



Removal of Chromium (VI) from Aqueous Solutions Using Composite Nanofibers



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Abstract

Chromium(VI) (Cr(VI)) is highly toxic, carcinogenic, mutagenic to most of the living organisms when its concentration level is higher than 0.05 ppm, and extremely mobile than Cr(III). Therefore, there is a great importance to remove Cr(VI) from aqueous solution, to prevent the deleterious impact of the Cr(VI) on the human health. This paper proposed a method that aims to remove Cr(VI) from water by composite nanofibers. A novel chitosan-polyvinyl alcohol-carbon nanotubes-magnetite (Chitosan-PVA-CNTs-Fe₃O₄) nanofiber composite was fabricated for the removal of Cr(VI) from aqueous solutions. The nanofiber composite was characterized using scanning electronic microscope (SEM) and transmission electronic microscope (TEM). The composite nanofibers had a positive effect on the absorption of Cr(VI) ions under neutral and acidic conditions. The saturated adsorption reached the highest when pH was 2 at (76.98%), whereas it was in low level when pH was 9 (59.13%), that was in composite nanofibers containing the same chemical components when CNTs (1g). This paper propose a method that aims to remove Cr(VI) from wastewater of the textile dyeing industry using composite nanofibers solution.

Keywords: Adsorption, Chromium (VI), Removal, Electrospinning, Composite, Nanofibers

1. Introduction

Chromium is a natural metal, commonly found in wastewaters, which are originated from several industrial processes such as electroplating industries, military purposes, textile dyeing, paint, leather tanneries, and pigment industries as critical industry materials [1, 2]. Chromium possesses two oxidation states Cr(VI) and Cr(III). Cr(VI) is highly toxic, carcinogenic, mutagenic to most of the living organisms when its concentration level is higher than 0.05 ppm, and extremely mobile than Cr(III) [3, 4]. Therefore, there is a great importance to remove Cr(VI) from aqueous solution, to prevent the deleterious impact of the Cr(VI) on the human health. Several methods, such as adsorption, reduction, solvent extraction, precipitation, reverse osmosis have

been used for the removal of Cr(VI) from industrial polluted wastewaters [5]. However, most of these techniques have several limitations and drawbacks, and they require high energy or massive use of reducing agents and they are not used widely. In particular, adsorption is considered to be simple, economical, and remains one of the most attractive approaches for treating Cr(VI) [6].

Several kinds of materials were used as an adsorbent for the removal of chromium, such as active carbon [7, 8], metal oxide nanoparticles [9, 10] and biomaterials [11, 12]. Among the adsorbents available currently, iron oxide (magnetite; Fe₃O₄) based adsorbents have been widely used for the effective removal of chromium from the polluted water. They have great advantages showing higher removal

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capacities owing to their outstanding adsorption activities [13]. Moreover, the presence of a high concentration of hydroxyl groups on the surface of Fe_3O_4 will interact with and adsorb pollutants in water [14]. The surface of CNTs have been applied recently to enhance the dispersion property and adsorption capacities of CNTs [15].

However, some of these adsorbents have drawbacks related to the complexity of the separation process of adsorbent from the solution after the adsorption stage, which will increase the operating cost. In order to avoid this problem, some researchers used nanofibers for the adsorption of several contaminants [16]. Polyvinyl alcohol, (Chitosan P.V.A) composite system was chosen as the template for loading CNTs- Fe_3O_4 NPs, because Chitosan possessed good crosslinked, simultaneously, a large number of hydroxyl groups and amine groups existing on the surface of composite nanofiber as well as its non-toxic nature [17, 18]. Chitosan-fibers with amine groups were used for the removal of several metal ions. In this point, nanofibers with nanoparticles were investigated for removal Cr(VI) from aqueous solution [19].

In the present work, a novel (Chitosan-PVA-CNTs- Fe_3O_4) composite nanofibers were fabricated for removal of Cr(VI) from aqueous solutions, which can be easily separated from the aqueous media [20]. The possible adsorption mechanism was provided by testing the adsorption performance under different solution pH values, and initial concentration of the substrate. In addition, the composite nanofibers (Chitosan-PVA-CNTs- Fe_3O_4) were characterized by scanning electronic microscope (SEM) and transmission electronic microscope (TEM) [21]. It is anticipated that this composite nanofiber showed promising potential for wastewater treatment.

