Removal chromium (VI) from water by magnetic carbon nano-composite made by burned straw

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Abstract. Magnetic activated carbon Nano composite was made by burning Gundelia tournefortii straw in a simple and inexpensive method. Effects of the magnetic activated carbon Nano composite on Chromium (VI) adsorption from water was measured in terms of various parameters. Adsorbent has been characterizing by FTIR, VSD, UV, SEM and XRD studies. Adsorption practical carried out systematization by batched practical in investigating the influence of differentiable factors, as such as absorbent dose, Chromium (VI) concentration, pH, contact time and temperature. Our results show that the prepared Nano composite is ferromagnetic and the optimal condition for removing obtained as follows: 50ppm concentrations, pH=5, 0.03 gr of adsorbent dose and 25°C temperature. We show that activated carbon magnetic Nano composite can be used as a potential absorbent for removing Chromium ions from water. The cleaning solution of synthetically waste of water possesses had been a successful performer by swift removals via chromium (VI) through Artichoke Straw particle from aqueous sol.

Keywords: Magnetic activated, carbon Nano composite, Gundelia tournefortii, Chromium (VI), adsorption.

1. Introduction

Heavy metallic ionized have a lethal effect on all formats of lifelong and these entering the food chain reaction through the disposal of wastes channelizing [1]. The various metal ions, lead, mercury, cadmium and chromium (VI) are in the top of toxicities listing [1]. Contaminants of water via toxic heavy metals through during the discharge of industrial waste water are worldwide of environmental problems. Rapid of industrialization has seriously of contributing to release of toxic heavy metals in the water stream. In order that configuration of ecological detoxification, different mechanism such as adsorption, sedimentation, ion exchange, reverse osmosis, electrochemical therapy, overlay filtering, vaporization, pontoon, corrosion and biosorption operation are applied extensively [2].

Waste water that much more industries, such as metallurgical, tannery, chemical, mining, and battery manufacturing industries, containing more than these toxic heavy metals. The concentration of metals is sometimes higher than the permissible discharge level in affluence [3]. The solutions not only cause environmental pollution and adverse of affected aquatics and humanness life, if so concentrating that particles are the level of top in pollution standard. Some advantages of using plants waste for wastewater processing includes the technique of suppleness, the little requirement of processes, good behaviour adsorption of capacitance, adsorptive selectively metal ions of heavy, low priced, availabilities of free and easy regeneration [4]. Anyway, applications plants wastes without treatment as adsorbents causes problems severally such as, little adsorption capacitances, increase chemically oxygen demanded (COD) and biologically chemical demanded (BOD). Chromium is an active redox of element, with statement of oxidation between “−2 to +6”, but only the “+3 and +6” state have prevalently in solutions of aqueous [5]. Hexa of Chromium has high toxicant pollutants generates from many sided industrial procession, for example, manufacture pigmentation in paint, ink, and plastic, anti-corrosive agencies in protectively coating, and in chrome plating, leather tanning, [6-7]. “This refers to the risk of developing lung cancer increases with amount of hexavalent chromium inhaled and the length of time the worker are
Exposed" [6-8]. Strong exposures to Chromium (VI) cause cancer in the digestive tract, lungs, epigastria pain and nausea [8]. It is urgent to clear Chromium (VI) from effluents to reach the industrial effluents standardization before its discharge into the environmental [9].

Straw Artichoke (GS) formally known as composite, this family is mostly composed of herbs that reside in temperate zones [10]. This is one of the largest families as it contains more than 25,000 species acharacteristic that is knowing from that group exists the presence of reverse, alternative sheets [11-13]. The buds of these organisms obtain a composite, which indicates that people do produce up of single buds. [12].

Aim of this study to build a magnetic Nano composites activated carbon for quick and easy separation of iron salts using Straw Artichoke hexa Chloride in addition to, production a new anionic absorbent and its effect on the removal Chromium (VI) from aqueous solution was conducted. Adsorption of Chromium (VI) of aqueous solvents undergone to the various dynamic and equanimity conditions must be investigational in part in the existing studying.

