Biosorption of Vanadium ions from aqueous solution by acid modified and unmodified sour orange peels

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ABSTRACT

Biosorption can be used as a cost effective and efficient technique for the removal of toxic heavy metals from wastewater using waste biomass derived from industries such as food processing. This study aimed to remedied vanadium (IV) ions from aqueous solution by batch adsorption system using both modified and unmodified sour orange peels (SORP) with a comparative investigation study. Optimization of Biomass, Time, Temperature, pH and Initial concentration parameters leads to the following results: metal ions adsorption onto the SOR biomass was established within 120 minute. The optimum pH for the metal binding to the biomass was found at pH=2, corresponding to the room temperature of $25C^{0}$, while maximum uptake was observed using an initial concentration of Vanadium equal to 100 ppm and 2gm of SOR biomass. These results indicate that modified and unmodified SORP sorbed more than eighty three percentage of the Vanadium ions. Confirmation of heavy metal ions binding with MSORP and UMSORP was achieved using Fourier Transform Infra Red Technique. Due to their low cost, good uptake capacity, and rapid kinetics, sour orange biomass is a promising biosorbent material warranting further study to release the environment from heavy metals contamination.

INTROUDACTION

Vanadium is a trace element of highly critical role in biochemical processes and of significant importance in environmental, biological and industrial analysis due to its toxicity [1].Vanadium has a rich chemistry mainly due to its complicated transitional chemical behavior and to its easy redox changes, both attributed to its mobile d electrons [2].

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Substantial amount of Vanadium is release to the environment mainly from the burning of fossil fuels, production of steel and the manufacture of pigments and paints[3],but unlike organic pollutants, Vanadium is not biodegradable and it may collect in certain ecosystems to the level which consider toxic to living organisms[4].Once consumed ,vanadium is stored primarily in fatty tissues, with the remaining amounts stored in the kidney,liver,spleen or bone, this element has both beneficial and detrimental properties,wherase vanadium exposure in a trace amount is essential in normal cell growth, inhibition cholesterol synthesis and increasing the oxidation of fatty acid [5],but chronic exposure up to exceed the tolerance level leads to sever health effect including nervous depression,coughing,vomiting,diarrhea,anaemia and lung cancer[6].In view of crucial role in different occupational hygiene, environmental science, toxicology and pharmacology fields, many types of adsorbents have been developed and tested for the recovery of vanadium from aquatic system[7,13].

Agricultural waste or by-products as biomass adsorbent have been investigated for bioremediation of heavy metals ions regarding to its capacity to bind and concentrate heavy metals from waste water streams by purely physic-chemical pathways(mainly adsorption)[14].However, using untreated agricultural waste or by-products as adsorbents can also bring sever problomes,such as low adsorption capacity, high chemical oxygen demand(COD) ,and biological chemical demand(BOP)as well as total organic carbon(TOC),due to the release of soluble organic compounds contained in the plant material into the solutions, the increase of COD,BOD and TOC can cause depletion of oxygen content in water and then threaten the aquatic life[15]. Literature has shown that metal ions affinity to biomass can be improved by its pretreatment with alkalis,acids,salts,detergents,and heat to increase the amount of metal absorbent[16].

The present communication reports the removal of pollutant Vanadium ions using Sour orange peels ,which has not been yet studied extensively[17,18]conducting the effect of biomass, contact time,temperature,pH and metal ions concentration to optimum the removal percentage of vanadium ions .

MATERIALS & METHODS

1-Chemicals and Reagents: All reagents and chemicals used in the present study were of analytical reagent grade including (Vanadyl sulphate,HCl, NaOH, HNO_3).A solution of 1000 mg/L of Vanadyl sulphate was

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prepared by dissolving the salt in deionized distilled water. The stock solution was diluted to prepare working solutions.

2-Original Sour orange peel (SORP): Samples were obtained from clean area far from those may be industrially polluted located in Baghdad, Iraq harvest in the year 2013.Samples were washed with deionized water, dried at room temperature, cut into small pieces ,blended, and sieved through a 250µm mesh size producing untreated Sour Orange peel(Untreated SORP).

3-Chemically Modified Sour Orange Peel (MSORP) or protonated peel: The Sour orange peel was activated by soaking 40 gm in 1000 ml (0.1 N) HNO3 overnight at room temperature. This was followed by washing the samples thoroughly with deionized distilled water .The samples were then filtered, air-dried and kept for the adsorption experiments.

