## **NATURAL OCCURRING RADIOACTIVITY IN THE ENVIRONMENTAL SAMPLES**

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**Abstract**

The objective of this study is to remove natural occurring uranium from polluted groundwater, coconut shells was converted into activated carbon (AC) by chemical activation using phosphoric acid. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were performed. SEM showed the presence variety of cavities at the surfaces of the prepared AC. The point of zero charge pH(PZC) was performed by batch technique using potentiometric titration. The pH(PZC) was found 8.8 confirming alkaline nature of AC surfaces. Speciation of uranium (IV) in ground water was simulated using VISUAL MINTEQA2 code. The prepared AC was found to contain a high fixed carbon, 64.8 % and low ash content, 11.2 %. Sorption tests were performed by batch technique AC removed around 80 % of aqueous U(IV) of concentration,100 mg/l, Sorption data were fitted to the Freundlich and Langmuir isotherms indicating of heterogeneous reaction with monolayer adsorption. and the kinetic data were fitted to the second order kinetic

1. **INTRODUCTION**

The presence of naturally occurring radioactive materials (NORM) in the environment are due to some industrial activities, in particularly uranium find its main way in nuclear industry, large amounts of this element have entered into the environment through human activities. The commercial phosphate fertilizers contain high activity concentrations of the natural uranium (238U) and radium (226Ra) series, it contains about 1500 Bq/kg of the natural uranium and radium series. 238U and 226Ra series may discharge into the environment and find its way into groundwater resources [1], Hence uranium pollution represents a threat to the ground and aquifer, therefore, the removal of uranium from the waste solution is important an inexpensive adsorbent is essential used for the removal of uranium from aqueous solutions. Activated carbon has been widely used for sorption of chemical species at aqueous solutions. Activated carbons are the most commonly used as adsorbents for removal of radioactive waste solutions. Different types of activated carbon were fabricated from agricultural solid waste products [2]. Coconut shells are suitable for making activated carbon as inexpensive adsorbent, the chemical of treatments of activated conditions are responsible for the properties of the resulting carbon active products [3, 4]. Activated carbon may be performed by two different methods of treatments, the physical and the chemical activation process. Phosphoric acid, zinc chloride, sodium hydroxide and potassium hydroxide may be used in the chemical process treatments [5-7]. Phosphoric acid is suitable for the removal of uranium from radioactive aqueous waste products [8]. The aim of the present study is to remove uranium from aqueous waste solutions by inexpensive adsorbent.

1. **EXPERIMENTAL**
   1. **Raw materials**

The raw materials of the coconut-shells samples were obtained from the Egyptian local market. Phosphoric acid (H3PO4 85% acid) and Sodium Hydroxide (NaOH) were obtained from Merck company. All chemicals used in our investigation are analytical grade.

* 1. **Sample preparation method**

Activated carbon is usually prepared in an inert nitrogen and nitrogen is a cost effective process, the preparation of inner environment for activated carbon is little bit inaccessible, the double crucible method are used [9]. A smaller silicon crucible containing coconut shells was put in a bigger porcelain crucible covered with a lid, the gap inside the bigger crucible is filled up by raw coconut-shells to reduce environmental oxygen inside the crucibles., the samples were dried overnight at 120 oC to remove the moisture content. Chemical activation was carried out by initially carbonizing the dried washed samples in a muffle furnace in closed system, the samples were heated at the temperature of 450°C for 1 hour . about 30 g of the carbonized samples was subsequently impregnated with 35% ortho-phosphoric acid (H3PO4) for 24 h of soaking duration, next, filtered and dehydrated overnight in the dryer oven at 105°C. The dried sample was then pyrolysis for activation at the temperatures of 500°C for 30 minutes, the sample was allowed to cool down at the room temperature, and washed with 0.1 M HCl , then washed with deionized water and grinded, the samples sieved using sieves have the grain particles size of 1.0 – 2.0 mm and preserved for analysis.

* 1. **Physical characterization of the sample**
     1. *Apparent density*

The standard test method was used. The weight of the adsorbent (g) was determined and divided by the volume (ml) to gives the apparent density (g/ml) of the adsorbent .