2. Experimental

2.1. Materials and Devices

Multi-walled carbon nanotubes (MWNTs, CNTs) has multiwall structure and size was about (L: >20 microns) and (W: 15 ± 5 nm). CNT synthesis procedure is described in [22, 23]. Glutaraldehyde (GA, 50 %), ethylene diamine, distilled water, acetyl acetone, sodium acetate, absolute ethanol, deionized water, polyvinyl alcohol (PVA), and ferric chloride. pH device, autoclaved sterilization, magnetic stirrer, suction funnel, filter paper, oven, centrifuge, electrospun, SEM, TEM, and the DR 3900 spectrophotometer

2.1.1. Preparation of Iron(III)-Acetyl Acetone

1. Iron chloride (1.7 g) was dissolved in 10 ml distilled water.
2. 1.9 ml of acetyl acetone was added into the iron(III) solution.
3. After 15 min, 6.25g of sodium acetate was added into the solution, taking care of slow stirring.
4. The solution was cooled to about 0-5 °C, this tends to result in red crystalline product as illustrated in Fig 1.
5. Recrystallization for iron(III)-acetyl acetone was done using absolute ethanol.



Figure 1. Red Iron(III)-acetyl acetone crystals.

2.1.2. Preparation of Iron Oxide Nanoparticles by Hydrothermal process

1. Iron(III)-acetyl acetone was dissolved in 70 ml deionized water in a beaker.
2. Then, ethylene diamine was added dropwise into the iron solution under stirring condition to maintain the pH at 10-11.
3. After that, the resulting suspension was transferred into the 100 ml Teflon lined autoclave and the hydrothermal reaction was carried out at 150 °C for 12 hrs.
4. After the reaction, the obtained precipitate was centrifuged.
5. The obtained precipitate was washed repeatedly with distilled water and finally with alcohol, then it was dried in an electric oven at 60 °C.

2.1.3. Preparation of Chitosan (CS)

The extraction of CS from the collected shrimp shellfish was carried out according to Brine's methodology (Brine 1984). This protocol consists of the following tasks:

1. Deproteinization where proteins related to chitin were removed via continuous stirring of 76.45g of shrimp shellfish in 760 ml of 0.1 N NaOH solution for 2 days.
2. Then, this solution was decanted at room temperature and filtered through a filter paper.
3. The obtained filtrate was afterward washed with distilled water until neutral pH.
4. Then, demineralization was carried out to remove the mineral matter bound to chitin. This step was performed by soaking the obtained filtrate in 200 ml

of 3–5% HCl solution for 8 days with continuous stirring, followed by decantation, filtration and rinsing with distilled water. After that, the obtained chitin (task 2) is chemically deacetylated in order to remove some or all of its acetyl groups. Amino groups in chitosan are soluble in aqueous solution, while acetyl groups in chitin are insoluble.

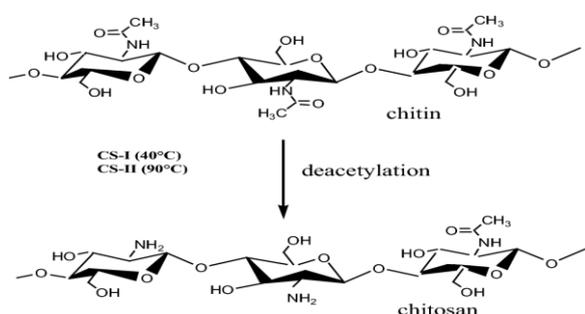


Figure 2. Deacetylation Mechanism

This chemical deacetylation as shown in Fig 2 is carried out by hydrolysis of chitin in a strongly alkaline medium with 50% NaOH under agitation for 4 hrs at a controlled temperature. In our case, two temperatures were used, 40 °C to prepare the first type of chitosan (CS-I) and 90 °C to get the chitosan second type (CS-II) which is a lighter pink than CS-I. The alkaline solution was filtered, and the filtrate was washed with distilled water at 50°C with stirring time for 5hrs until reaching a neutral medium. The resulting powders correspond to CS-I and CS-II.