2. Materials and Techniques

2.1. Modified Straw Artichoke (GS)

Straw Artichoke (GS) collected from the mountains of Taqe Bostan (the city of Kermanshah, Iran), using distilled water washed for 24 hours at a temperature 60 °C in oven dried, then straw, dried (ratio 2 = 3FeCl / GS) in a solution of 96 percent ethanol and O2H6.3FeCl was placed for 24 hours. The solution was diluted to the required concentration for experiments. Then a good piece of straw was cremated with fire, and to get powder.

2.2. Batch Adsorption Tests

The adsorption experiments were carried evaluating the effect of pH, contact time, adsorbent dose and metal ion concentration [15], batch adsorption studies were performed by mixing 1250 mg/L Kr2Cr2O7 obtained made via dissolving amount during deionized H2O 100 mL so become standard liquid. All desired chromium (VI) experiments were obtained from concentrations by dilutions of the stock solution. The adsorption balance experiments were conducted in thermostatic thermostat controller working at 200 rpm. Experiments were conducted by contacting the adsorbent of 2-10 mL of chromium solution (VI) in 10-100 ml of plastic bottles placed in a shaker at 100 rpm for two hours. The effect of pH on chromium (VI) was studied from removal by artichoke by changing the pH solution from 2.03 to 11.02. The initial concentration of chromium solution (VI) was 100 mg / L, and the pH solution was adjusted either 0.1 mL hydrochloric acid, 0.1 mL NaOH. Chromium and iron concentrations were measured by atomic absorption (UV). All experiments were done in two versions and the mean values were reported. The removal efficiency of Cr (VI) (removal %) was calculated using equation pH using Equation 2.1[12-14]:

\[
\text{%removal} = \frac{C_o - C_e}{C_o} \times 100
\] 

Where,

\(C_o\) : the initial equilibrium of concentration Chromium (VI).
\(C_e\) : the final equilibrium of concentration Chromium (VI), in mg/L.

Initial Chromium (VI) concentration was variedly from 10 - 100 mg/L, and a solution pH was kept at 2.03. stability of ability sorption was restricted using the Equation 2.2 [16-17]:

\[
q_e = \frac{C_o - C_f}{m} \times V
\]
Where,

$q_e$: stability value of Cr (VI) adsorbed through a unit quantity of adsorbent (mg/g),

$V$: volume (L) of a sample. The competitive influences of different to coexisting ions such as Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ on Cr(VI) discharges were examining. Adsorption tests were an investigation including 25 mL of 100 mg/L Cr(VI) solution includes several components in two concentrations (10 - 100 mg/L) and 20 mg from adsorbent about pH 2.03. Next adsorption approached an equilibrium case, this adsorbent separated of the solvent. Each filtrate obtained the remaining Cr (VI) concentration. Finally, the potential applicability concerning Artichoke to Cr (VI) elimination of existing wastewater specimen carried out toward batch method via applying a mining industry wastewater specimen [18]. In this study, Strew Artichoke particles were famously employed for chromium elimination and Restoration. The studies conveyed applying various concentrations from chromium eliminated 99.18% chromium within 2 minutes [20].

2.3. Adsorption Studies

Batch adsorption investigations were conducted through Cr (VI) adsorbed Artichoke. Originally, adsorption study obtained performed employing 0.03 mg/L of the Artichoke and 100 mg/L of Cr (VI) solution about pH 2.03. Later, adsorption tests were carried out with shaking the Cr (VI) loaded adsorbent with 0.1 mL NaOH solution among various concentrations (10 M–100 M) during 2 h. Next adsorption and/or desorption ended stability, the adsorbent was conveniently classified through a surface magnetic field and the solution was collected for metal concentration steps. The concentrations of metal ions were reported by examined spectrophotometrically employing a UV–visible spectrophotometer (PerkinElmer, Landa-35, Singapore) at 540 nm after handling in accordance by standard Method [19].

