Removal of Zinc ions from industrial wastewater with wool fibers

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Abstract:

In this research, the efficiency of low-cost unmodified wool fibers were used to remove zinc ion from industrial wastewater. Removal of zinc ion was achieved at 99.52% by using simple wool column. The experiment was carried out under varying conditions of (2h) contact time, metal ion concentration (50mg/l), wool fibers quantity to treated water (70g/l), pH(7) & acid concentration (0.05M). The aim of this method is to use a high sensitive, available & cheep natural material which applied successfully for industrial wastewater& synthetic water, where zinc ion concentration was reduced from (14.6mg/l) to (0.07mg/l) & consequently the hazardous effect of contamination was minimized.

Key words: Ion Exchange, Wool Fibers, Wastewater, Zinc Ions

Introduction:

Nowadays the contamination of water by heavy metals become the concern of the scientific community. These heavy metals can occur from leaching of ore deposits & from anthropogenic source, which include mainly industrial effluent & solid waste disposal. The hazards associated with the contamination of water have led to the development of various technologies for industrial wastewater purification, which include; precipitation, coagulation /flotation, filtration, membrane process, electrochemical techniques, ion exchange, biological process & chemical reaction. The adsorption process with modified wool fibers is attracted by many scientists because of the effectiveness for the removal of heavy metal ions at trace quantities [1-4]. But because of its high cost, the needs for low cost materials as sorbet have been widely used. One of the exploitation is the use of natural low cost materials like wool fibers [5-7]; cotton [8]; onion skin [9]; coffee grounds [10,11]; tea leaves [12]; apple waste [13]; peanut [14]; wheat straw [15]; soybean hull [16] & etc [17-20]. In this research, the keratin wool fibers resin was subjected to remove zinc ion. Wool fibers are highly complex portentous materials of different types of keratin cell [Fig.1] which include eighteen amino acid [Table1] [21]. It consist of three layers, an outer layer, the cuticle with its three subdivision, an inner layer, the cortex which includes semi-crystalline micro fibrils imbeded into the amorphous elastic inter filament matrix & the medulla [Fig.2].

From the previous study we notice that metal ions act on the outer layer of the wool fibers which the last considered a good adsorbent [22-24]. Here in, the need for economical & effective material to remove zinc ion from industrial wastewater has resulted in the search for material like wool fibers that show it usefulness in reducing the contamination of water.

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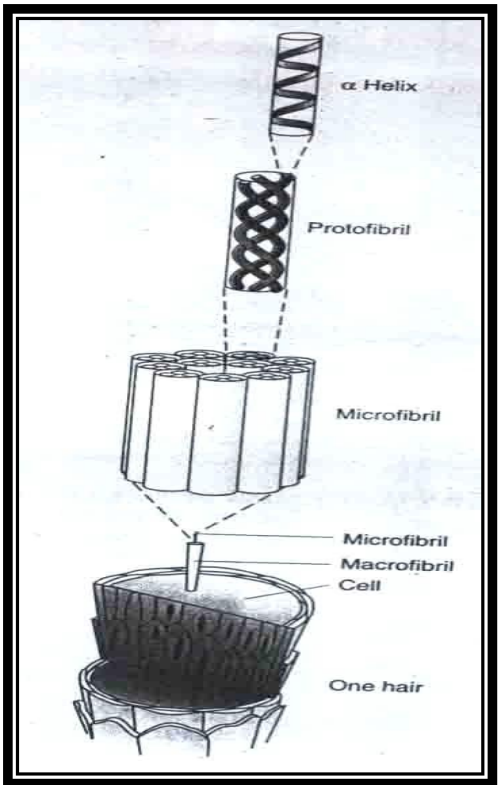