2.1.4. Preparation of Electrospun Composites Nanofibers

2g of Chitosan was dissolved in 98 ml of acetic acid and stirred for 24h with heating at 40 °C, until the chitosan solution was obtained. A polyvinyl alcohol solution is prepared by dissolving 8g of polyvinyl alcohol in 92 ml distilled water with heating at 90 °C and constant stirring for 2h to obtain the polyvinyl alcohol solution. However, after several experiments, the best solution obtained from nanofibers of CS was a mixture between CS solution and polyvinyl alcohol solution where this mixture consists of 30% CS and 70% polyvinyl alcohol. This is due to chitosan solution alone does not give nanofibers for the occurrence of large scattering on the receiver board in the electric spinning device as shown in Fig 3. After the addition of the polyvinyl alcohol solution by the above-mentioned weight, there was a significant reduction of the dispersal which gave nanofiber on the receptor plate.

This is due to the mitigation of the positive charge present in CS and its equivalent to the negative charge found in the polyvinyl alcohol as shown in Fig 4. After obtaining this nanofiber, different concentrations of MCNTs were used with only one concentration of iron

oxide (as shown in Fig 5) and a solution of glutaraldehyde (GA; 2.5 wt.%) wherein nanoparticles were kept at room temperature after dipping in a solution of GA (2.5 wt.%) for 24 hrs.



Figure 3. Electrospun Device

2.2. Characterization

The morphology and microstructure of the composite nanofiber (Chitosan-PVA-CNTs-Fe₃O₄) were recorded by scanning electron microscopy (SEM, LEO 1430 VP, GRESHAM) and transmission electron microscope (TEM, JOEL JEM-2100). The HR-TEM is operating at 200 kV equipped with Gatan digital camera Erlangshen ES500. They were used in the surface analysis of the resulting composite nanofiber (Chitosan-PVA-CNTs- Fe₃O₄) adsorbent. The concentration of Cr(VI) was measured using-DR 3900 Spectrophotometer. pH was measured using a pH-meter (WTW pH-330, Germany).



Figure 4. Fiber produced after the Electric Spinning Process



Figure 5. Fiber Produced after the Addition of glutaraldehyde

2.3. Adsorption of Cr(VI)

The adsorption of Cr(VI) in aqueous solution was carried out in (1.5 diphenylhydrazine) reactor containing 0.25 mg of composite nanofibers and 25 ml of 12.5 ppm Cr(VI) solution. The pH values of Cr(VI) solution were measured using a pH-meter and adjusted at pH 2 and 9 by the addition of HCl or NaOH solutions.

Composite nanofibers were dispersed in Cr(VI) solution under shaking condition at room temperature, then 3 ml of the suspension was taken from the reactor at a scheduled interval. The concentration of chromium prior and after adsorption was measured using DR 3900 spectrophotometer.

The equilibrium adsorption capacity (q_e) was determined using Eq (1), while % removal of Cr(VI) was calculated using Eq (2).

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

$$(\%) \text{ Removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (2)$$

where C_0 is the initial chromium(VI) concentration (mg/l) and C_e is the chromium(VI) concentration in the aqueous solution at equilibrium (mg/l), V is the total aqueous volume (L), and (m) is the mass of the composite nanofibers (g).

3. Results

3.1. Characterization of (Chitosan-PVA-CNTs-Fe₃O₄) and (Chitosan-PVA) nanofibers

Figure 6 (a, b, c) represents SEM images of the (Chitosan-PVA) nanofibers, the diameters is about 250 nm. Figure 7 (d, e, f, g) represents (Chitosan-PVA-CNTs-Fe₃O₄) nanofibers. The TEM micrographs clearly show that, the as-prepared CNT has multiwall structure and size was about (L: >20 micron) and (W: 15 ± 5 nm) (Figures 8, 9).