* + 1. *Moisture content*

About 2.0 g of the carbonized sample was heated in a ventilated drying oven at 150 oC for 3 hours and cooled in a desiccator and re-weighed. The loss in weight of the adsorbent represents the moisture content as percentage [9]

* + 1. *Volatile matter conten*t

About 1.0 g of activated carbon is taken in a pre-dried crucible, it was covered with the lid and heated in a muffle furnace regulated at 950 oC for 30 min, the sample cooled in a desiccators and weighed.

* + 1. *Ash content*

The crucible is ignited in the muffle furnace at 650 oC for 1 hour. After heating, the crucible is placed in a desiccator and cooled at room temperature and the weight was taken.

* + 1. *Fixed* *carbon*

The fixed carbon content is determined by subtracting sum of percentage compositions of the moisture content, volatile matter content, and ash content form 100. It is calculated using the following Equation:

% fixed carbon = 100 – (% ash content + % volatile matter content) (1)

* 1. **Determination the pH of the point of zero charge (pH PZC)**

The pH of the point of zero charge (pH PZC) corresponds to the pH at which the surface net charge of adsorbent (AC) is zero. A series of 50 ml 0.01 M NaCl solution was added to 0.15 g of AC in the glass flasks, the pH was adjusted between 2 and 10 using 0.1 M of HCl and NaOH with a pH meter, each AC sample was agitated at 150 rpm for 48 h under atmospheric conditions. The initial pH values was plotted against the difference between the initial pH and the final pH values (ΔpH ) of the solutions. The point of zero charge is the intersection of the two curves [10].

* 1. **FTIR spectrum study**

The surface chemistry of the prepared activated carbon was analyzed by identifying the surface active functional groups. .Fourier transform infrared spectroscope (FTIR-2000, Perkin Elmer) at 4000 to 500 cm-1 resolution was used for analysis of the sample.

* 1. **Batch Equilibrium Studies**

Sorption of U(IV) was carried out using batch technique. Factors such as, effects of AC dosage, U(IV) ion concentration and contact time were investigated. Sample aqueous solutions were withdrawn from the solid contact with aqueous U(IV) at equilibrium, concentrations of U(IV) at the desired sample was compared with the standard U(IV) curves, the standard curves if U(IV) was determined from Lambert Beers Law relationship that obtained between the absorbance and concentration at equilibrium. Concentration of U(IV) in solution before and after adsorption was determined using a double UV-Vis spectrophotometer (UV-1100 Shimadzu, Japan), the residual U(IV) concentrations was measured by colorimetric technique using 1-(pyrdyl-2-azo)-resorcino (PAR) indicator at the wavelength 510 nm. The sensitivity of the measured U(IV) by this method is 0.02 µg/ml, [11].For equilibrium studied, 20 ml of U(IV) standard aqueous solutions (100 mg/l) was added in each 0.05 g of AC sample in 30 ml bottles. The bottles were shacked at 30 rpm for certain time, amount of U(IV) adsorbed at equilibrium, Qe (mg/g), was calculated using the following equation [12]:

.V (mg/g) (2)

The U(VI) removal percentage is calculated [13, 14].

The amount of U(VI) adsorbed (Qt) after different contact time(t) intervals at equilibrium was calculated by the following:

(4)

Where Co and Ce are the initial and the equilibrium uranium concentration

concentrations in the solution (mg/L) respectively, V is the solution volume (L) and m is the mass of activated carbon (g). Qt is the amount of U(IV) adsorbed (mg/g) at t (h.) and Cto and Ct (mg/L) are the liquid phase concentrations at initial and any time t.

1. **RESULTS AND DISCUSSIONS**
   1. **Physical properties of the modified activated carbon**

The physical properties of the prepared AC is given in Table 1. AC was found to have a low ash content (11.2%) and a high fixed carbon (64.8%),. the cation exchange capacity is 760 meq/g. The pHzpc of the AC corresponds to the solution pH at which the carbon presents zero net charge on its surface. The prepared activated carbon is a good adsorbent because it has a low ash content, a high fixed, high specific surface area and high cation exchange capacity. The point of zero charge is 8.8 indicating that the prepared activated carbon using coconut shells has selectivity towards cation species [10, 14].

