

Research Article

Synthesis of polypyrrole coated oxidized multi-walled carbon nanotubes nanocomposite for the removal of Cr (VI) from potable water

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Abstract: Polypyrrole (PPy) coated oxidized multi-walled carbon nanotube (PPy-OCNT NC) based nanocomposites were successfully synthesized. They were used as novel adsorbent for the removal of hexavalent chromium Cr (VI) from aqueous solution. Effects of various parameters that include pH, dose of PPy-OCNT NC, initial concentration of Cr (VI) and percentage loading of PPy on OCNTs were explored. The optimum pH for Cr (VI) removal was found to be 2. Cr (VI) adsorption followed Langmuir isotherm with maximum adsorption capacity of 555.56 mg/g while the sorption kinetics followed the pseudo second order kinetic model. Ion exchange mechanism was found to be the predominant mechanism in the removal of Cr (VI) from aqueous solution where the doped Cl⁻ on polypyrrole exchanged with either monovalent bichromate, HCrO₄⁻ or divalent dichromate Cr₂O₇²⁻ ions, as these ions are dominating species at pH <6.

Keywords: Carbon nanotubes, nanocomposite, Heavy metals, isotherms, Pollution

INTRODUCTION

As the world becomes more industrialised and smaller due to infrastructure and trade, accidental and premeditated hazardous dumping of waste has contributed to the problem of water pollution. Heavy metals, in particular pose a huge threat to human health due to their toxic nature, bio-viability and non-biodegradability. The most toxic heavy metals that may be found in waste are lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As)[1, 3].

Chromium exists frequently in either trivalent Cr (III) or hexavalent Cr (VI) form in aqueous solution. Cr (III) is an indispensable nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. However, the uptake of high levels of Cr (III) can cause harsh health effects such as skin rashes. Cr (VI), on the other hand, is more mobile, more soluble in aqueous solutions and compared to Cr (III), it is extremely toxic, carcinogenic and mutagenic to living organisms. Furthermore, intake or too much exposure to Cr (VI) may and can have adverse health effects such as vomiting, severe diarrhoea, nausea, liver and kidney damage, respiratory problems[4, 5]. Numerous water treatment methods have been used to remove Cr (VI) from wastewater; these include reverse osmosis, chemical precipitation, ion exchange, solvent extraction, electrocoagulation, and adsorption [6-13]. The disadvantages associated with most of these methods are the consumption of large amounts of reagents and as a consequence they produce large

amounts of toxic sludge that needs further treatment. Another limitation is the high equipment capital cost, requirement of the specialized personnel and time consumption. However, the adsorption method has received a lot of attention recently due to its versatility, robustness, simplicity and cost effectiveness for the removal of pollutants from water. Natural adsorbents such as wool, egg and coconut shell, banana peel, seaweed and many others are readily available but they have low affinity for Cr (VI) and slow process kinetics [4, 5], whereas other common adsorbents like activated carbon, hybrid materials, micro-algae, and resins have irregular adsorption sites with chemical heterogeneity and thus low adsorption capacity for Cr (VI) [14-16]. This has lead research to the development of more innovative adsorbents that are effective both industrially and environmentally with large surface area and short diffusion paths.

Carbon nanotubes (CNTs), which are allotropes of carbon with a cylindrical structure are ideal because of the nanosize nature that provides high surface area [17]. They are chemically stable and easily modified by chemical treatment procedures to suite the needed conditions. For instance, CNTs can be modified to remove different kinds of elements like heavy metals, dyes and/or volatile organic compounds (VOCs) [17]. Moreover, CNTs have different features such as greater tensile strength, high thermal conductivity that is better than the purest diamond and electrical conductivity similar to copper but with the ability to carry much

higher currents [27], are of well-developed mesopores and are building blocks of nanotechnology [19]. Since CNTs are flat sheets of graphite, they can easily aggregate due to the π - π interactions between the sheets thus reducing dispersion. Moreover, CNTs have a low sorption capacity for Cr (VI) [17], hence there is a great need to modify the CNTs to increase their sorption capacity for Cr (VI). The CNTs were first oxidized in order to introduce oxygen containing surface groups which have affinity for anionic chromate (CrO_4^{2-}). Secondly, they are coated with polypyrrole (PPy). PPy is a conducting polymer which displays particular electronic properties including conductivity, environmental stability, nontoxicity, low cost and ease of preparation [33,34]. It was found that PPy carries charges via some of positively charged nitrogen atoms in the polymer matrix. To maintain charge neutrality, some of the counter ions are incorporated into the growing polymer chain [35]. The existence of positively charged nitrogen atoms in PPy provides a good prospect for its applications in adsorption [33]. It has been previously studied that sorption of Cr(VI) onto PPy/ Fe_3O_4 and showed that the mechanistic interaction between Cr(VI) ions at pH 2 and the PPy was governed by ion exchange [19].