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM) of the Adsorbents

Scanning electron microscopy (SEM) described the structural morphology and structural physical characteristics to produced adsorbents (FEI Quanta FEG 200 High-resolution SEM). SEM micrographs of natural Straw Artichoke (GS) beside Cr (VI) were presented in Patterns (1). It is obvious that (GS) produces a considerable amount of foramina with high homogeneity and there was a considerable decrease in the pores nature of Cr (VI) filled biomass [21]. In Figure (1) FESEM image can be made magnetic nanocomposites. Be seen on the surface of nano-sized particles of the straw burned Fe$_3$O$_4$ was have been formed. “It shows that the Straw Artichoke material has good porosity and high adsorption capacity” [21-23].
Magnetic nanocomposites were made using AGFM were identified (Figure 2). As the Hysteresis Curve can be observed ferromagnetism is magnetic nanocomposites. “The relationship between field strength H and magnetization M is not linear in such materials. If a magnet is demagnetized (H=M=0) and the relationship between H and M is plotted for increasing levels of field strength, M follows the initial magnetization curve. This curve increases rapidly at first and then approaches an asymptote called magnetic saturation. If the magnetic field is now reduced monotonically, M follows a different curve. At zero field strength, the magnetization is offset from the origin by an amount called the remanence. If the H-M relationship is plotted for all strengths of applied magnetic field the result is a hysteresis loop called the main loop. The width of the middle section along the H axis is twice the coercivity of the material” [23].
3.2. Dose Effect Absorbent MCG:

Effect of activated carbon absorbent magnetic chromium removal using different amounts of MCG, including (0.005/ 0.007/ 0.009/ 0.01/ 0.03/ 0.05/ 0.07/ 0.09/ 0.1 g) was investigated. Testing of the dose effect absorbent of chromium concentration in 30 ppm in conditions 25 ml and 7 = pH (pH typical) at room temperature, and the time was 120 minutes. Results of the experiments showed that the highest percentage of absorbed dose for 0.03 gr of the amount of absorbent. Best absorption when 0.03 gr of the MCG was adsorbent. The effect of different amounts of MCG on the adsorption capacity and efficiency under the optimal condition is illustrated in figure (3) it can be observed that with an increase in the adsorbent dosage. The rise in the adsorption efficiency is related to the increase in the availability of active sites of the MCG, which can give rise to the adsorption of chromium (VI) ion. The specific absorption rate to the surface depends on the total volume of pores. with increasing doses of adsorbent more than 0.03 gr for sticking composite nanoparticles, the adsorbent agglomerate, as a result decreased surface available to absorb all the sites and areas did not participate in the process of absorption, therefore increasing the absorption rate was fixed and did not increase the dose adsorbent as shown in(Figure 3).

![Figure 3](image)

Figure 3. Show increasing the absorption rate is fixed and will not increase the dose adsorbent

3.3. Effect of Chromium Concentration (VI)

Nano-composites MCG effected upon absorption from chromium (VI) of water to various concentrations of Cr (VI) in the range of steps 10 ppm – 100 ppm with steps 10 ppm that was studied. 03/0 g MCG of chromium was added to the solution and was stirred for 2 hours. The best absorption for ppm50 concentration was observed as shown in Figure (4). The removal efficiency was found to be (99.43%, 99.18%, 98.20%, 97.12%, 94.99%, 74.04%, 79.98%, 75.58%, 75.47%, and 52.72%) sequentially for various concentrations of chromium. The dependence of adsorption of chromium on the dosage of Straw Artichoke (GS) is shown in figure (3). “The percentage of chromium removal increased from 52.72% to 99.43% when adsorbent dosage was increased from 0.01-0.1g/l, and this was due to the availability of more binding sites as the dosage of adsorbent increased”. Therefore, the amount of Cr (VI) adsorbed (mg/g) was found to
decrease with increasing adsorbent dosage. The strong decrease in adsorption capacity could be due to the overlapping or aggregation of the adsorption sites caused by the overcrowding of the adsorbent particles [22-23].

\[ \text{Figure 4. Diagram percent absorbed by different concentrations solution of Chromium} \]