4-Analytical methods:

A-Determination of Vanadium contents or concentration:

After biosorption,biosorbents were separated from the solution by sieving through a (CNABO 44-Q, China) filter paper (No.18.0 cm) filter paper and the filtrated were subjected to residual vanadium concentration determination. The vanadium concentration was analyzed by Shimadzu(AA-680) Atomic Absorption Spectrometer supplied with graphite Furnace atomizer type Shimadzu(GFA-graphite Furnace atomizer 4A) and determined mathematically using the equation below:

$$Removal\% = \frac{C_\circ - C_e}{C_\circ} *100$$

Where $C_\circ$ and C_e are the initial and equilibrium concentrations of V(VI) ions in solution (gm/L), and the amount of V(VI) ions adsorbed (qe in mg/g) was calculated as follows:

$$Q_e = \frac{(C^\circ - C_e)V}{m}$$

Where V is the volume of solution (L) and m is the mass of adsorbent (g).This test was performed in Ibn-Sina company,Baghdad,Iraq.

B-FT-IR characterization of UMSORP and MSORP

Samples of Orginal, protonated, and protonated Sour orange peel loaded with vanadium were characterize by a FT-IR spectrophotometer (830-Shimadzu spectrophotometer).The samples were grounded well to make KBr pellets under hydraulic pressure of 400 Kg/cm^2 and spectra were

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recorded in the range of 400-4000 cm^{-1}.In each scan, the amount of the sample and KBr were kept constant in order to know the changes in the intensities of characteristic peaks with respect to the structural changes. This test was performed in the university of Al-Mustansiriyah, College of Science, Chemistry Department.

C-Batch Biosorption Experiments

I-Effect of contact time variation:

One gram of SORP powdered samples were taken and shaken with fifty cm^3 of a metal ion solution whose concentration was 100 mg.cm^{-3} at various contact time intervals of 30 to 120 min. at 25 C°.At the end of each contact time the concentration of metal ion in simulated wastewater filtered and analyzed by Atomic Absorption Spectrophotometer.

II-Effect of Temperature variation:

The ideal Temp. was determined by varying the Temp. from (25-65)C° for five plastic stopper bottles containing 50 ml metal ions concentration of 100 mg.cm^{-3} for90 minute.These samples were shaken, filtered and residual metal ions concentration analyzed using Atomic Absorption Spectrophotometer.

III-Effect of Biomass variation:

For this experiment four plastic stopper bottles were prepared with the following amount of dry biomass(0.5,1,1.5,2) gm ,to each bottle it was added 50 ml of vanadium ions solution in a concentration of 100 mg. cm^{-3}.The bottles were shaken in a rotary shaker at pH=2 for 90 minute. Consequently the equilibrium concentration of Vanadium was determined by AAS.

IV-Effect of pH variation:

For optimum pH biosorption of vanadium by SORP, a study carried out ranging the pH from (1-6) by drop wise addition of 1M HCl and 1M NaOH using a pH meter (WTW Terminal 740,Germany) for six bottles containing one gram of SORP, fifty cm^3 of 100 ppm metal ions, which were incubated in a thermostatic rotary machine (BS-11).for 90 minute. Finally the samples were analyzed.

V-Effect of Metal ions concentration variation:

In order to determine the effect of metal ions concentration,50 ml of various concentration ranging from(25-150) mg.cm^{-3}were prepared in five bottles for vanadium fromVO(SO$_4$).H$_2$O.One gram of the adsorbent was added to each bottle, agitated for90 minute,pH adjusted to 2,and analyzed by Atomic Absorption Spectrophotometer.

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Unmodified and modified Sour orange peel was examined for each Batch Biosorption Experiment.

RESULT and DISCUSSION

A comparison between modified and unmodified sour orange peel vanadium ion adsorption for biomass, contact time, temperature, pH, and initial concentration effects are illustrated in Fig(1,2,3,4 and 5)while Fig(6,7 and 8) demonstrate the FT-IR before and after modification with acid media.