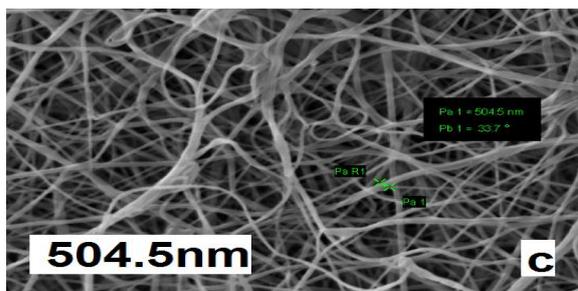
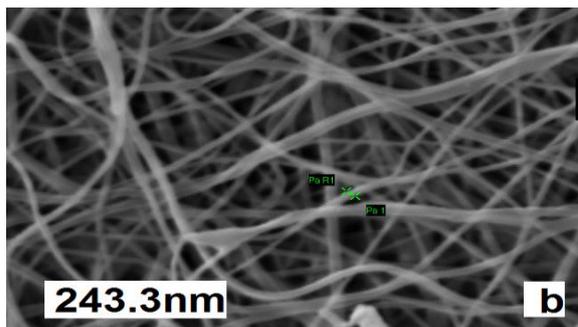
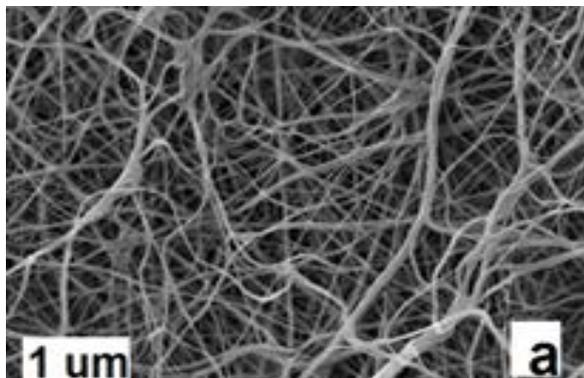
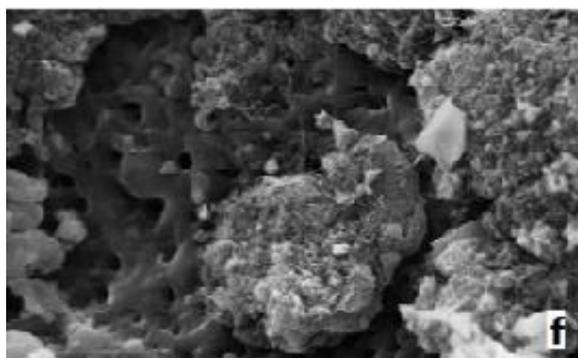
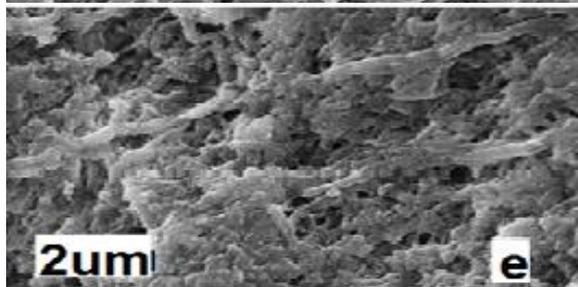
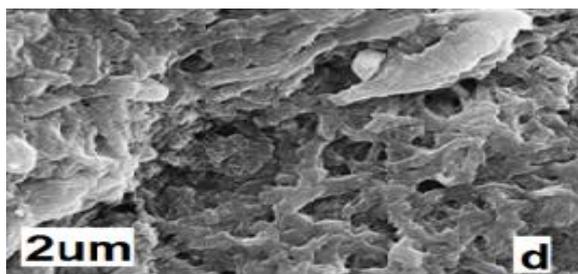


Figure 6. (a, b, c). SEM Images of (P.V.A–Chitosan)



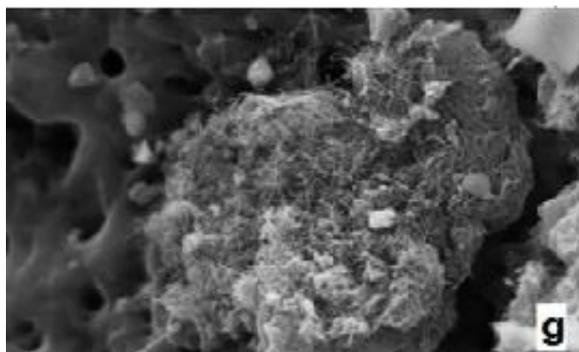


Figure 7 (e, d, f, g). SEM Images of different concentrations of (PVA-Chitosan-Fe₃O₄-CNTs) composite nanofibers.

