

Uranium adsorption on modified activated carbon and charcoal and investigation of uranium adsorption chemistry.

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Abstract

In this research the chemistry of surface oxidation of activated carbon and charcoal and its effect on the uranium adsorption were investigated. First, five commonly used oxidants were chosen: H_2SO_4 , HNO_3 , $H_2SO_4-HNO_3$, H_2O_2 , and $K_2Cr_2O_7$ then the surface of activated carbon and charcoal was oxidized by these oxidants and optimum conditions like, the best oxidants, time of reaction and concentration were determined. The results show that surface oxidation changes the surface functional groups such as carboxylic, phenolic and lactonic. These functional groups, especially carboxylic acid, are able to form some complexes with uranyl. These complexes increase the capacity of activated carbon to adsorb ions.

Keywords:

Uranium, Activated carbon, Adsorption, oxidation, Chemical modification.

1- Introduction:

It is obvious that Uranium and its related compounds consist a large amount of nuclear wastes. Uranium mainly exists in two forms in solutions: uranyl (UO_2^{2+}) and uranus (U^{4+}). These ions form large amounts of nuclear wastes [1]. The uranium contents in these wastes is applicable after recycling. Therefore, devising new methods for recycling of uranium from wastes is so crucial. There are a lot of methods have been presented for Uranium recycling such as, precipitation, solvent extraction, ion exchange resins and adsorption methods [2].

For some reasons like, easy handling, low cost and selectivity, adsorption methods are more considered. There are many adsorbents for Uranium recycling but, one of the most prominent of which is activated carbon. Activated carbon has a great affinity to adsorb large varieties of species, specially ions. This ability, for ion adsorption, results from the structure of large aromatic plates with oxygenated functional groups enabling it to adsorb ions. These plates are formed by the condensation of carbonaceous materials in high temperature [3]. These plates also carry some polar functional groups like: carboxyl, phenol, lactones and amines. This results in

an increase in ion chemical adsorption Because, these functional groups are susceptible to form complexes with ions [4].The position of these plates and amounts of functional groups depend on the preparation conditions [5].with some kind of modifications, higher adsorption is accessible. One of this methods is The surface modification of activated carbon which is mainly used to increase the adsorption capacity. One of these modifications is the oxidation of activated carbon with some oxidants. It can introduce some oxygenated functional groups like, carboxyl, lactonesand phenol which form stable complexes with many heavy metals with chemical bonding. As the amount of these functional groups increases, the capacity of heavy metal adsorption increases [5]. The main aim of this research was the study of oxidation effects on the activated carbon and charcoal surface and the relationships between the amount of oxygenated groups and chemistry of adsorption, for this purpose a type of commercial activated carbon and industrial charcoal were selected and some types of oxidants commonly used in industrial chemistry, have been treated with samples [6]. After experiments, the relationship between oxygenated functional groups and uranium adsorption, the optimum concentrations of oxidants, time of reaction, and types of oxidants were studied.

2- Experimental:

2-1- sample preparation

1gr sample was washed throughly with excess amount of hot double distilled water until pH of filtrate remains constant. Then it was dried in the oven at 110 °C for 24h.

2.2. pH measurement:

For all samples, 0.2 gr of dried sample was added to 25 ml double distilled water in 50 ml beaker and it was stirred for 24 hr. then pH with pH meter was determined.

2.3. Measurement of uranium adsorption:

0.100 gr sample was added to a 100 ml beaker and 25 ml 1000 ppm U^{6+} solution was poured. Then 25 ml double distilled water was added and was stirred for 5 hr at room temperature. Then was filtered and the absorbance of remaining uranium was determined with Arsenazo method

2.4. Oxidation of activated carbon and charcoal with oxidants:

100 ml of oxidant solution was added to a 250 ml round bottom flask and 0.500 gr sample was added. It was stirred for 5 h at 90 °C . Then it was cool and 300 ml double distilled water was added to the flask. it was filtered under vacuum and the residue was washed with excess amount of hot double distilled water until the pH of filtrate remains constants then it was dried for 24 hrs at 110 °C. For oxidation with $K_2Cr_2O_7$ and H_2O_2 , 4 ml concentrated H_2SO_4 in 1N

concentration of oxidant was added. And for $K_2Cr_2O_7$ and H_2O_2 , 20 ml concentrated H_2SO_4 in 5N concentration of oxidant was added.

2.5. Base neutralization capacity (BNC):

BNC was determined via the adsorption from aqueous solutions of different bases, namely NaOH, Na_2CO_3 and $NaHCO_3$ onto prepared activated carbon.

In glass bottles 0.1 gr sample in 20 ml (0.4 N) base is shaken for 24 hr then is titrated Vs 0.4 N HCl.