Variation Optimization:

1-Effect of Biomass:

as can be concluded from Fig(1)the removal percentage of V (IV) is increased with increasing adsorbent biomass until the surface became saturated and further increase leads to a decrease in removal percentage. The increase was highest with (1 gm) for both modi. And unmodi, this can be explained by a greater availability of exchangeable sites or surface area at higher amount of the adsorbent [19].
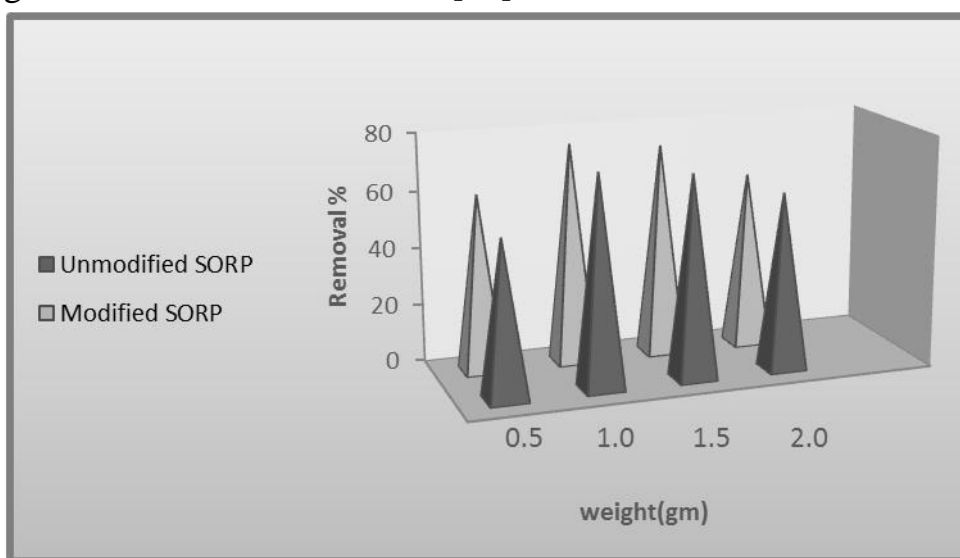

Fig (1): Trend of Percentage V(IV) ions adsorbed by different biomass of Nitric acid modified and unmodified Sour orange peels.

2-Effect of Contact time:

The effect of the contact time on the adsorption of V (VI) ions by both unmodified and modified SORP is presented in Fig (2).The results show that for initial metal ion concentration of 100 ppm, there was an increase in the amount for metal ions bound as the contact time increased for both mod. and unmodi. Substrate. After the contact time of (90 minute), as the time increased further, the amount remained steady. This means that

equilibrium was reached at (90 minute), and the adsorption sited became saturated to maximum uptake capacity[20].
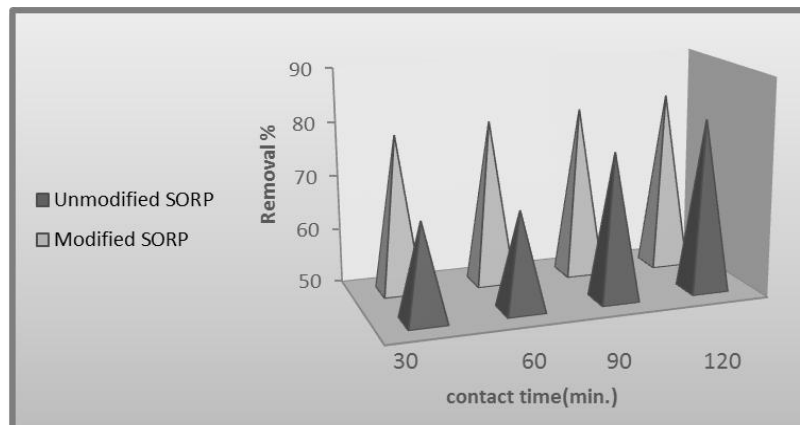

Fig (2): Trend of Percentage V(IV) ions adsorbed by different contact time of Nitric acid modified and unmodified Sour orange peels.