MATERIALS AND METHODS

Materials and reagents

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium carbonate, pyrrole (Py, 99 %), anhydrous ferric(III) chloride (FeCl_3), sodium hydroxide (NaOH), hydrochloric acid (HCl) and 1,5 diphenylcarbazide were purchased from Sigma-Aldrich, Germany. All chemicals used in this work were of analytical grade. The stock solution of 1000 mg/L Cr(VI) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water.

Oxidation of carbon nanotubes (O-CNT)

1g of MWCNTs was dispersed in 100 mL of concentrated nitric acid (8 N) in a 100 mL round bottom flask equipped with a condenser. The dispersion was refluxed at 353 K while stirring constantly for about 16 hrs. This was followed by the vacuum filtration and simultaneous washing of the resulting oxidized MWCTs with distilled water until their pH was close to 7. The final mass was then left in the oven to dry at 333 K over night.

Synthesis of the PPy/O-CNT nanocomposites

PPy-OCNT NC was prepared via *in situ* chemical oxidative polymerization technique. The OCNT loading (percentage in parentheses) was varied from 0.025 g (8.89 %) – 0.1 g (32.2 %) with the aim of optimizing the nanocomposite for efficient Cr(VI) sorption. In a typical polymerization technique, the specified amounts of OCNTs were added in 20 mL of deionized water in separate 100 mL conical flasks and ultrasonicated for 30 min for a better dispersion of the OCNTs. Subsequently, 0.2 mL of pyrrole monomer was

syringed to each mixture, followed by addition of 1.5 g of the oxidant, FeCl_3 . This mixture was then stirred for 3 hrs at room temperature. Finally, the reactions were stopped by addition of acetone. The black mass formed was then filtered and washed with distilled water until the filtrate became colourless and then washed with acetone to remove oligomers [21]. The nanocomposites, were then dried at temperature of 333 K for 8 hrs in an oven. The total weights of the nanocomposites after drying were 0.28 g, 0.31 g and 0.35 g for the OCNTs loading percentages of 8.89 %, 17.0 % and 32.2 %, respectively. The nanocomposites were then named PPy-OCNT NC 1, PPy-OCNT NC 2 and PPy-OCNT NC 3 for 8.89 %, 17.0 % and 32.2 % OCNT loading, respectively.

BATCH EXPERIMENTAL PROCEDURE

Effect of Ph and sorbent dosage

Adsorption experiment were carried out in temperature controlled thermostatic shaker operated at 200 rpm and required concentrations Cr (VI) solutions were prepared by diluting the stock solution of 1000 mg/L. To evaluate the effect of the O-CNT loading on Cr (VI) sorption, 0.025 g of PPy-OCNT NC 1 - PPy-OCNT NC 3 was added to 50 mL of 300 mg/L Cr (VI) solution, then agitated at 200 rpm in a thermostatic shaker at 298K. After 24 hrs of contact, the adsorbent was then separated from the solution by filtration and the filtrate was analysed for Cr(VI) residual concentration. The Cr (VI) percentage removal was determined by the following equation Eq.(1)

$$\% \text{ removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

Where C_o and C_e are initial and equilibrium concentration (mg/L) of Cr(VI), respectively. The nanocomposite with the optimum O-CNT loading for Cr (VI) sorption was then used throughout the experiment. The effect of pH on adsorption of Cr (VI) by PPy-OCNT NC was studied by varying the pH from 2-11 using either HCl or NaOH. At optimum pH, the effect of the adsorbent dosage on the removal of Cr (VI) was studied by varying the PPy-OCNT NC mass from 0.01 g – 0.1 g using 50 mL of 200 mg/L Cr(VI) at 298 K. The removal percentages were calculated using Eq. (1).