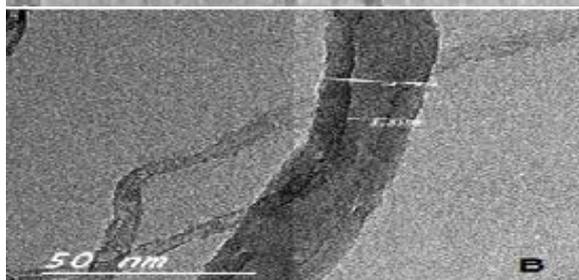
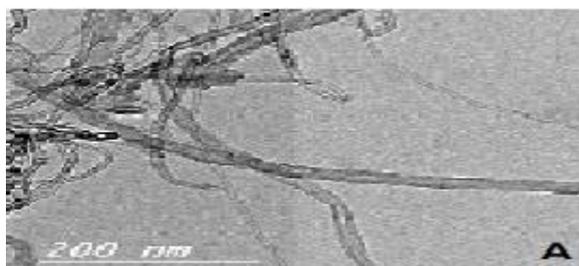


Figure 8 (a, b). TEM Images of MCNTs

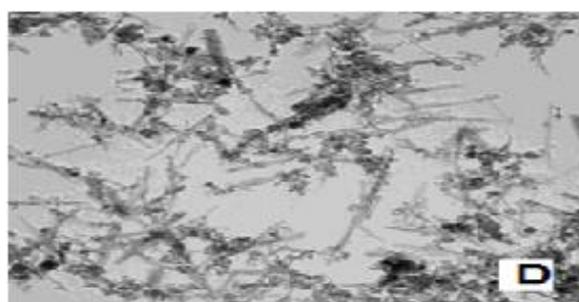
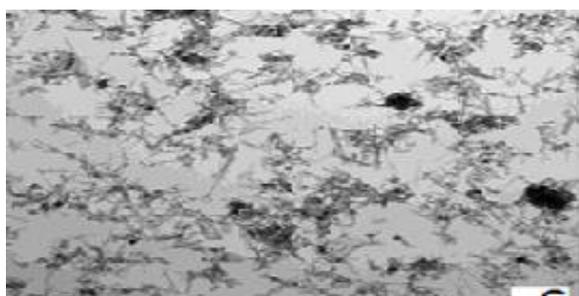


Figure 9 (c, d). TEM Image of Iron Oxide (Magnetite)

Table 1. Removal of Cr(VI) at pH 9
T= Time, Sa= Sample, R= Removal

T	Sa 1	Sa 2	Sa 3	Sa 4	Sa 5	Sa 6	Sa7
0	1.008	1.008	1.008	1.008	1.008	1.008	1.008
5	0.986	0.994	0.991	1.000	0.981	1.004	0.985
10	0.933	0.924	0.956	0.946	0.967	0.992	0.979
15	0.904	0.898	0.934	0.908	0.946	0.907	0.971
20	0.876	0.869	0.908	0.894	0.934	0.876	0.963
25	0.854	0.861	0.884	0.851	0.922	0.800	0.959
30	0.809	0.811	0.849	0.812	0.909	0.754	0.951
40	0.775	0.785	0.811	0.796	0.889	0.713	0.943
50	0.752	0.725	0.787	0.745	0.882	0.694	0.939
60	0.723	0.701	0.766	0.712	0.874	0.632	0.932
70	0.694	0.679	0.726	0.659	0.851	0.572	0.928
80	0.673	0.645	0.704	0.611	0.84	0.511	0.928
90	0.655	0.611	0.677	0.588	0.836	0.464	0.927
100	0.636	0.597	0.676	0.545	0.835	0.421	0.925
110	0.634	0.596	0.674	0.533	0.834	0.414	0.925
120	0.634	0.595	0.673	0.530	0.834	0.412	0.925
R%	37.10	40.97	33.23	47.42	17.26	59.13	8.23