3-Effect of Temperature:

There was a plateau in per cent adsorption with increase in temperature of the aqueous solution. Vanadium adsorption plummeted from 83.57 to 80.86 % by UMSORP in contrast with MSORP which ranged from 84.49 to 81.01 % as the temperature was increased from $25C^0$ to $65C^0$. This is because increasing the temperature will lead to the attractive forces between biomass and metal ions becoming weaker thereby leading to sorption decreses.Also at high temperature, the thickness of boundary layer decreases due to the tendency of the metal ion to escape from the biomass surface to the solution phase which result in a decrease in adsorption as temperature is increased [21].
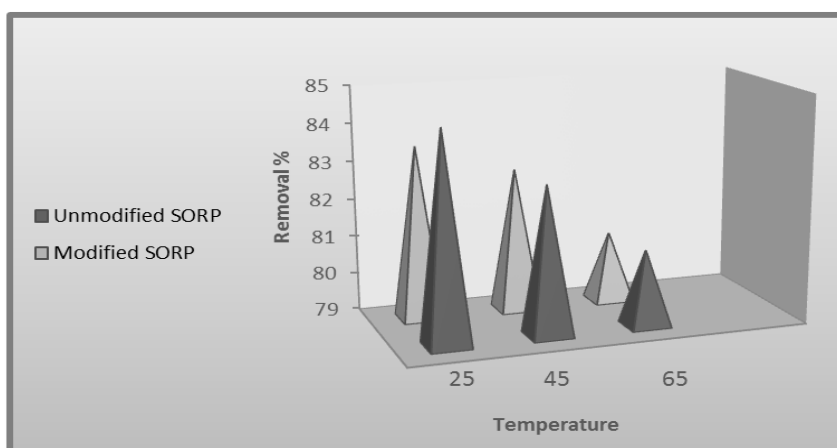

Fig (3): Trend of Percentage V(IV) ions adsorbed by different Temperature of Nitric acid modified and unmodified Sour orange peels.

4-Effect of pH:

The value of (pH=2) was established as the optimum pH for vanadium biosorption by modi and unmodi. SORP as can be seen from Fig(3).Increasing pH values leads to a decline in adsorption capacity, the reason for this trend is due to vanadium chemistry, correlating ionic forms,pH and concentration. At basic pH the anionic form begin to be formed, such as $VO_3(OH)^{-2}, V_3O_4^{-3}, V_{10}O_{27}(OH)^{-5}$ etc.,while at acidic pH range between(1.0 to 4.0) the cationic form predominates, as well as the neutral form[22],the distribution of species of Vanadium in solution is therefore highly dependent on this parameter ,It is thus important to work in the acidic pH so that, in solution, positively charged species occurs and bioremediation can take place.
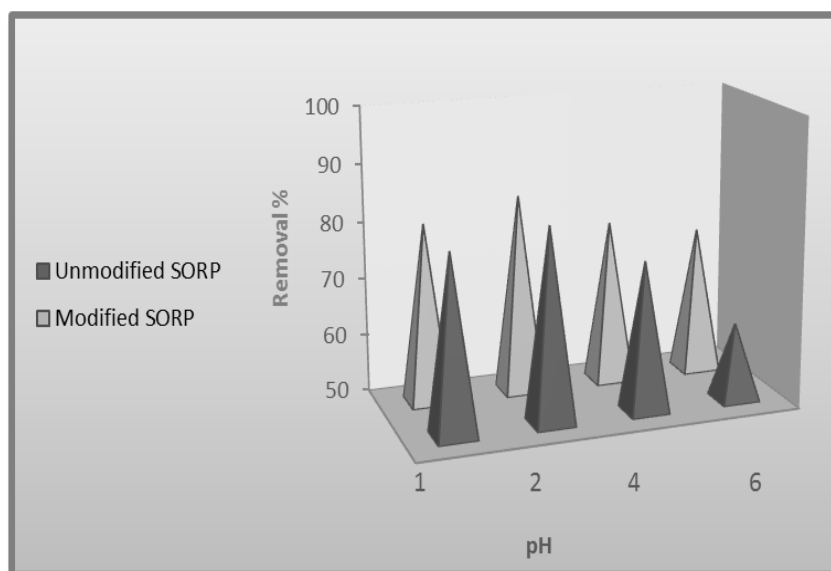

Fig (4): Trend of Percentage V(IV) ions adsorbed by different pH of Nitric acid modified and unmodified Sour orange peels.