3.4. Fourier transforms infrared spectroscopy analysis

The successful modification of the Nano composite surface for their stabilization was confirmed by Fourier Transform Infrared Spectroscopy measurements (FTIR) [23]. “The presence of absorption peaks in the region of waves numbers 500-3500 cm\(^{-1}\) corresponding to the C-H stretching vibration the peak at 1616.09 cm\(^{-1}\) and 556.59 cm\(^{-1}\) in figure (5) were related to the C-H stretching oscillation of the (-CH2-) group The peak around 457.38 cm\(^{-1}\) agree to the carbonyl group in a quinone as well as representing a γ-pyrone structure beside big oscillations from a mixture of C=O and C=C [19]”. The chemical composition of Straw Artichoke (GS) as obvious from FTIR spectrum showed that Straw Artichoke (GS) was the best sorbent for element binding. With increasing of pH, HCrO\(_4\) kind transfers to different kinds of CrO\(_4\) and Cr\(_2\)O\(_7\). The decrease in adsorption of Cr (VI) through increasing the pH stays due to the action between the anions CrO\(_4\) and OH\(^-\). Comparable considerations described in other studies [16]. According to the results of Zeta Potential in Table (1) were made in an acid environment- magnetic nano-composites have a positive surface charge that the alkaline environment of positive surface charge is reduced figure (6). This noted that the highest elimination of Cr presented at about pH= 4. The Cr (VI) elimination rate significantly depends on the pH of the solution because the solubility of precipitate occurs strongly reliant upon pH [25].
Table 1. Results of Zeta Potential

| The Surface Charge (mv) | pH |
|-------------------------|----|
| 8.44                    | 2  |
| -17.1                   | 7  |
| -21.1                   | 9  |

The most important parameter in the design of water treatment systems optimum the time impact of the exposure is absorbent and adsorbs contaminants [22]. In figure (7) the time of contact with the MCG Nano composites with the help Chromium solution (VI) at constant concentration 50 ppm, pH=4 and adsorbent dosage 0.03 gr it was observed that by increasing the time with absorption rate is increased. The adsorption behavior of Cr (VI) by burning Gundelia tournefortii straw in relation to the effect of contact time was carried out by varying the equilibrium time from 30 min to 240 min at a Cr concentration of 10-100 ppm. The results showed after 120 min is enough to remove more than 90% of Cr (VI) indicating that the reaction is fast and the adsorption sites are open and the metal ions interacts easily with the sites and hence a higher rate of adsorption is observed. The rapid metal removal has significant practical importance, as this will facilities the use of small adsorbent volumes to ensure efficiency and economy [26].

Figure 5. FTIR spectra of native Straw Artichoke (GS)
Figure 6. Curve the percentage of absorption of various time duration

Figure 7. Curve the percentage of amounts solution at the time the adsorption
3.5. X - Ray Diffraction Analyses

X-ray diffraction is a versatile and non-destructive method which is applied for classification of the crystalline phases present in dense materials and investigating the structural characteristics of the states such as stress, grain size, phase structure, crystal direction and defects [14]. In the Figures (8-a, b, c) XRD analyses confirmed that the synthesized nano-composite were Magnetite (Fe$_3$Cl$_3$) as shown in Figure (8). Seven Characteristic peaks were marked by their indices (012), (104), (110), (311), (024), (116), and (300) sequentially, were observed for both samples reveal that the resultant nano-composite were Fe$_2$O$_3$ with inverse-spinel structure [14]. In the pattern of XRD diffraction, the broad nature of the diffraction bands indicated that MCG have small particle sizes. The particle sizes can also be quantitatively evaluated from the XRD data using the Debye - Scherrer equation the particle size of the Straw Artichoke and flaxseed stabilized Fe$_2$O$_3$ nano-composite.

The X-ray diffraction spectrum of Fe$_3$Cl$_3$ indicates a cubic spinel structure with a grain size of about 10 nm. Other phases, Fe$_2$O$_3$, which is the common products in chemical co-precipitation process, were not detected. To estimate the average dimension of the crystallites, the Debye - Scherrer equation was applied [21-26]:

\[
D = \frac{K \lambda_{Cu-K\alpha}}{\beta \cos \theta} \text{FWHM}
\]

\[
D = 0.9 \frac{\lambda}{\beta \cos \theta}
\]

Where;
D: crystallite dimension,
K: a coefficient (0.89),
$\lambda_{Cu-K\alpha}$: wavelength of the emission from the diffraction tube, FWHM: full width at half maximum of diffraction in the 2 $\theta$ scale (rad),
$\theta$: diffraction Bragg angle.