Table 2. Removal of Cr(VI) at pH 2
T = Time, Sa = Sample, R = %Removal

T, min	Sa 1	Sa 2	Sa 3	Sa 4	Sa 5	Sa 6	Sa7
0	1.008	1.008	1.008	1.008	1.008	1.008	1.008
5	1.004	0.997	1.000	0.987	0.987	1.003	1.004
10	0.957	0.978	0.800	0.856	0.971	0.992	0.997
15	0.908	0.908	0.731	0.803	0.958	0.875	0.978
20	0.867	0.886	0.718	0.756	0.936	0.748	0.967
25	0.849	0.812	0.645	0.700	0.902	0.608	0.949
30	0.835	0.754	0.626	0.636	0.806	0.46	0.935
40	0.802	0.621	0.601	0.600	0.800	0.423	0.902
50	0.789	0.598	0.593	0.513	0.758	0.397	0.889
60	0.665	0.432	0.582	0.503	0.732	0.373	0.865
70	0.645	0.412	0.570	0.423	0.728	0.352	0.845
80	0.584	0.411	0.557	0.411	0.715	0.314	0.844
90	0.544	0.400	0.555	0.388	0.686	0.286	0.844
100	0.499	0.387	0.554	0.359	0.671	0.272	0.844
110	0.488	0.376	0.554	0.358	0.668	0.267	0.844
120	0.487	0.374	0.552	0.358	0.667	0.261	0.844
R%	51.69	62.90	45.24	64.48	33.83	76.98	16.27

3.2. Effect of pH on the Performance of Removal

As shown in Figure 10, the best result was obtained at pH 2 compared to pH 9 (Tables 1, 2), because of the composite nanofibers in acid medium gives a better performance for the removal of Cr(VI) as well as the adsorption process.

In addition, the best performance at pH 2 was for sample 6 (Chitosan-PVA-0.5g Fe₃O₄-1g CNT), whereas the worst performance was in sample 7 which contains (Chitosan-PVA). The amine groups and hydroxyl groups of chitosan chain can be modified

chemically to form nano particles, nano sheets, hydrogels etc. with unique properties.

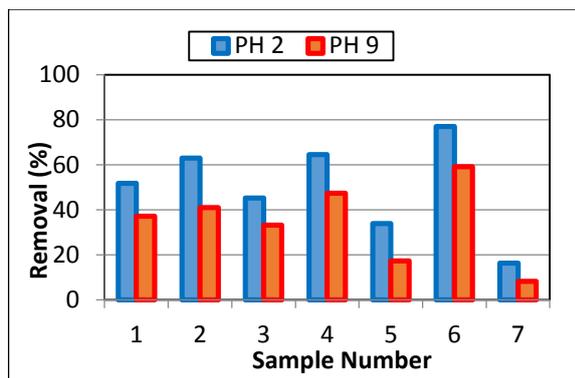
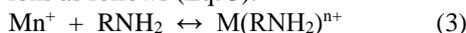


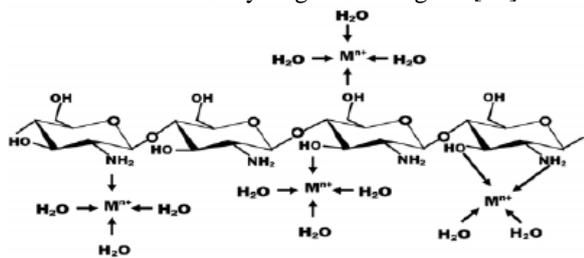
Figure 10. Effect of pH on the Performance of Removal

3.3 Mechanism of Heavy Metals Removal

Heavy metals like chromium, copper, nickel, mercury, lead, zinc, arsenic etc. are extremely toxic and are bio persistent in nature. Chitosan tends to bind/chelate with such metal ions. The amine groups present along the polymer chain are strongly active with metal ions [24]. At pH close to neutral (when NH_2 groups are not protonated), CS reacts with metal ions as follows (Eq. 3).