Fig. (1): Structure of α-keratins

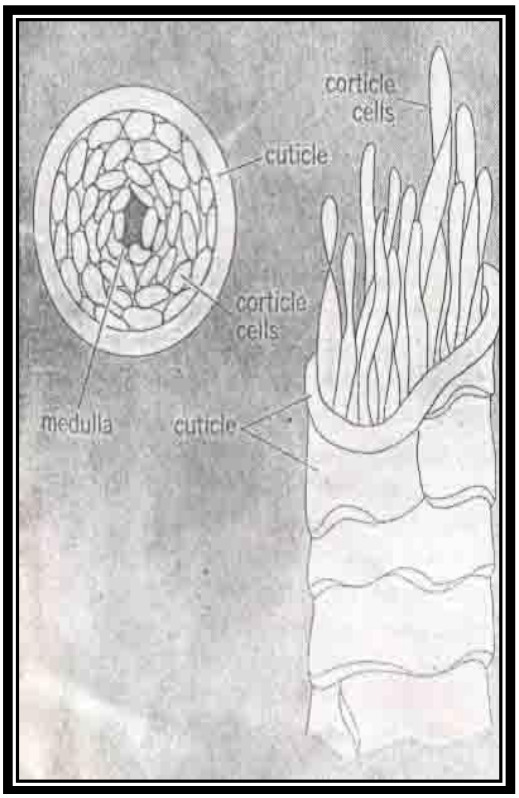

Fig. (2): Cuticle, cortex & medulla of wool fiber

Table (1): Amino acid composition of wool

Amino acid	Approximate percentage present in wool	Grams of residue per 100 g of wool	Grams of side chain per 100 g of wool
Glycine	6.5	4.94	0.09
Alanine	4.4	3.52	0.74
Serine	9.41	7.80	2.76
Proline	6.75	5.69	2.46
Valine	4.72	3.99	1.73
Threonine	6.76	5.54	2.59
Cystine	12.72	10.83	4.89
Leucine	11.3	9.75	4.92
Aspartic acid	7.27	6.28	3.22
Lysine	3.3	2.89	1.63
Glutamic acid	15.27	13.40	7.58
Methionine	0.71	0.62	0.36
Histidine	0.7	0.62	0.37
Hydroxylysine	0.21	0.19	0.11
Phenylalanine	3.75	3.34	2.07
Arginine	10.4	9.33	5.97
Tryosine	5.8	5.23	3.43
Tryptophan	0.7	0.64	0.45
Total Ammonia nitrogen	110.67	94.80	45.37

Material and Methods:

reagents:

Wool fibers were obtained from young sheep (one year old). Sodium acetate & citric acid anhydrous (pH solution) were from CHEM (South Australia). Magnesium chloride, Eriochrome Black-T (EBT) & hydroxyl- amine hydrochloride were from Merck (Germany). The ethanolic solution of Eriochrome Black-T was used as indicators. A (0.01M) solution of the disodium salt of ethylenediamine tetracetic acid (EDTA) was from Fluke & used for titration. Zinc was used as $ZnSO_4.7H_2O$ solution in synthetic water & the industrial wastewater samples were from Al-Noaman Factory (Zafrania).

Resin preparation:

The unmodified wool fibers resins (10-70g/l) were packed as long fibers into seven glass columns of 5cm diameter to 1L length. Each column was washed (4-5) times with demineralized water until it become clean. Then it was washed with ethanol to remove the odor of wool to be ready to use.

Synthetic water preparation:

The synthetic water samples, Zn^{2+}, were prepared from $ZnSO_4.7H_2O$ (10-500mg/l).

Each solution was adjusted by pH (1-9) respectively (pH was measured with a HANNA digital pH meter (Hungary-Europe) HI 9811).

Industerial wsatwater sample:

Industrial wastewater sample is taken from Al-Noaman factory. The concentration of zinc ions in wastewater is (14.6 mg/l). After adjust all the conditions of experiment on synthetic water, we applied the perfect conditions on the sample of Al-Noaman factory.