Equilibrium isotherms and kinetics

Sorption isotherm data were generated by contacting 0.025 g of the PPy-OCNT NC with 50 mL Cr(VI) solution of varying concentrations at 298 K inside 100 mL plastic bottles. The Cr(VI) concentrations were varied from 200-600 mg/L at pH of 2.0. The bottles were then placed in a thermostatic shaker and shaken for 24 hrs at 200 rpm. At the end of the experiment, the samples were filtered through syringe filters and the residual Cr(VI) concentrations were analyzed. The equilibrium sorption capacity was determined using Eq. (2):

$$q_e = \left(\frac{C_o - C_e}{m} \right) V \quad (2)$$

Where q_e is the equilibrium amount of Cr (VI) adsorbed per unit mass (m) of adsorbent (mg/g) and V is the sample volume (L).

The kinetics of adsorption were carried out in a 1 L batch reactor with initial Cr (VI) concentrations of 100, 150 and 200 mg/L. The adsorbent mass was fixed at 0.5 g. The reactor was stirred with an overhead stirrer operated at 200 rpm. At predetermined time intervals, 10 mL samples were withdrawn from the reactor, filtered through syringe filters and analysed. Amounts of Cr (VI) ions adsorbed per unit mass of adsorbent at any time were calculated by Eq. (3):

$$q_t = \left(\frac{C_o - C_t}{m} \right) V \quad (3)$$

where q_t is the time-dependent amount of Cr (VI) adsorbed per unit mass of adsorbent (mg/g) and C_t (mg/L) is the bulk-phase Cr (VI) concentration (mg/L) at any time t .

Effect of co-existing ions and regeneration experiment

To evaluate the competitive effects of various ions such as Zn^{2+} , Pb^{2+} , Ni^{2+} , NO_3^- on Cr(VI) adsorption, 50 mL of 200mg/L Cr(VI) solution was mixed with varying concentrations (50, 100, 150 and 200mg/L) of the above mentioned ions in binary sorption systems. The pH of the mixtures was adjusted to pH 2 whereby a fixed amount of the PPy-OCNT NC was added, shaken to equilibrium, filtered and analyzed for Cr(VI) residual concentration.

Chromium analysis method

The concentrations of Cr (VI) ions were measured using a UV-VIS spectrometer, PerkinElmer, Lambda-35 at 540 nm according to the 1,5-diphenylcarbazide method.

RESULTS AND DISCUSSIONS

Effect of Ppy and O-CNT mass loading on the nanocomposite

To evaluate the effect of percentage loading of PPy and O-CNTs in the PPy-OCNT NC for Cr (VI) removal, 0.025 g of PPy-OCNT NC 1, PPy-OCNT NC 2 and PPy-OCNT NC 3 were contacted with 50 mL of 300 mg/L Cr(VI) containing solutions and left to adsorb to equilibrium. Table 1 shows the removal percentages of respective nanocomposites for Cr (VI).

Table-1: Effect of percentage loading on the adsorbent

| Material | % of OCNT loading | % of PPy loading | % Removal | Ads. Cap (mg/g) |
|---------------|-------------------|------------------|-----------|-----------------|
| PPy-OCNT NC 1 | 8.89 | 91.75 | 47.10 | 283.29 |
| PPy-OCNT NC 2 | 17.0 | 83.43 | 69.32 | 555.0 |
| PPy-OCNT NC 3 | 32.2 | 67.79 | 63.16 | 379.00 |
| OCNT | 100.00 | 0.00 | 2.00 | 10.87 |
| PPy | 0.00 | 100.00 | 37.45 | 196.72 |

It is evident that a maximum adsorption removal percentage 69.32 % is achieved at a percentage loading of 17 % OCNTs and 83 % PPy (PPy-OCNT NC 2). The decreased efficiency when the percentage loading of O-CNTs and PPy was 32.2 and 67.79, respectively, may be due to the increased O-CNTs loading given that other O-CNTs may have not been fully dispersed therefore restricting the exposure of other available O-CNTs adsorption sites to the Cr (VI) ions. Under the same experimental condition, only 2.00 % Cr (VI) removal was achieved for the O-CNTs alone and 37.45 % removal for the homo polymer. This shows that PPy plays an important role in adsorption. However, since polypyrrole alone tend to agglomerate thus limiting the adsorption sites for adherence of

chrome ions, it needs a supporting material thus OCNTs support and increase the adsorption capacity of polypyrrole. From these results, PPy-OCNT NC 2 was chosen for all subsequent experiments.