3- Results and discussion:

In this research, five types of oxidants commonly used in industries were selected. Some applications of these oxidants are: removing odors and impurities, degradation of organic compounds, in oxidative reactions, etc. a type of commercial activated carbon was selected and oxidized with these oxidants. Before oxidation, the total amount of functional groups on the surface and other characteristics were determined. Then the activated carbon was reacted with each oxidant separately. Initial concentration was 1M for all oxidants, and the results are shown in figure (1). It is obvious that the sample oxidized by $K_2Cr_2O_7$ in acidic media has the most adsorption. $K_2Cr_2O_7$ results in large amount of uranyl adsorption but, it has some difficulties. Cr is one of the most toxic metals in the environment, working with this oxidant is hard and reaction conditions are out of control. For example, it oxidizes activated carbon severely and decreases the yield. The increase in adsorption is due to the increase of oxygenated functional groups on the surface forming complexes with uranyl ion.

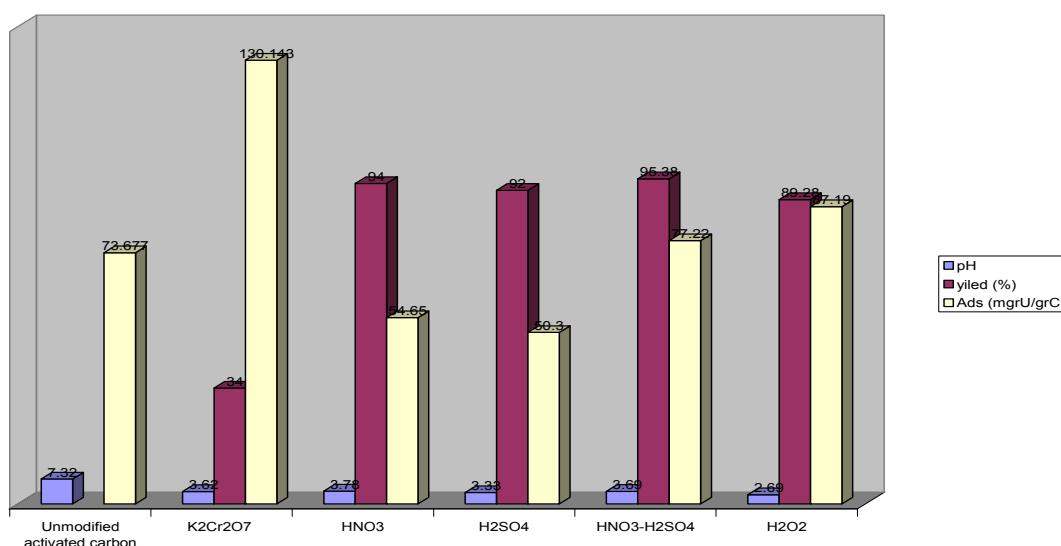


Figure (1): efficiency of some oxidants to modify trade activated carbon

Because the yield and the amount of adsorption are the most important factor, $\text{HNO}_3\text{-H}_2\text{SO}_4$ and H_2O_2 were selected as the best oxidants. They result in high yield and adsorption. In the case of $\text{K}_2\text{Cr}_2\text{O}_7$, the adsorption is high but the yield is low. It is concluded from pH comparison, surface pH has become more acidic than unmodified activated carbon. It shows that, oxidation results in introduction of acidic functional groups on the surface

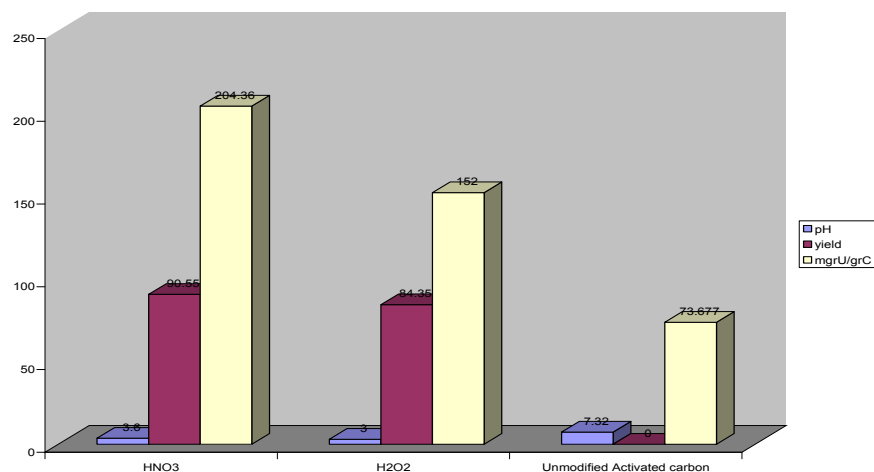


Figure (2): efficiency of two oxidants to modify trade activated carbon

As it mentioned above, two types of oxidants ($\text{HNO}_3\text{-H}_2\text{SO}_4$, H_2O_2) were selected and the reaction was repeated in higher concentration (5M), for all materials, to discriminate between two types of oxidants. The results are shown in figure (2). It is obvious that $\text{HNO}_3\text{-H}_2\text{SO}_4$ system has the best results. Because of the industrial importance of this procedure, the research was continued with one type of industrial charcoal. Charcoal has the similar structure to activated carbon and it is expected to produce similar results like Activated carbon. Furthermore, it is economical to be used the reaction was carried out in 5M $\text{HNO}_3\text{-H}_2\text{SO}_4$ and H_2O_2 with charcoal. The differences between the results for charcoal and activated carbon are shown in table (1).