Ion exchange processs:

After the preparation of the solutions of synthetic water, they were poured in each column separately. Then they left there for a contact time of (0.5-5h). The columns were then rinsed with distilled water. The zinc ion content of the effluent solution was determined titrimetrically by using disodium salt of EDTA & EBT. After that the zinc ion was eluted with acid solution of 100ml HCl (0.05-4M) & the eluting solutions were analyzed.

Analysis of the samples:

The concentrations of zinc ion in both industrial wastewater & synthetic water were analyzed by Atomic Absorption spectrophotometer. (Perkins Elmer (USA) 5000).

The wool fibers structure before & after the ion exchange process was mention in FT-IR spectrum (SHIMADZU- JAPAN 212). Wool fibers sample was taken as a film slid without any additions.

Results and Discussion:

Effect of metal ion concentration:

As shown in (Table2 & Fig.3), at different amount of $ZnSO_4$ solutions from (10mg/l) to (500mg/l), the zinc ion concentration removal was increased to the optimum $ZnSO_4$ solution value at (50ml/g), which led to the maximum removal. It was found that more increasing $ZnSO_4$ solution led to decrease in zinc ion removal, from which the optimum operating condition of each experiment was found to be (50mg/l) $ZnSO_4$ solution. The removal was found to be 99.90%, at operating conditions parameter, pH(7), (70g/l) of wool fibers for (2h) contact time & at (0.05M) acid concentration comparing with the other $ZnSO_4$ solutions.

Table (2): Effect of zinc Ion Conc. In Solution

No. of Samples	$ZnSO_4$ conc.(mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
1	10	0.36	96.4
2	50	0.05	99.9
3	100	8.6	91.4
4	500	400	20

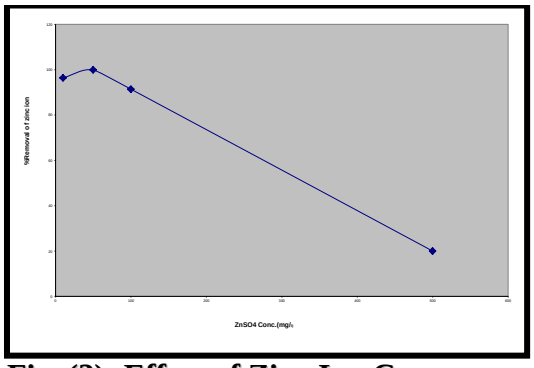

Fig. (3): Effect of Zinc Ion Conc.

Effect of pH parameter:

The pH of a solution is of significance for its effect on the wool fibers & zinc solution. The functional groups of the amino acid of wool fibers are affected by the pH value of the solution. The relation of zinc ion removal as a function of pH was studied at a wide range of (1-9) as shown in (Table3 & Fig.4). This relation can be applied in the operating conditions of (70g/l) wool fibers at a concentration of (50mg/l) with (2h) contact time & (0.05M) acid concentration. It was observed that removal of zinc ion concentration increasing with increasing of the (pH) value, were the maximum removal efficiency can be observed at (99.92%) on pH equal to (7). Increasing of pH above (7) led to decrease in percentage zinc ion removal.

Table (3): Effect of pH

No. of Samples	pH	Initial Zn^{2+} conc. (mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
1	1	50	45	10
2	2	50	40	20
3	3	50	36	28
4	4	50	30.0	39
5	5	50	22	56
6	6	50	14.5	71
7	7	50	0.04	99.92
8	8	50	0.07	99.86
9	9	50	4.5	99.10

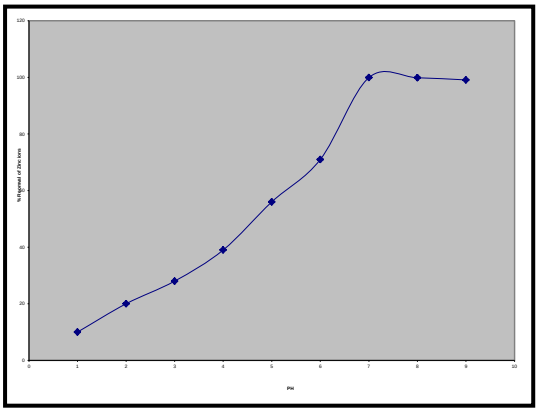

Fig. (4): Effect of pH

Effect of resin dosage:

To study the effect of wool fibers on the removal of zinc ions, different dosage of wool fibers were taken (10-70g/l) at constant pH(7) for 2h in zinc ion concentration of (50mg/l) & acid concentration of (0.05M) HCl. When the wool dosage was increased, the removal percentage was increasing (Table 4 & Fig.5). The complete removal of zinc ions was (99.96%) at wool dosage (70g/l).

Table (4): Effect of Wool Dosage

No. of Samples	Wool dosage(g/l)	Initial Zn^{2+} conc. (mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
1	10	50	8	84
2	20	50	6.2	87.6
3	30	50	4.4	91.2
4	40	50	2.7	94.6
5	50	50	1.45	97.1
6	60	50	4.5	99.1
7	70	50	0.02	99.96

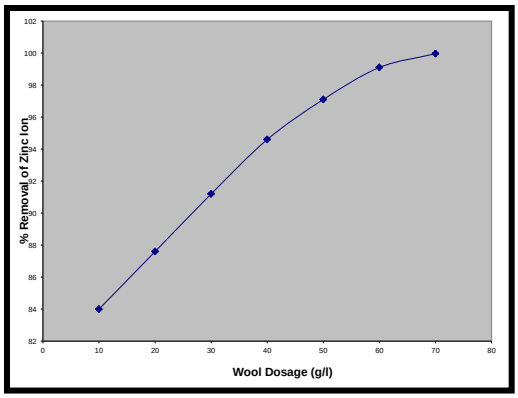

Fig. (5): Effect of Wool Dosage

Effect of acid concentration:

The effect of acid concentration on the removal of zinc ions was carried out on (0.05-4M). The effect of HCl acid on zinc ions & wool fibers is shown in (Table 5 & Fig.6). It was observed that removal of zinc ions decreased with increasing in acid concentration at optimum operating parameter of (70g/l) wool fibers, pH(7) with (2h) contact time & (50mg/l) zinc ions. The maximum

removal efficiency was found to be (99.95%) at (0.05M) HCl concentration.

Table (5): Effect of acid Concentration

No. of Samples	Acid conc. (M)	Initial Zn^{2+} conc. (mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
1	0.05	50	0.025	99.95
2	0.1	50	0.183	99.63
3	0.5	50	0.545	98.91
4	1	50	1.145	97.71
5	2	50	1.84	96.32
6	3	50	2.525	94.95
7	4	50	3.045	93.91

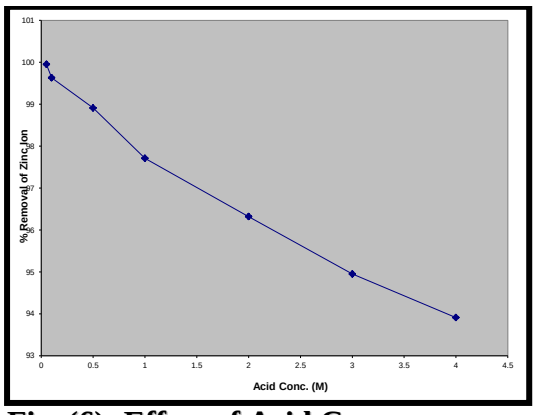

Fig. (6): Effect of Acid Conc.