* 1. **Scanning** **electron** **microscope** (**SEM**)

The surface morphology of the modified activated carbon (coconut-shells) is given in Fig. 1, indicated by development of many pores with cavities. An early work has been conducted on various concentration of H3PO4 activation using frond waste of Saudi Arabian [14].

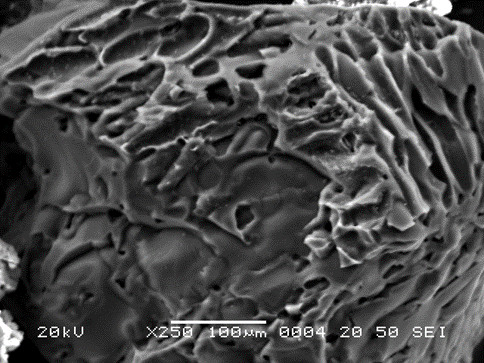
* 1. FTIR **analysis.**

The FT-IR spectra of the carbonized coconut-shells is given in Fig.2. The transmission band at 3413 cm-1 can be assigned to the OH stretching vibration of the hydroxyl groups, the small band is observed at 1714 cm-1 assigned to the C=O stretching vibrations of ketones, aldehyde or carboxylic groups, strong band is observed at 1594 cm-1 due to the vibration of C-C in aromatic rings, other band is observed at 1402 cm-1 corresponds to the aromatic skeleton generally found in carbonaceous material of activated carbon, the broad band at 1191 , 885 cm-1 are usually found within the oxidized carbon assigned to C=O stretching in acids, it is also an indication of the presence of phosphorous carbonaceous compounds in the phosphoric acid activated carbon and the plan deformation mode of

C-H for different substituted benzene rings [15].

TABLE 1: Physical properties of AC prepared from coconut-shells by chemical activation.

|  |  |
| --- | --- |
| Parameter | Value |
| Apparent Density (g/m3) | 0.44 |
| Moisture content (%) | 2.1 |
| Volatile matter (%) | 22.4 |
| Ash content (%) | 11.2 |
| Fixed carbon (%) | 64.8 |
| pH | 6-7 |
| Specific surface area (m2/g) | 560 |
| pHPZC | 8.8 |



*FIG. 1: The morphology of the modified activated carbon with phosphoric acid.*

FIG.2: FTIR spectra of AC prepared by chemical activation with H3PO4.

* 1. Speciation of uranyl ion in aqueous solution.

Using VISMINTEQA2 simulation software code to determine uranyl species in aqueous groundwater at equilibrium. The maximum anion concentrations were used at natural pH value 7.8. The species of U(IV) in ground water samples depend on the anion concentration in the groundwater aquifer. The maximum anion concentrations were used at the groundwater samples of the Egyptian rural regions are given by the following; CO32-  ,500 mg/l, PO43- , 1.0 mg/l, Cl- , 160 mg/l , NO2- , 2.0 mg/l and NO3- , 30 mg/l . simulation of U(IV) species, 3.0 mg/l, can be found in solution as:U(HPO4).4H2O and U(OH)2SO4 , UO22+ and uranite species,

* 1. **Sorption studies**
     1. *Effect of dosage weight*

The sorption was found increased by increasing of the dosage weight (Fig. 3) and remained to have a constant value 80 – 82.5 % for U(VI) at the dosage weight ranged between 0.04 to 0.08 g. Therefore 0.05 g is the sample dosage weight is used at all batch experiments.

* + 1. *Langmuir isotherm model*

The linear form of the Langmuir isotherm model for the formation of monolayer adsorption is given by the following equation [16]:

(5)

Where, m is the maximum adsorption capacity, (mg g-1), is the equilibrium ion concentration (mg L-1) and is the Langmuir adsorption constant (L/mg).

* + 1. *Freundlich* isotherm

The linear form of the Freundlich equation was given by the following [17]:

(6)

Where, , (Lg-1) is the Freundlich constant, n is heterogeneity factor .