Effect of pH

The pH of a solution is one of the most important variable that govern metal adsorption on an adsorbent [22], since it reflects the nature of the physicochemical interaction of the species in the solution and the adsorptive sites of the adsorbents. Experiments were carried out to study the effects of pH (2-11) on the removal of Cr (VI) by PPy-OCNT NC data is shown in Fig. 1.

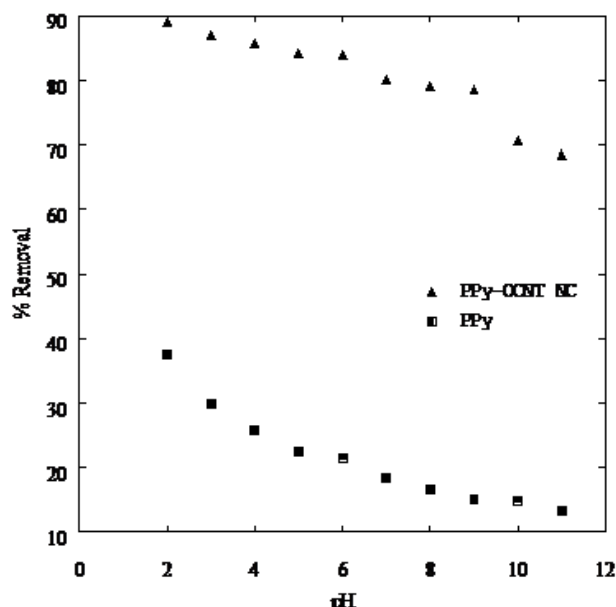


Fig-1: Effect of pH on Cr (VI) adsorption onto PPy-OCNT NC and PPy

The highest Cr (VI) removal efficiency was achieved at pH 2 with 89.07 % using PPy-OCNT NC 2, whereas only 37.45 % removal efficiency was achieved with PPy homopolymer. The increase in removal efficiency of the PPy-OCNT NC 2 is a result of the increased surface area of the OCNTs as well as the adsorptive ion exchange properties of PPy [19]. It has been reported that the speciation of Cr(VI) in aqueous solution is strongly pH dependent and that Cr exist as both monovalent bichromate, HCrO_4^- and divalent dichromate $\text{Cr}_2\text{O}_7^{2-}$ ions (especially at high concentrations) at $\text{pH} > 6$ [23,26]. The removal of these metal ions is due to anionic exchange property of PPy in the nanocomposite, where the doped Cl^- is exchanged with either HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$. However, ion exchange mechanism is not the sole mechanism responsible for the removal of Cr (VI). Surface complexation by functional surface groups on OCNTs is also responsible for Cr (VI) removal. It is important to note that the oxidized OCNTs are carbonaceous material as C_xOH where C_x is carbon and those hydroxylated surface groups vary at different pH values due to protonation and deprotonating processes. There are two possible mechanisms that occur between the carbonaceous material and chromium; first type is the direct ion

exchange where OH^- is exchanged with either HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$ and thus forms a complex. The second kind of mechanism rely on the reduction of Cr (VI) to Cr (III). It is known that Cr (VI) is reduced to Cr (III) in the presence of a reducing substrate C_xOH [6,7] on the occurrence of a redox reaction between the surface groups and the Cr (VI) at low pH values [27].

Dosage effect

The amount of adsorbent in solution is also an important parameter as it determines the capacity of an adsorbent for a given adsorbate concentration. Varying amounts of PPy-OCNT NC 2 (0.01 g - 0.1 g) were used for Cr (VI) sorption experiments at speed of 200 rpm, 298 K and pH 2 for 24 hrs. As shown in Fig. 2, the Cr (VI) removal percentage increased with increasing sorbent dosage. This indicates that the number of adsorption sites for Cr (VI) is directly proportional to the sorbent dosage. This dose-dependent behaviour allows the optimum and most economical dose for water treatment to be determined. In this case, specifically 22 % Cr (VI) removal was recorded at 0.005 g of PPy-OCNT NC 2 while 99.99 % Cr (VI) removal was recorded at 0.075 g sorbent dosage.