Effect of contact time:

The removal phenomenon of metal ions is mainly dependent on contact time. The effect of contact time was studied by contacting the wool fibers & zinc solution for times of (1-5h),the results are represented in (Table 6 & Fig.7). Maximum removal of zinc ions (99.44%) occurs within 2h for optimum value of (50mg/l) concentration of zinc ions at pH7 on (70g/l) wool fibers & (0.05M) acid concentration. It was found that it is very important to increase the contact time, because the wool fibers will be toxin with the observe zinc ions from wastewater which leads to necessary process of regeneration of wool fibers media by acid solution of HCl as shown in samples (3,4 and 5).

Table (6): Effect of Contact Time

No. of Samples	Contact time (hr)	Initial Zn^{2+} conc. (mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
1	1	50	4.9	90.2
2	2	50	0.28	99.44
3	3	50	1.45	97.1
4	4	50	2.82	94.36
5	5	50	4.2	91.6

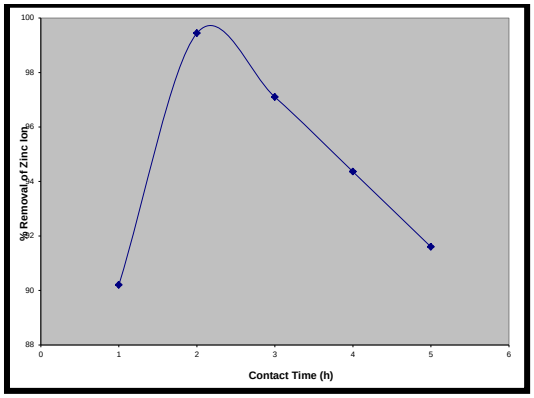

Fig. (7): Effect of Contact Time

Analysis of the wastewater samples:

From the results of preliminarily experiments to determine the optimum operating conditions of zinc removal on synthetic water, it was observed with $ZnSO_4$ concentration (50mg/l), pH(7) , wool fibers dosage (70g/l), acid concentration (0.05M) & (2h) contact time, the maximum removal of zinc ions from industrial wastewater was (99.52%) as shown in (Table7) . The experiments were conducted under the same conditions as in the ion exchange process by using synthetic water of $ZnSO_4$. $7H_2O$ solution.

Table(7):Analysis of the wastewater sample

Factory	pH	SO_4 (mg/l)	Pb (mg/l)	Cl (mg/l)	Initial Zn^{2+} conc. (mg/l)	Final Zn^{2+} conc. (mg/l)	Removal of Zn^{2+} (%)
Al-Noaman	6.7-8.5	280	0.01	193.5	14.6	0.07	99.52

Relationship between the zinc ion behavior and the wool fibers structure:

Wool fibers are composed of eighteen amino acids as shown in Table(1). Amino acids can be classified into polar & non polar amino acids. Wool fibers contain (32.33%) non polar amino acids, (41.19%) polar with uncharged side chain (R) group, (22.54%) polar with negative charged (R) group & (14.61%) polar with positive charged (R) group. The FT-IR spectra of wool exhibit absorption bands associated with their characteristic amide group, the structure unit common to all molecules of this type is present in the peptide linkage which the last conjugated one amino acid by another . An isolated planar amide group give rise to four in plane modes (Fig.9). The in-plane modes are due to C=O stretching, C-N stretching, N-H stretching & O-C-N bending. The most useful FT-IR band for the analysis of the secondary structure of protein (wool fiber) in aqueous media which occurs in 1666.38 cm^{-1} is represents 80% of the C=O stretching vibration of the amide group, coupled to the in- plane N-H bending modes. The exact frequency of this vibration depends on the nature of the hydrogen bonding involving the C=O & N-H groups, & this was determined by the particular secondary structure adopted by the wool protein. Proteins generally possess a verity of domains containing polypeptide fragments in different conformations. As a consequence, the observed C=O amide band is usually a complex composite, consisting of a number of overlapping component bands representing α- helices, β-structures, turns & random structures. The second important band is N-H bending that occur at 1519.80 cm^{-1} & 748.33 cm^{-1}. Secondary amides in the trans-configuration exhibit two characteristic bands at (3217.04 & 3093.61 cm^{-1}). The band is due to the stretching mode of the N-H bond, which is hydrogen bonded. Other bands represent the C-N stretching at 1288.36 cm^{-1} & O=C-N bending at 678.90 cm^{-1} In addition, the FT-fibers must be considered IR contributions of the side chains of the amino acids which form the wool. The characteristic side-chain FT-IR frequencies of amino acid can be expressed in O-H deformation of CO_2 asymmetric stretching of Glutamic acid that exist in 1519.80 cm^{-1}, NH_3 deformation of lysine that appears in 1666,38 cm^{-1}, NH_3 rocking of Arginine can be exist in 1010.63 cm^{-1}, ring vibration of Phenylalanine at 702.04 cm^{-1}, & C-S stretching of Cystine which occurs in 586.32 cm^{-1}.These results suggest that biological active component of the side-chain for the amino acid in wool fiber such as polar uncharged Serine & Cystine , polar Glutamic acid with negative charged (R) group , polar lysine & Arginine with positive charged (R) group & the non polar Phenylalanine contributed to the removal of zinc ion from industrial waste water[25,26].