The amine groups form coordinate bonds with the metal ions as shown in Scheme 1, by the donation of free electrons present on nitrogen and oxygen in the amine groups and hydroxyl groups, respectively, to the vacant orbitals of the metal. The metal binding efficiency of chitosan depends on the availability of the amine groups (high degree of deacetylation) for interaction with metal ions, chain length, extent of inter/intra molecular hydrogen bonding etc [24].



Scheme 1. Mechanism of removal of metal ions using CS.

4. Conclusion Future Prospects

The article illustrates the importance of chitosan in the field of water filtration/purification. Apart from this, chitosan based nano materials can be explored to evaluate their potential in a wide range of promising applications. Different methods can be adopted to synthesize chitosan based nano composites/nano hybrids with more advanced water purification capabilities. The (CS-PVA-CNTs- Fe_3O_4) composite

nanofibers were successfully prepared by the electrospinning technique, which was used as an adsorbent. The composite nanofibers showed an excellent ability to remove Cr(VI) ions in water, especially in the acidic environment of the textile dyeing industry. The highest removal capacity of (CS-PVA-CNTs- Fe_3O_4) for Cr(VI) was found to be 76.98% at acidic media and the Cr(VI) adsorption processes reached their equilibrium state in about 120 min with a final concentration of 0.261 ppm of Cr(VI) ion. Whereas, at pH = 9, 59.13% of Cr(VI) removal was achieved with a final concentration of 0.412 ppm of Cr(VI) ion. There can be some change of the materials, where titanium oxide or zinc oxide can be used instead of iron oxide, because they are cheaper and available. In addition to this, modifications in chitosan can be carried out to tailor different properties like cationic and anionic.

References

- [1]. L. Khezami, Richard Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, *J. Hazard. Mater.* 123 (1–3) (2005) 223–231.
- [2]. X. Guo, Guang Tao Fei, Hao Su, Li De Zhang, High-performance and reproducible polyaniline nanowire/tubes for removal of Cr(VI) in aqueous solution, *J. Phys. Chem. C* 115 (5) (2011) 1608–1613.
- [3]. J.A. Giménez, M.A. Aguado, S. Cervera-March, Photocatalytic reduction of chromium(VI) with titania powders in a flow system. Kinetics and catalyst activity. *J. Mol. Catal. A: Chem.* 105(1) (1996) 67–78.
- [4]. [L.B.M. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination, *Appl. Catal. B: Environ.* 17(3) (1998) 267–273.
- [5]. J.-H. Zhu, Xi-Luan Yan, Ye Liu, Bao Zhang, Improving alachlor biodegradability by ferrate oxidation, *J. Hazard. Mater.* 135 (1–3) (2006) 94–99.
- [6]. C.K.P. Ahn, Donghee Park, Seung H. Woo, Jong M. Park, Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants, *J. Hazard. Mater.* 164(2–3) (2009) 1130–1136.
- [7]. R.M.C. Schneider, C.F. Cavalin, M.A.S.D. Barros, C.R.G. Tavares, Adsorption of chromium