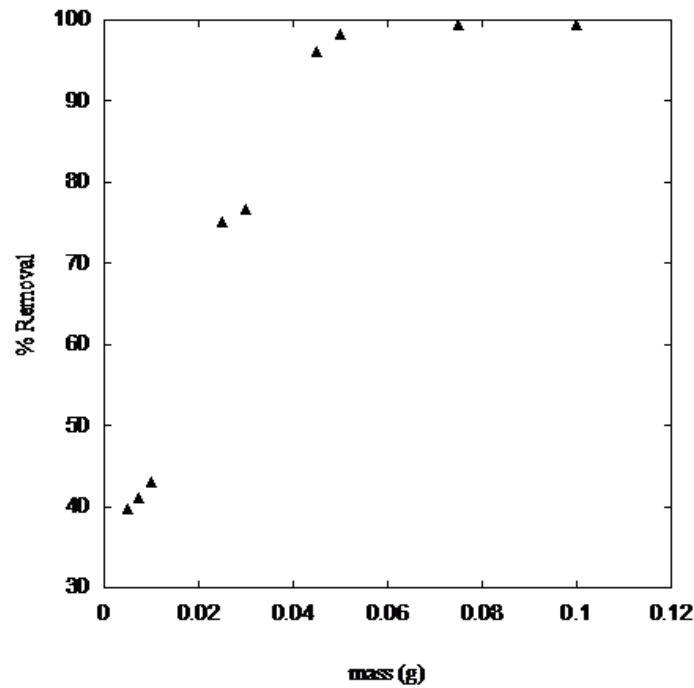


Fig-2: Effect of PPy-OCNT NC dosage on Cr(VI) adsorption

Adsorption isotherms

The relationship between metal ions and adsorbents is very essential to reach an effective adsorption. In order to demonstrate the effect of the Cr (VI) ion concentration on adsorption, experiments were carried out at different initial concentration ranging from 150 mg/L to 600 mg/L (Fig. 3). It is observed that the adsorption capacity increases with an increase in initial Cr (VI) concentration. Specifically, 300 mg/g

was recorded at 150 mg/L Cr (VI) and 545 mg/g recorded for 500 mg/L. The increase initial Cr(VI) concentration results in increased number of moles of Cr (VI) available to the adsorbent surface area therefore the number of collisions between the Cr (VI) ion and the adsorbent are increased and a driving force to overcome all mass transfer resistance between the aqueous and the solid phase is developed [28].

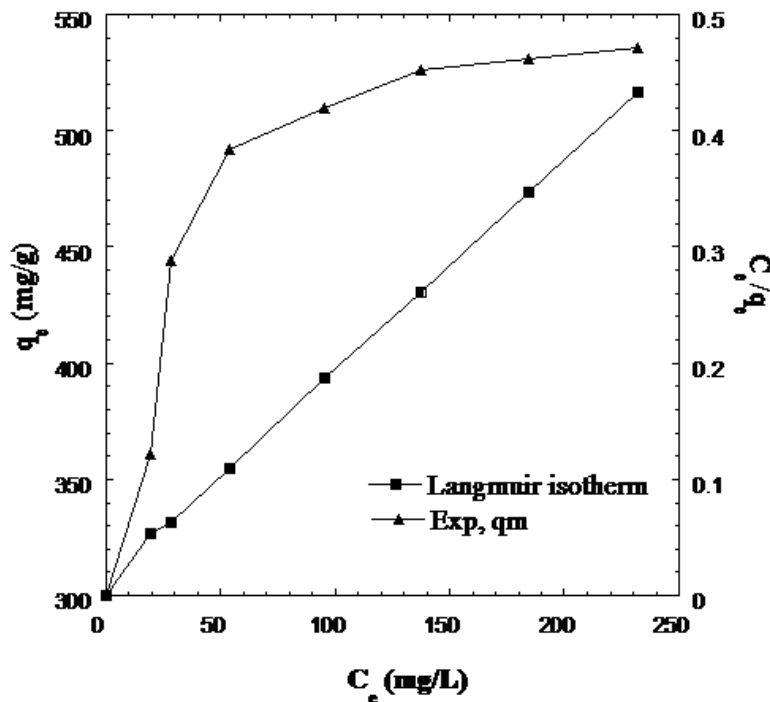


Fig-3: Isotherms of Cr (VI) sorption onto PPy-OCNT NC

The relationship between adsorbed Cr (VI) and its concentration in solution under equilibrium is described by the widely accepted Langmuir and Freundlich models. The Langmuir isotherm is valid monolayer adsorption on energetically homogenous surface with limited number of identical sites [24]. Both linear and nonlinear forms of Langmuir isotherm can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (4)$$