5-Effect of Initial concentration:

The initial concentration of metal ions is an important factor for effective biosorption.Fig (5) shows that increasing the concentration of vanadium in the solution is expected to result in the increase of biosorption until the saturation of biomass is attained. A maximum value of removal percentage was observed with a concentration of 100 ppm; this might be due to the saturation of binding sites and increase in the number of ions competing for the available sites in the biomass for binding of vanadium at higher concentration [23].
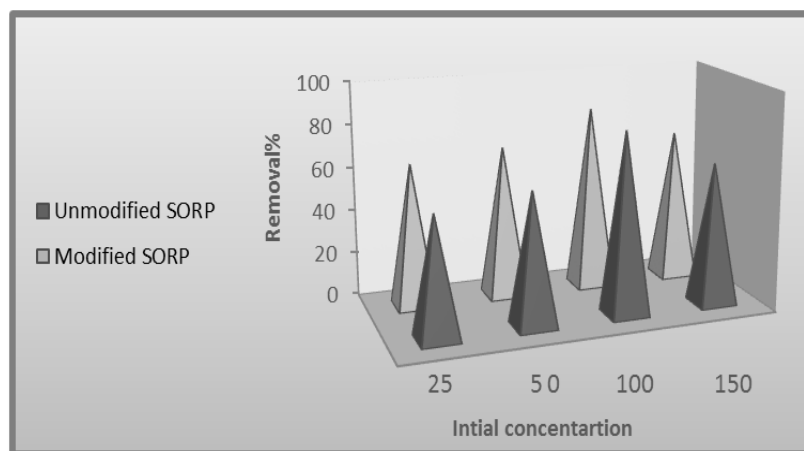
Fig (5): Trend of Percentage V(IV) ions adsorbed by different initial concentration of Nitric acid modified and unmodified Sour orange peels.

FT-IR characterization:

Pectin, anionic plant cell wall polysaccharide based on α-(1-4) linked D-galacturonic acid [24], which contains carboxyl, and hydroxyl groups as an important sites for sorption due to their attraction the positively charged metal ions and binding occurs.Thus,metal ion binding to the biomass is in essence an ion-exchange mechanism which involves electrostatic interaction between the negatively charged groups in the cell walls and metallic cations.In an attempt to gain an insight into the mechanism of V(IV) binding by the SORP ,FT-IR spectra for original,protonateted SORP before and after vanadium ions binding were recorded as shown in Fig(6,7,8).These spectra showed the characteristics peaks in agreement with the presence of O-H broad peaks (3417.98cm^{-1}), alkyl C-H (2924.18cm^{-1}), C=O bond of carboxylic acid and COO^{-} carboxylate ion stretching bond (1734.06,1612.54cm^{-1}), and C-O stretching of carboxylic acids and alcohols (1057.03cm^{-1}).It can be conclude that overall weakening intensity of peaks indicated that the functional groups mentioned above are involved in the adsorption of vanadium onto the biomass.
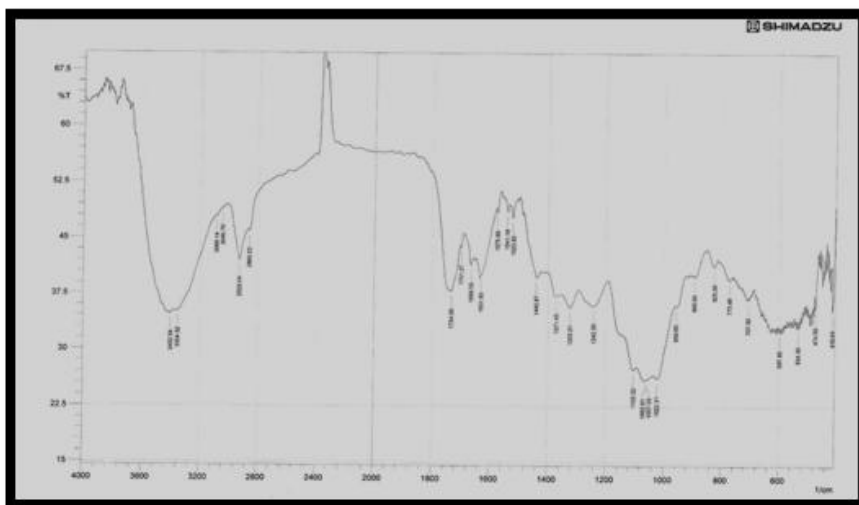
Fig (6): Unmodified SORP FT-IR chart
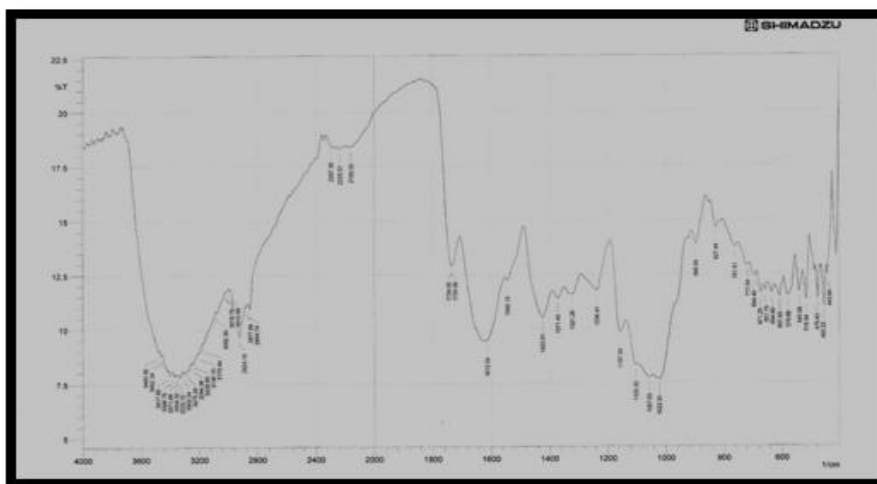
Fig (7): Modified SORP FT-IR chart
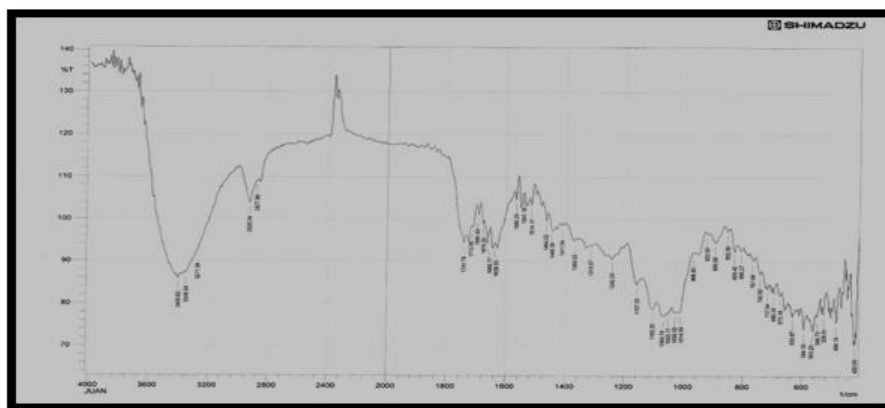
Fig (8): Modified SORP after biosorption FT-IR chart