High intensity and sharpness of the peaks related to the nano-composite are due to the higher stereo regularity of Straw Artichoke inside channels [20-25-26]. Therefore it can be concluded that Straw Artichoke a kind of order in lattice stacking of the chemical structure. According to the results the mean particle size of less than 100 nm can be obtained for Straw Artichoke material.
Figure 8(a), (b), (c). XRD patterns of the Artichoke Straw by magnetic carbon nano-composite sample

4. Conclusion

The optimal conditions absorption and absorbed a high percentage of activated carbon magnetic Nano-composites can be a good absorbent for the removal of Chromium (VI) from the water. This method is very simple and easy without any facilities can be everywhere, even in the field of Nano-composite structure and use it. Another advantage this method is the ability to separate the magnetic Nano composites activated carbon adsorbent solution after the absorption process by the magnetic field is without filtration. Of the FT-IR analysis, it was observed, that the hydroxyl and C-H groups near the cover of the adsorbent add to chromium adsorption. The results from FTIR analysis showed that all of the nanoparticles had the functional groups expected.
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References

[1] Makeswari, M., Santhi, T., 2014, Adsorption of Cr(VI) from aqueous solutions by using activated carbons prepared from Ricinus communis leaves: Binary and ternary systems, Arabian Journal of Chemistry, Production and hosting by Elsevier B.V, Department of Chemistry, Karpagam University, Coimbatore 641021, Tamil Nadu, India.

[2] Bin Qiua, Cuixia Xua, Dezhi Sunb, Qiang Wangb, Hongbo Gua, Xin Zhangd, Brandon L., Weeksd, Jack Hoppera, Thomas C., Hoa, Zhanhu Guoa, Suying Weic, 2014, Polyaniline coating with various substrates for hexavalentchromium removal, Applied Surface Science, Elsevier.

[3] Jing, Hu., Irene M.C., Lo., Guohua Chen, 2007, Performance and mechanism of chromate (VI) adsorption by (γ-FeOOH) coated maghemite (γ-Fe2O3) nanoparticle, Separation and Purification Technology 58, pp 76–82.

[4] Babak Kakavandi, Roshanak Rezaei Kalantary, Mahdi Farzadkia, Amir Hossein Mahvi, Ali Esrafilii, Ali Azari, Ahmad Reza Yari and Allah Bakhsh Javid, 2014, Enhanced chromium (VI) removal using activated carbon modified by zero valent iron and silver bimetallic nanoparticles, Journal of Environmental Health Science & Engineering, pp 12-115.

[5] Madhumita Bhaumik, Hyoungh J., Choi, Mathapeo P., Seopela, Rob I., McCrindle, and Arjun Maity, 2014, Highly Effective Removal of Toxic Cr(VI) from Wastewater Using Sulfuric Acid-Modified Avocado Seed, Industrial & Engineering Chemistry Research, American Chemical Society, 53, pp 1214–1224.

[6] Wei Wang, Xuejiang Wang, Xin Wang, Lianzhen Yang, Zhen Wu, Siqing Xia, Jianfu Zhao, 2013, Cr(VI) removal from aqueous solution with bamboo charcoal chemically modified by iron and cobalt with the assistance of microwave, Journal of Environmental Sciences, 25(9) pp 1726–1735.

[7] Aditya Dhagat, Bhushan Goyal, Lalsangzela Sailo, 2013, Removal of Cr (VI) in aqueous solution using iron oxide coated sand (IOCS), International Journal of Scientific & Engineering Research, Vol 4, Issue 5, ISSN 2229-5518.

[8] Naseema Khatoon, Altaf Husain Khan, Vinay Pathak, Neeraj Agnihotri, Masihur Rehman, 2013, Removal of hexavalent chromium from synthetic wastewater using synthetic nano zero valiant iron (NZVI) as adsorbent, International Journal of Innovative Research in Science, Engineering and Technology, Vol 2, Issue 11,
[9] Gandhi, N., Sirisha, D., Chandra Sekhar, K.B., 2014, Adsorption of chromium from aqueous by using mutiny miti, *International journal of research in pharmacy and chemistry*, ISSN: 2231-2781, *Vol 4*, Issue 1, pp 168-180.

[10] Serpil Cetin, Erol Pehlivan, 2007, the use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 298, pp 83–87.

[11] Abhradip Pal, Ardhendu Shekhar Chaudhury, 2012, Biosorption of chromium using Anabaena and Vetiveria, *International Journal of Pollution Abatement Technology*, *Vol 1*, Issue 1, pp 15-19.

[12] Wen Liu, Jinren Ni, Xiaochen Yin, 2014, Synergy of photocatalysis and adsorption for simultaneous removal of Cr(VI) and Cr(III) with TiO2 and titanate nanotubes, pp 12-25.