Where q_o (mg/g) is the maximum amount of Cr (VI) ions per unit mass of adsorbent to form a complete monolayer on the adsorbent surface and b (L/mg) is the binding energy constant. The Langmuir plot is shown in Fig. 3. Furthermore, the dimensionless separation factor, R_L , which is an essential characteristic of the Langmuir model for defining the favourability of an adsorption process was used. The R_L is given by (Eq. 5);

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates a favourable adsorption. Freundlich isotherm describes multilayer adsorption well on an energetically heterogeneous surface [23]. Freundlich isotherm describes multilayer adsorption well on an energetically heterogeneous surface. Both linear and nonlinear forms of Freundlich isotherm are described as:

$$\ln(q_e) = \ln K_f + \frac{1}{n}(C_e) \quad (6)$$

Where K_f (mg/g) and $1/n$ constants are related to the adsorption capacity and intensity of adsorption respectively. The Langmuir and Freundlich parameters are shown in Table 2.

Table 3 shows the comparisons of the adsorption capacities found in literature with the PPy-OCNT NC for Cr (VI) sorption.

Table-2: Langmuir and Freundlich isotherm constant for Cr (VI) adsorption onto OCNTs/PPy

| Temp. (K) | Langmuir constants | | | | Freundlich constants | | |
|-----------|--------------------|------------|--------|-------|----------------------|-------|-------|
| | q_m (mg/g) | b (L/mg) | R_L | R^2 | K_f (mg/g) | $1/n$ | R^2 |
| 298 | 555.56 | 0.175 | 0.0199 | 0.999 | 266.29 | 0.137 | 0.826 |

Table-3: Comparison of adsorption capacity of chromium with carbon nanotube based adsorbent and polymer based adsorbent

| Adsorbent | q_m (mg/g) | pH | t_e (min) | Reference |
|--|--------------|-----|-------------|--------------|
| Polypyrrole-polyaniline nanofibers | 227-294 | 2.0 | 30-180 | [22] |
| Polypyrrole/Fe ₃ O ₄ | 169.4 | 2.0 | 30-180 | [19] |
| Polyacrylamide grafted sawdust | 45.0 | 3.0 | - | [20] |
| Polyaniline/ humic acid composite | 150 | 5.0 | 120 | [37] |
| Polyethylenimine-modified fungal biomass | 279.2 | 4.6 | - | [36] |
| PVP coated silica gel | 30.0 | 5.0 | - | [21] |
| Polyacrylonitrile fibers | 35.0 | 5.0 | 120 | [22] |
| AFC | 65 | 3.0 | 300 | [23] |
| O-CNT | 10.87 | 2 | - | Present work |
| ACNT/CeO ₂ | 30.2 | 7.0 | 300 | [17] |
| MWCNT/nZVI | 25 | 7.0 | 120 | [24] |
| SWCNT/SSN | 20.3 | 4.0 | 60 | [25] |
| PPy-OCNT NC | 555 | 2.0 | 240 | Present work |

Kinetic Analysis

Another profound experimental parameter is time because to achieve an effective sorption process, it is essential that an adsorbent offers rapid sorption kinetics for efficient adsorbate removal from solution

and as a result, kinetic analysis offers a revelation of the transport mechanism involved in a reaction. Figure 4 represents the relationship between adsorption contact time and sorption amounts at the initial Cr (VI) concentrations of 100, 150 and 200 mg/L.