Conclusions:

- This method has the advantages of simplicity & rapidity in removal of zinc ion from wastewater.
- Wool fibers can be used in the wastewater treatment process as a good resin compared with the expensive modified resins.
- The experiment is applicable to select the optimum operating condition to remove the zinc ions dissolve in wastewater. These optimum condition is (500mg/l) concentration of $ZnSO_4$, pH value (7), (0.05M) acid concentration and (70g) wool fiber dosage with contact time of(2h).

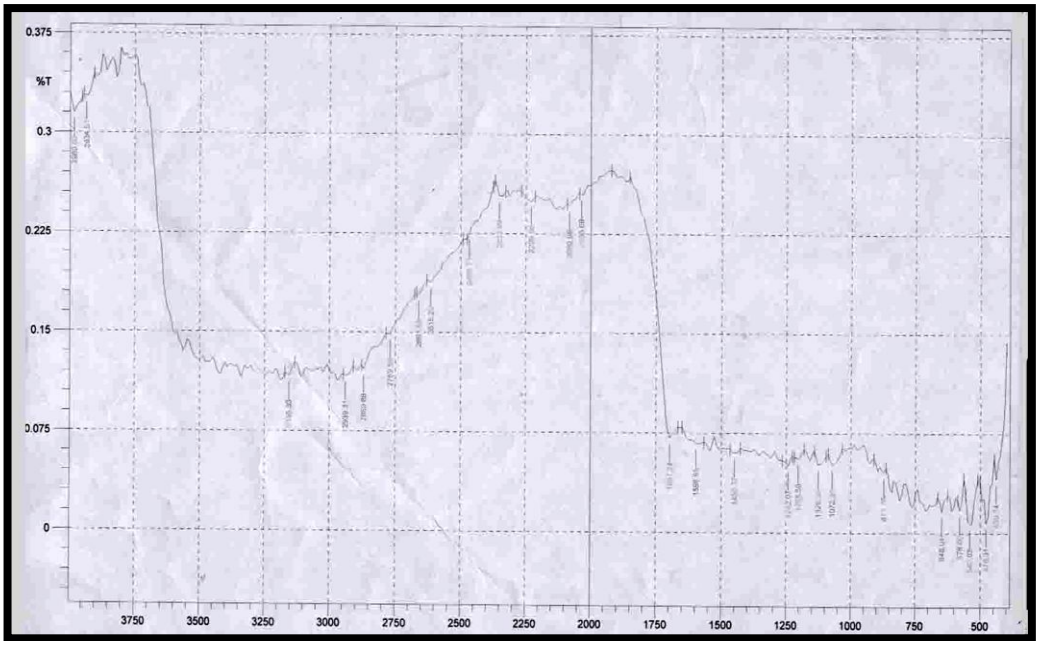

Fig.(8): FT-IR SPECTRUM OF WOOL FIBER BEFORE ION EXCHANG PROCESS

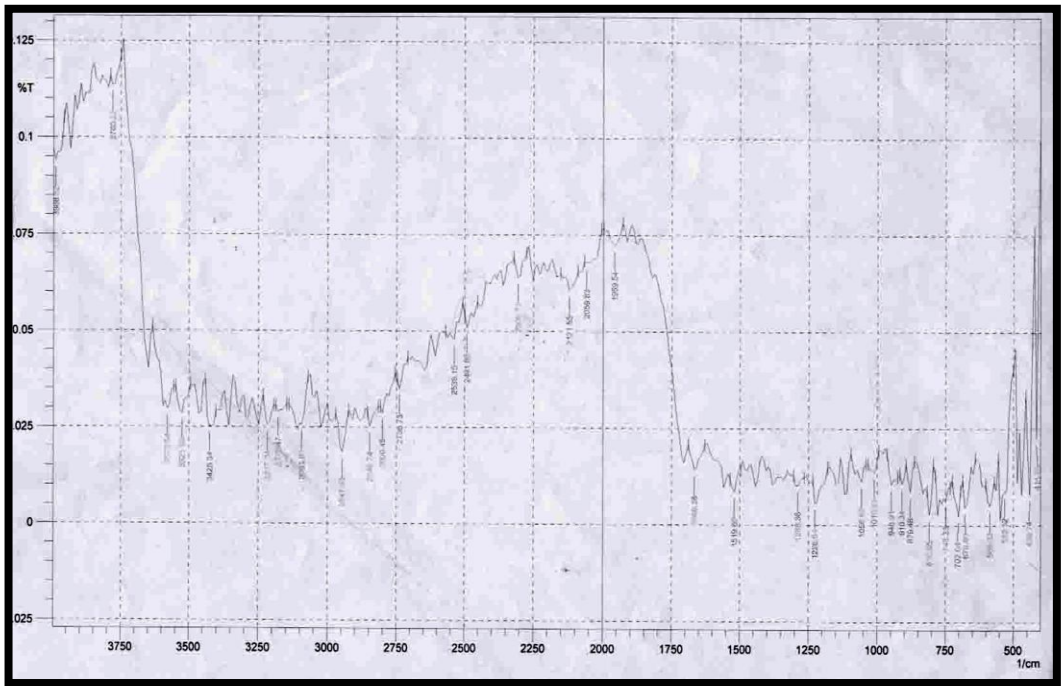

Fig.(9): FT-IR SPECTRUM OF WOOL FIBER AFTER ION EXCHANG PROCESS

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ازالة ايونات الخارصين من مياه المجاري الصناعية بواسطة الياف الصوف

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الخلاصة:

في هذا البحث، تمت الاستفادة من كفاءة الياف الصوف غير المحسنة واطئة الكلفة لازالة ايون الخارصين من مياه المجاري الصناعية. تم ازالة ايون الخارصين بنسبة 99.52% باستخدام عمود الصوف البسيط. تم تنفيذ التجربة عند ظروف مختلفة، حيث ان زمن الاستبقاء (2 ساعة) وتركيز ايون الخارصين (50 ملغم/لتر) وكمية الياف الصوف الى الماء المعامل (70 غم/لتر) والدالة الحامضية(7) وتركيز الحامض (0,05 مولاري). ان الهدف من التجربة هو استخدام مادة طبيعية رخيصة الثمن ومتوفرة بكثره و ذات حساسية عاليه للايونات والتي تم تطبيقها بنجاح على مياه المجاري الصناعية والمياه المصنعة، حيث تم تقليل تركيز ايون الخارصين في هذه المياه من (14.6 ملغم/لتر) الى (0.07 ملغم/لتر) وهكذا تم خفض مستوى التلوث.