Table (1): the comparison with oxidation results of trade activated carbon and (Acid = $\text{HNO}_3\text{-H}_2\text{SO}_4$) charcoal with different oxidants

Starting material	pH	% yield	U Ads(mgrU/grC)
Activated carbon (H_2O_2)	3	84.35	152
Charcoal (H_2O_2)	3.41	51.36	175.85
activated carbon (Acid)	3.6	90.55	204.36
Charcoal (acid)	3.54	92.3	183.683

It is obvious that $\text{HNO}_3\text{-H}_2\text{SO}_4$ results in more adsorption and yield in comparison with H_2O_2 . for this reason, other experiments were carried out for charcoal with this oxidant. In

the next step, some experiments were carried out to find the best oxidant concentration. After each experiment the surface functional groups were investigated by boehm titration method[]. The results are shown in figure (3).

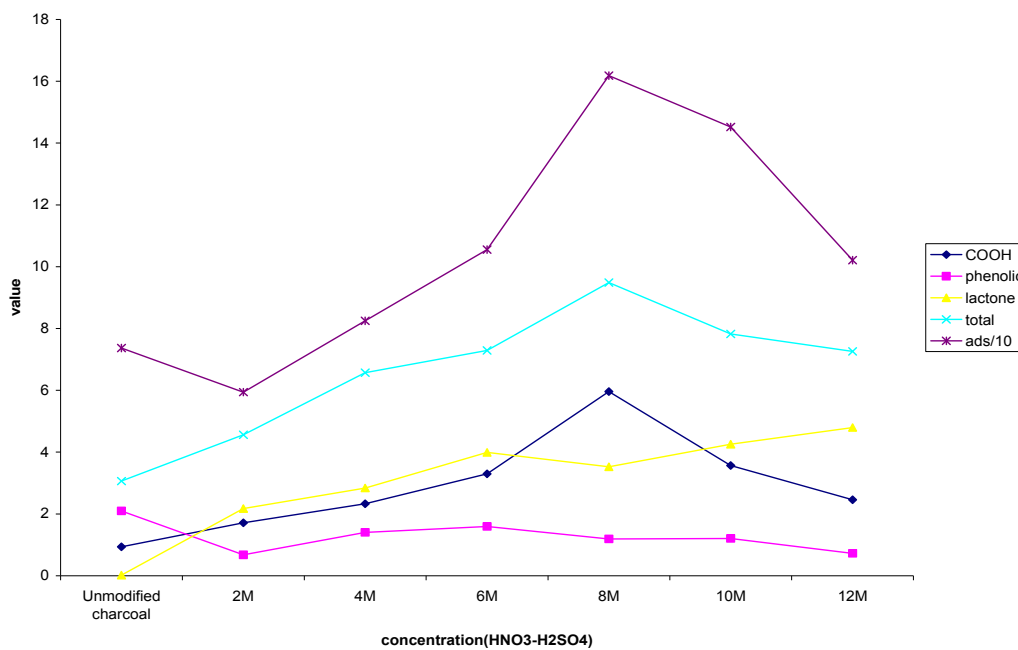


Figure (3): effects of different concentrations of oxidants and amount of oxygenated functional groups and amount of adsorption.

As the concentration of oxidant increases, the amount of total acidic groups and amount of adsorption increases. The maximum adsorption is in 8M concentration of both acids. In higher concentrations, the adsorption and total acidic groups decrease. It is obvious that there are a lot of aromatic plates on the surface of activated charcoal. The edge of these plates is susceptible for oxidation []. In this kind of oxidation, these edges were oxidized to carboxylic groups or other groups. The amounts of these groups depend on the oxidant concentration and distribution of other functional groups. There are three main types of acidic groups on the charcoal surface: carboxylic, phenolic, lactones. These three types of functional groups form chemical bonds with uranium but, the major share is for carboxylic groups. Because uranyl ion can form stable complexes with carboxylic acids, as the amount of these carboxylic acids groups increase, the amount of adsorption increases. Other functional groups like phenolic groups can form some weaker complexes the amount of acidic groups on modified charcoal are more than unmodified one, especially in higher concentration of oxidants. After optimum concentration, the amount of adsorption and total acidic sites especially carboxyl groups are decreased. It is because of the surface decomposition in high concentration of oxidant. In



addition, the increase of lactonic groups indicates the condensation of acidic groups to form lactones. That is decreases the uranium adsorption. For determining the optimum time, all experiments repeated in 8M HNO₃-H₂SO₄ as the optimum concentration, and the optimum time of reaction is determined 8 hrs.

4-Conclusion:

The increase of acidic groups on charcoal surface can increase the amount of uranium adsorption. With chemical or physical activation of charcoal the best result can be achieved. And all parameters such as concentration and reaction time have limited range, upper these limits decomposition of surface occurred and some modification for selective adsorption can be carried out.

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4- References:

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