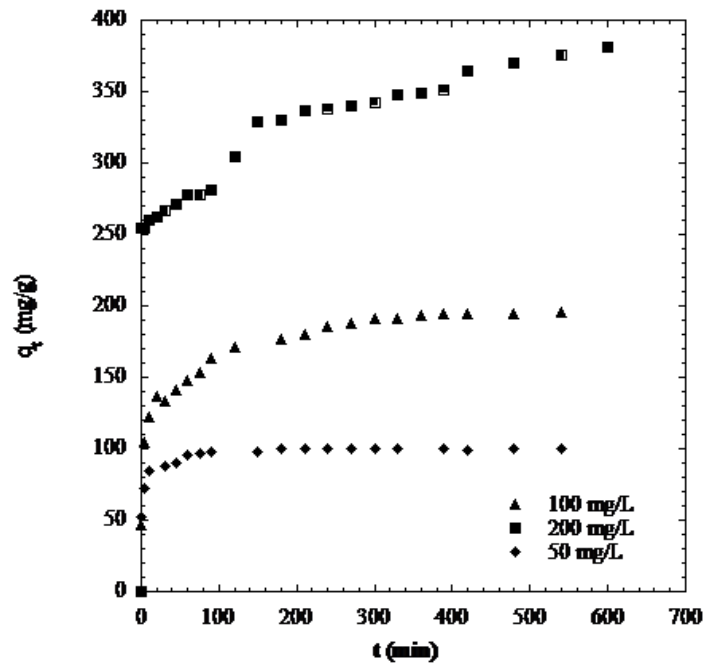


Fig-4: Relationship between adsorption contact time and sorption amounts at the initial Cr (VI) concentrations of 100, 150 and 200 mg/L.

Traditionally, adsorption occurs in three steps and this behaviour was observed on Fig. 4 where adsorption of Cr (VI) onto PPy-OCNT NC 2 for all the considered initial concentrations was rapid with an increase in time between 0-50 min and slowed down considerably as reaction approached equilibrium. The first step was a rapid adsorption that proposes that there is a readily available, large surface area on the nanocomposite. While the second step of the reaction was rather slower between (50-150min) and this is due to intraparticle diffusion of the adsorbate to the internal matrix of the adsorbent while on the third step (>150 min) the reaction stopped which is indicative of equilibrium. The rapid uptake would be ideal for lowering capital and operational costs for industrial application. This behaviour can be best explained considering the concentration gradient. Adsorption is a process where the adsorbed species concentration gradient acts as a driving force during the reaction. Accordingly, the higher the initial concentration, the higher the adsorption driving force, hence an increase in adsorption capacity. The increase in the initial concentration results in the increased number of moles

of Cr (VI) available to the adsorbent surface area, therefore the number of collisions between chromium species and adsorbent get increased and a driving force to overcome all mass transfer resistances between the aqueous and solid phases is developed [28]. In order to analyse the nature of kinetics and the rate of adsorption of total Cr (VI) by PPy-OCNT NC 2, data were further treated with Lagergren pseudo first order model and the Ho and Mckay pseudo second kinetic order model. The linearized forms of the pseudo first order (Eq. 7) and second order (Eq. 8) models are given by;

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_1 (1/min) and k_2 (g/mg/min) are the pseudo first order and second order rate constants, respectively, q_t is the amount of Cr(VI) adsorbed at any time (mg/g) and q_e is equilibrium adsorption capacity (mg/g). A linear plot of t/q_t versus t for the pseudo second order kinetic model was employed (Fig. 5).

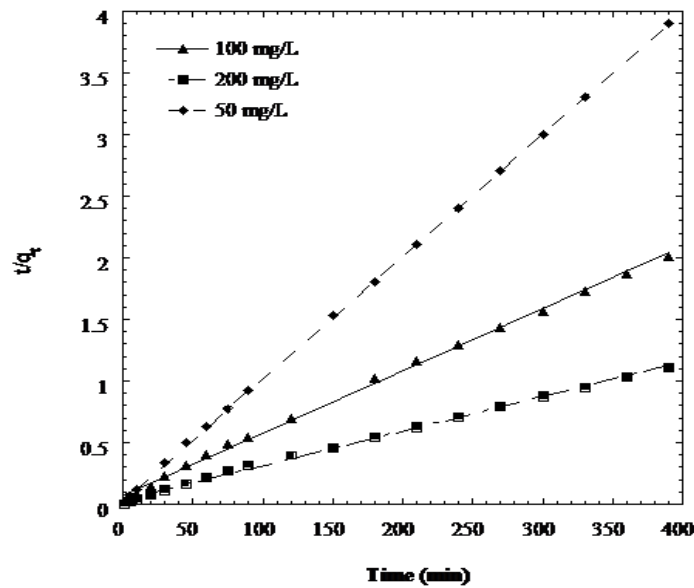


Fig-4: Pseudo second order kinetic plot of Cr (VI) sorption onto PPy-OCNT NC

Compared values of reaction rates and correlation coefficients of first order and second model for varying initial concentration of Cr (VI) is shown in

Table 4. According to the correlation coefficients and the calculated uptakes values, data is best described by the pseudo second order kinetic model.

