Equilibrium isotherm experiments for the miswak powder were carried out by placing 0.25 g of powder with 50 mL lead solution in a batch adsorption unit. The concentration of lead ion solution ranged from 50 to 800 ppm. The particle size of the miswak powder was 0.125 mm. The equilibrium experiments were run for a total period of 3 h to ensure that the adsorption process is in a state of equilibrium. After termination of the experiment, samples were collected, filtered and the concentration of Pb was measured by atomic absorption spectroscopy. The amount of Pb ion adsorbed on the surface of miswak powder was calculated using the following Equation (1):

$$q_e = \frac{v(C_0 - C_e)}{M} \qquad (1)$$

where M is the mass of miswak powder in g, V is the volume of the solution in liters, q_e is the amount of ion adsorbed mg g^{-1}, C_o is the initial concentration of lead ion solution as mg/L and C_e is concentration of Pb ion at equilibrium in mg/L. The equilibrium adsorption isotherm curves were prepared from the amount of lead ion adsorbed on the surface of the miswak powder and the Pb concentration in solution.

3 RESULTS AND DISCUSSION

3.1 Ion removal efficiency of Miswak powder

The Pb ion concentration in the solution after treatment was less than 285.17 ppm and the removal efficiency of Pb ion by miswak powder was more than 58.81 %.

3.2 Initial concentration vs. Pb ion adsorption

The data in **Figure 2** shows that the adsorption capacity of the sPb ion increased with increasing the initial concentration. The maximum adsorption capacity of the miswak powder was 18.2 mg g^{-1} and 20.79 mg g^{-1} at 25 °C and 45 °C, respectively. The process of Pb-ion adsorption on the negative sites of the miswak powder is due to the electrostatic attraction between these negative sites and the lead ions. Furthermore, the formation and number of negative sites on the surface of the miswak powder are mainly due to the presence ofa carboxyl group. The miswak powder has chemical functional groups such as carboxylic acid (COOH), as shown by FT-IR analysis (**Table 1**). The study's findings agree with many researchers who reported that the metal uptake capacity of the root for different metals was in the order of: Ni>Cd>Pb>Cu>Cr; stem Ni>Pb>Cu>Cd>Cr; and leaf Ni>Cd>Cu>Pb>Cr. They also reported that Ni adsorption was the highest in the root and its concentration was 428.4 ng/g dry wt. Also the trend of adsorption of the phytomass was similar for Ni and Cd, i.e., root>leaf>stem.[9–12]

3.3 Temperature vs. adsorption capacity of Miswak powder

The adsorption capacity of miswak powder increased with increasing temperature (**Figure 2**), thus indicating that the adsorption process of Pb ions on miswak powder is an endothermic process. Therefore, the adsorption of Pb ions on the surface of the miswak powder is favorable. The results agree with those of S. A. Aljlil et al.[13]

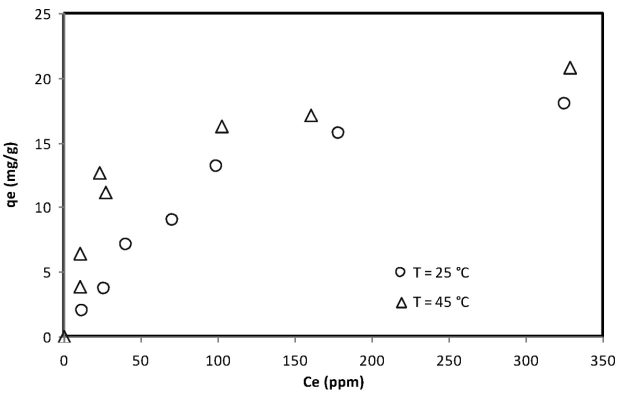

Figure 2: Equilibrium isotherm for lead ions adsorption on miswak powder
Slika 2: Ravnotežna izoterma za adsorpcijo ionov svinca na miswak prahu

who reported similar behavior when increasing the solution temperature.

4 SAUDI MISWAK STICK POWDER VS. COMMERCIAL ADSORBENTS

The maximum adsorption capacities of miswak powder, activated carbon and silica were taken from the equilibrium isotherm experimental data for comparing the ion-removal efficiency among these different adsorbents (**Table 4**). The results in **Table 4** indicated that miswak powder proved to be the best bio-adsorbent compared to other similar adsorbents. Because it seems cheaper, has a relatively high saturation capacity, a natural biomaterial and easily available locally.

Table 4: Comparison between miswak powder and other commercially available adsorbents for the adsorption of lead ions

Tabela 4: Primerjava med miswak prahom in drugimi komercialno dostopnimi adsorbenti za adsorpcijo ionov svinca

Adsorbent	Saturation (maximum) capacity, (mg g^{-1})
Activated carbon	7.49
Miswak powder	18
Silica	5.15

5 ANALYSIS OF THE EQUILIBRIUM EXPERIMENTAL RESULTS

Two types of equilibrium isotherm models were used in this paper, i.e., the Langmuir and Freundlich models.