- ions in activated carbon, *Chem. Eng. J.* 132(1–3) (2007) 355–362.
- [8]. Z. Hu, Lin Lei, Yijiu Li, Yaming Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, *Sep. Purif. Technol.* 31 (1) (2003) 13–18.
- [9]. T. Burks, A. Uheida, M. Saleemi, M. Eita, M.S. Toprak, M. Muhammed, Removal of chromium(VI) using surface modified superparamagnetic iron oxide nanoparticles, *Separat. Sci. Technol.* 48(8) (2013) 1243–1251
- [10]. D. Lu, Gaoke Zhang, Zhen Wan, Visible-light-driven g-C₃N₄/Ti³⁺-TiO₂ photocatalyst co exposed {0 0 1} and {1 0 1} facets and its enhanced photocatalytic activities for organic pollutant degradation and Cr(VI) reduction, *Appl. Surf. Sci.* 358 (Part A) (2015) 223–230.
- [11]. A.B. Albadarin, Chirangano Mangwandi, Gavin M. Walker, Stephen J. Allen, Mohammad N.M. Ahmad, Majeda Khraisheh, Influence of solution chemistry on Cr(VI) reduction and complexation onto date-pits/tea-waste biomaterials, *J. Environ. Manage.* 114 (2013) 190–201.
- [12]. Y. Hou, Huijuan Liu, Xu Zhao, Jihui Qu, J.P. Chen, Combination of electroreduction with biosorption for enhancement for removal of hexavalent chromium, *J. Colloid Interf. Sci.* 385 (1) (2012) 147–153.
- [13]. Alaa Mohamed, T.A. Osman, M.S. Toprak, M. Muhammed, A. Uheida, Surface functionalized composite nanofibers for efficient removal of arsenic from aqueous solutions, *Chemosphere* 180 (2017) 108–116.
- [14]. Alaa Mohamed, S. Yousef, M.A. Abdelnaby, T.A. Osman, M.S. Toprak, M. Muhammed, B. Hamawandi, A. Uheida, Photocatalytic degradation of organic dyes and enhanced mechanical properties of PAN/CNTs composite nanofibers, *Sep. Purif. Technol.* 182 (2017) 219–223.
- [15]. Waleed Khalil, A. Mohamed, Mohamed Bayoumi, T.A. Osman, Tribological properties of dispersed carbon nanotubes in lubricant, Fullerenes, Nanotubes, Carbon Nanostruct. 24 (7) (2016) 479–485.
- [16]. Bahaa M. Kamel, A. Mohamed, M. El Sherbiny, K.A. Abed, M. Abd-Rabou, Tribological properties of graphene nanosheets as an additive in calcium grease, *J. Dispersion Sci. Technol.* 38 (10) (2016) 1495–1500.
- [17]. Alaa Mohamed, T.A. Osman, M.S. Toprak, M. Muhammed, Ramy El-Sayed, A. Uheida, Composite nanofibers for highly efficient photocatalytic degradation of organic dyes from contaminated water, *Environ. Res.* 145 (2016) 18–25.
- [18]. Alaa Mohamed, T.A. Osman, M.S. Toprak, M. Muhammed, Eda Yilmaz, A. Uheida, Visible light photocatalytic reduction of Cr(VI) by surface modified CNT/titanium dioxide composites nanofibers, *J. Mol. Catal. A: Chem.* 424 (2016) 45–53.
- [19]. M. Avila, T. Burks, F. Akhtar, M. Göthelid, P.C. Lansåker, M.S. Toprak, M. Muhammed, A. Uheida, Surface functionalized nanofibers for the removal of chromium(VI) from aqueous solutions, *Chem. Eng. J.* 245 (2014) 201–209.
- [20]. S. Xing, Dongyuan Zhao, Wenjuan Yang, Zichuan Ma, Wu Yinsu, Yuanzhe Gao, Weirong Chen, Jiao Han, Fabrication of magnetic core-shell nanocomposites with superior performance for water treatment, *J. Mater. Chem. A* 1 (5) (2013) 694–1700.
- [21]. F. Liu, Xinhong Wang, Bor-Yann Chen, Shilin Zhou, Chang-Tang Chang, Removal of Cr(VI) using polyacrylonitrile/ferrous chloride composite nanofibers, *J. Taiwan Inst. Chem. Eng.* 70 (2017) 401–410.
- [22]. Alaa Mohamed, T.A. Osman, Ali Khattab, M. Zaki, Rheological behavior of carbon nanotubes as an additive on lithium grease, *J. Nanotechnol.* 2013 (2013) 4.
- [23]. Bahaa M. Kamel, A. Mohamed, M. El Sherbiny, K.A. Abed, Rheology and thermal conductivity of calcium grease containing multi-walled carbon nanotube, Fullerenes, Nanotubes, Carbon Nanostruct. 24 (4) (2016) 260–265.
- [24]. T.C. Maponya, K.E. Ramohlola, N.H. Kera, K.D. Modibane, A. Maity, L.M. Katata-Seru, M.J. Hato, Influence of Magnetic Nanoparticles on Modified Polypyrrole/m-Phenyldiamine for Adsorption of Cr(VI) from Aqueous Solution, *Polymers*, 12 (2020) 679.