By plotting Ce/Qe against Ce , straight line was given in Fig.4 The sorption data were fitted both Freundlich and Langmuir isotherms. A high regression coefficient (R2 = 0.975) for the Langmuir isotherm due to the formation of monolayer of uranyl adsorption and the sorption data were also fitted the Freundlich isotherm with high regression coefficient (R2 = 0.9967) . The parameters of the Langmuir and Freundlich sorption isotherms are given in Table 2. The maximum sorption capacity is Qm 60.606 mg/g calculated from the slop of the straight line (FIG.4) using U(IV) concentration ranges 25 to 75 mg/l, application of Langmuir and Freundlich sorption isotherms were used by other studies for the removal of rhodamine B dye from aqueous waste solution by acid activated coconut husk [2].

TABLE2: Langmuir and Freundlich sorption parameters of U(IV) sorption on AC

|  |  |  |  |
| --- | --- | --- | --- |
| Sorption isotherm | Parameters |  | Regression coefficient (R2) |
| Langmuir | *Qm*  60.606 (mg/g) | KL  0.023998 (L/mg) | 0..975 |
| Freundlich | 1/n = 0.817 | *KF* = 1.531 | 0.997 |

* 1. **Kinetic** **studies**

The kinetics of U(IV) adsorption on AC was analyzed using two adsorption kinetic models, these are pseudo first order kinetic model [18 ] and pseudo second order kinetic model [19], the adsorption data obtained in our study were performed using 0.05 g of AC, 100 mg/l U(IV) solution and contact time up to 96 h. Fig. 6 shows the relationship between the sorption capacity (Qt)) at different contact time, the steady state was attained after 48 h.

* + 1. *Pseudo First order kinetic model*

pseudo-first order kinetic (Lagergren) model was given by the following equation:

) = *Qe* – *K1*.t/2.303 (7)

where Qe andQt are amount of the solute adsorbed at equilibrium and after different contact time intervals, t, time (min), and K1 is the Lagergren rate constant (min–1).

The plots of *Log* (*Qe* – Qt ) versus t is given in Fig. (7) for the pseudo first order reaction with the correlation coefficient R2 is 0.935 , *Qe* and *K1* were calculated from the slop and intercept of the straight line plot respectively.

* + 1. *Pseudo second order kinetic.*

pseudo second order kinetic was given by the following equation:

= + (8)

where qe and qt are the amount of iodide adsorbed (mg g-1) at equilibrium and at the time t (min.), respectively, and k2 is the second order rate constant (min–1).

The straight line relationship between t/Qt and different contact time t (h) was given by the straight line (Fig.8) with the regression coefficient of R2 = 0.993 for the pseudo second order kinetic model, therefor the sorption data was fitted to the second order kinetic. The sorption capacity (Qt) of AC was found to be 62.89 mg/g calculated from the slop of the straight line relationship and the rate constant K2 calculated from the intercept of the straight line. Moreover it can be observed that there is a conformance between the maximum adsorption capacity calculated by the Langmuir isotherm and second order kinetic . other studies were applied both Langmuir isotherm model and kinetic reaction on activated carbon for the removal of rhodamine B dye from aqueous waste solution by acid activated coconut husk and other studies [20. 21]

**CONCLUSIONS**

In the present study, adsorption experiments of uranium U(VI) was carried out onto the prepared activated carbon (AC) obtained by chemical activation of coconut shells using phosphoric acid. Characterization of the adsorbent was performed through ash content, fixed carbon, bulk density, FT-IR and SEM morphology. a series of batch adsorption tests were performed. AC could be successfully used for the removal of U(IV) ion from aqueous solutions. the experimental results have been analyzed by the Langmuir and Freundlich sorption isotherms. Sorption of U(IV) could be fitted by the Langmuir sorption isotherm indicating by the formation of monolayer and kinetic data were fitted to pseudo second order kinetic, there was a conformance between the capacity of AC determined by the Langmuir isotherm model and pseudo second order kinetic model, this prepared AC may be used for the removal of uranyl ion from aqueous waste solutions.

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