[13] Lei Wang, Wen Liu, Ting Wang, Jinren Ni, 2013, Highly efficient adsorption of Cr (VI) from aqueous solutions by amino-functionalized titanate nanotubes, *Chemical Engineering Journal* 225 pp 153–163.

[14] Caroline Bertagnolli, Arnaud Uhart, Jean-Charles Dupin, Meuris Gurgel Carlos da Silva, Eric Guibal, Jacques Desbrieres, 2014, Biosorption of chromium by alginate extraction products from Sargassum filipendula: Investigation of adsorption mechanisms using X-ray photoelectron spectroscopy analysis, *Bioresource Technology* 164, pp 264–269.

[15] Iman Y., El-Sherif, Joseph Y., Farah Girgis E., Ola Mohamed, A., 2013, Removal of chromium from tannery wastewater using magnetic nanoparticles, *Journal of Applied Sciences Research*, *Vol 9*, Issue 3, pp 1564-1572.

[16] Attia, A. A., Khedr, S. A., Elkholy, S. A., 2010, Adsorption of chromium ion (VI) by acid activated carbon, *Brazilian Journal of Chemical Engineering*, ISSN 0104-6632, *Vol 27*, No. 01, pp 183 - 193.

[17] Muthusamy Shanmugaprakash, Venkatachalam Sivakumar, Manickavelu Manimaran, Jeyaseelan Aravinda, 2013, Batch and Dynamics Modeling of the Biosorption of Cr(VI) from Aqueous Solutions by Solid Biomass Waste from the Biodiesel Production, *Environmental Progress & Sustainable Energy* DOI 10.1002/ep, American Institute of Chemical Engineers.

[18] Suhong Chen, Qinyan Yue, Baoyu Gao, Qian Li, Xing Xu, 2011, Removal of Cr(VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study, *Chemical Engineering Journal* 168, pp 909–917.

[19] Hoda Beheshti, Mohammad Irani, Layla Hosseini, Arash Rahimi, Majid Aliabadi, 2015, Removal of Cr(VI) from aqueous solutions using chitosan/MWCNT/Fe3O4 composite nano fibers batch and column studies, *Chemical Engineering Journal*, 158.
[20] Min Gan, Shengjie Sun, Zhihe Zheng, Haojia Tang, Jingrui Sheng, Jianyu Zhu, Xinxing Liu, School, 2015, Adsorption of Cr(VI) and Cu(II) by AlPO_4 modified biosynthetic Schwertmannite, *Applied Surface Science* 356, pp 986–997.

[21] Yingxin Zhao, Shengjiong Yang, Dahu Ding, Jie Chen, Yingnan Yang, Zhongfang Lei, Chuanping Feng, Zhenya Zhang, 2013, Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay, *Journal of Colloid and Interface Science* 395, pp 198–204.

[22] Rumi Chand, Takanori Watari, Katsutoshi Inoue, Toshio Torikai, Mitsunori Yada, 2015, Evaluation of wheat straw and barley straw carbon for Cr(VI) adsorption, *Separation and Purification Technology* 65, pp 331–336.

[23] Palanisamy, K. L., V. Devabharathi, N., Meenakshi Sundaram, 2013, The utility of magnetic iron oxide nanoparticles stabilized by carried oils in removal of heavy metals from wastewater, (IMPACT: IJRANSS) ISSN 2321-8851, Vol 1, Issue 4, pp 15-22.

[24] Qiaoyu Hu, Hari Paudyal, Junmei Zhao, Fang Huo, Katsutoshi Inoue, Huizhou Liu, 2014, Adsorptive recovery of vanadium(V) from chromium(VI)-containing effluent by Zr(IV)-loaded orange juice residue, *Chemical Engineering Journal* 248, pp 79–88.

[25] Jun Dai, FengLian Ren, ChunYuan Tao, 2012, Adsorption of Cr(VI) and Speciation of Cr(VI) and Cr(III) in Aqueous Solutions Using Chemically Modified Chitosa, *International Journal of Environmental Research and Public Health*, ISSN 1660-4601, Vol 9, pp 1757-1770.

[26] I. Villaescusa, N. Fiol, M. Martines, N. Miralles, J. Poch, J. Serarols, 2004, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38, 992–1002.