5.1 Langmuir isotherm model

The Langmuir isotherm model assumes that a monolayer of lead ions is adsorbed on the miswak powder particles and is also used to estimate the maximum capacity. The Langmuir isotherm Equation (2) is written as follows:

$$q_e = \frac{KC_e}{1+bC_e} \quad (2)$$

The Langmuir model in the linear form is:

$$\frac{c_e}{q_e} = \frac{1}{K} + \left(\frac{b}{K}\right) C_e \quad (3)$$

The equilibrium parameters, K and b, can be determined by using the non-linear regression method with Equation (3).

Figure 3 shows the relationship between C_e and q_e at T = 25 °C and T = 45 °C. The equilibrium constants, K and b, were estimated using the nonlinear regression method and are tabulated in **Table 5**. As shown in **Figure 3**, the Langmuir model fits the experimental data well at T = 45 °C.

Table 5: Langmuir equilibrium parameters for lead ions adsorption on Miswak powder

Tabela 5: Parametri Langmuir ravnotežja za adsorpcijo ionov svinca na Miswak prahu

Temperature	K (L/g)	b (L/mg)	R^2
T = 25 °C	0.2024	0.00644	0.8895
T = 45 °C	0.3758	0.01529	0.9230

5.2 Freundlich isotherm model

The Freundlich isotherm model was applied to describe the data from equilibrium adsorption experiments for a heterogeneous surface. The Freundlich model is written as follows in Equation (4):

$$q_e = K_F C_e^{1/n} \quad (4)$$

The equilibrium parameters, K_F and n, can be calculated by using the non-linear regression method with Equation (4). The adsorption of metal ions on miswak powder is favorable when the values of n are greater than one[14].

The Freundlich model in the linear form is:

$$\lg(q_e) = \lg(k_F) + \frac{1}{n} \cdot \lg(C_e) \quad (5)$$

Figure 4 shows the relationship between C_e and q_e at T = 25 °C and T = 45 °C. The equilibrium constants were

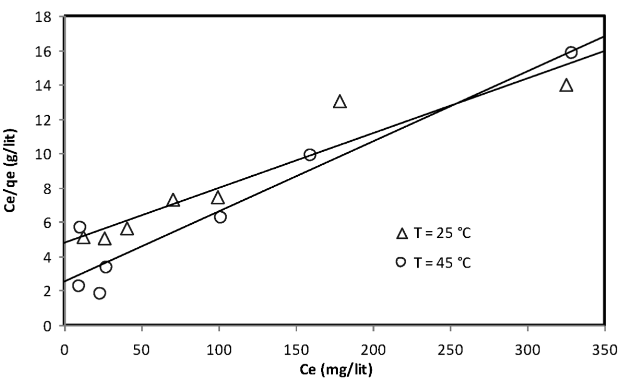

Figure 3: Langmuir equilibrium isotherm for lead adsorption on Miswak powder

Slika 3: Langmuir ravnotežna izoterma za adsorpcijo svinca na Miswak prahu

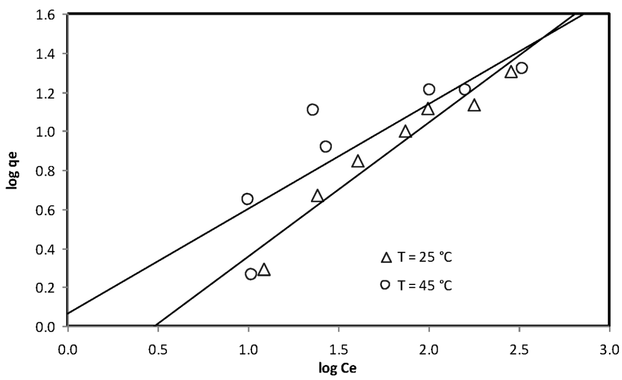

Figure 4: Freundlich equilibrium isotherm for lead adsorption on Miswak powder

Slika 4: Freundlich ravnotežna izoterma za adsorpcijo svinca na Miswak prahu estimated using the nonlinear regression method and are tabulated in **Table 6**. As shown in **Figure 4**, the Freundlich model also correlates the experimental data well at T = 25 °C.

Table 6: Freundlich equilibrium parameters for lead ions adsorption on Miswak powder
Tabela 6: Freundlich ravnotežni parametric za adsorpcijo ionov svinca na Miswak prahu

Temperature	K (L/g)	b (L/mg)	R^2
T = 25 °C	0.7207	1.457	0.941
T = 45 °C	1.0690	1.862	0.720

6 CONCLUSIONS

The adsorption of lead ions on the surface of miswak powder was studied. The study on the influence of the initial concentrations on the adsorption capacity of the Saudi miswak powder indicated that the saturation capacity increased with increasing the initial solution concentration. The maximum adsorption capacity of miswak powder (SPRP) for lead ions was 18.2 (mg g^{-1}) and (0.79 (mg g^{-1}) at 25 °C and 45 °C, respectively. The application of Langmuir and Freundlich models showed that this model fitted the experimental data well at T = 45 °C, while, the Freundlich model correlated the experimental data well at T = 25 °C.

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