Conclusion:

The ideal metal ion removal should be not only suitable, appropriate and applicable to the local conditions,but also able to meet maximum contaminant level standards established, this results in biosorption being considered as an alternative technology for trace metal remendation.Therefore in this paper SORP was used to remove vanadium ions from wastewater under optimum conditions(Biomass(1 gm),time(90 minute),Temperature(25 C^0),pH(2), and initial concentration(100 ppm)) using Biosorption technology ,this is regardless the SORP is in the modified or unmodified form, however the modified SORP showed an enhanced level of metal ion adsorption as compared with the modified type.

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امتزاز ايونات الفناديوم من المحيط المائي بواسطة قشور النارنـج المحورة والغير محورة.

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<div align="center">

جوان عدي عبدالستار   اروى محمود حسين   هند احمد

كلية العلوم / قسم الكيمياء / الجامعة المستنصرية

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الخلاصة

تم الاستفادة من فعالية تقنية الامتزاز لازالة العناصر الثقيلة من النظام المائي بأستخدام مخلفات من صناعات مختلفة مثل صناعة الغذاء ،بتطبيق تقنية الدفعات لكل من قشور النارنج الغير محورة والمحورة بحامض النتريك لازالة عنصر الفناديوم الملوث.وتم الحصول على النتائج التالية: زمن الامتزاز الامثل(١٢٠ دقيقة)،الدالة الحامضية (٢)،بينما درجة الحرارة الامثل (٢٥درجة مئوية) والوزن الامثل (١ غرام) واما التركيز الابتدائي لافضل نسبة ازالة فهو (١٠٠ جزء في المليون).كما وتم تشخيص المجاميع الفعالة المرتبطة مع ايون الفناديوم عن طريق استخدام تقنية تحول فورييه للاشعة تحت الحمراء.أستنادا الى الكلفة القليلة،نسبة الازالة الجيدة والحركية السريعة امكن اعتبار قشور النارنج كسطح ماز لتخليص البيئة من التلوث الناتج من العناصر الثقيلة.

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