Table-4: Pseudo first and second order kinetic model parameters for removal of Cr (VI) adsorption onto PPy-OCNT NC 2

| C _o (mg/g) | Pseudo-first –order model | | | Pseudo-second order model | | |
|-----------------------|---------------------------|-----------------------|----------------|---------------------------|-----------------------|----------------|
| | K ₁ (L/min) | q _e (mg/g) | R ² | K ₂ (L/min) | q _e (mg/g) | R ² |
| 50 | 0.029 | 32.08 | 0.939 | 0.0044 | 100 | 0.999 |
| 100 | 0.0085 | 86.44 | 0.983 | 0.0003 | 200 | 0.999 |
| 200 | 0.0077 | 188.58 | 0.906 | 0.0001 | 389 | 0.998 |

Effect co-existing ions

Competing anions and metal ions are known to influence Cr (VI) uptake [28-32]. Nitrate ion was selected as a possible competing ion because this ion is

chemically similar to dichromate ion with respect to charge. In addition to this anion, metal ions (Zn²⁺, Pb²⁺ and Ni²⁺) were also investigated for their effecting in adsorption of Cr(VI)

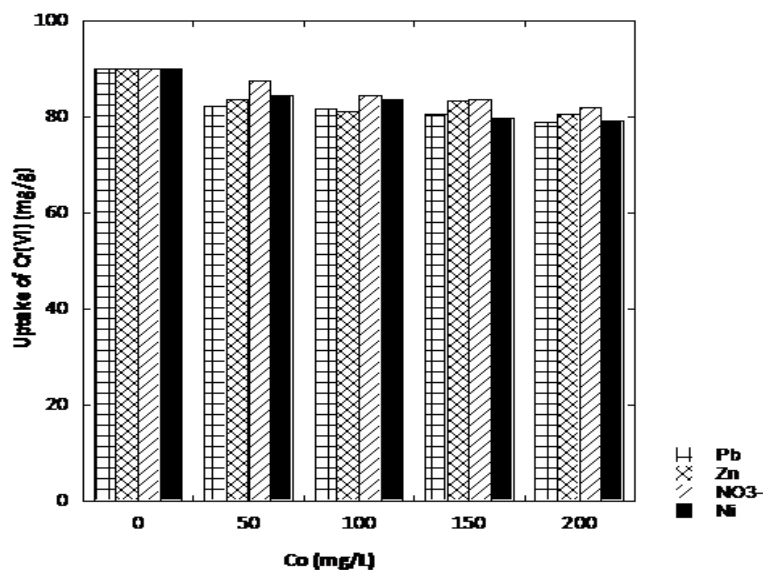


Fig-5: Effect of co-existing ions on Cr (VI) removal by the PPy-OCNT NC

Thus, the experiment was carried out in a batch mode where 0.025 g of the sorption media was contacted with 50 mL of aqueous solution containing Cr(VI) ions and known quantities of commonly occurring ions (Ni^{2+} , Zn^{2+} , Pb^{2+} , NO_3^- , Zn^{2+}) in wastewater. Figure 5 shows a typical example of the adsorption of Cr(VI) in binary components of $\text{Cr}^{6+}/\text{Ni}^{2+}$, $\text{Cr}^{6+}/\text{Pb}^{2+}$, $\text{Cr}^{6+}/\text{Zn}^{2+}$ and $\text{Cr}^{6+}/\text{NO}_3^-$. The uptake of Cr(VI) in a single component adsorption at initial concentration of 200mg/L was found to be 389.6413mg/g. It is observed that the uptake of Cr(VI) is not affected by the presence of other occurring ions, implying that the PPY-OCNT NC is selective for Cr(VI). One possible reason for Cr(VI) selectivity in the binary system with cations may be that, at lower pH, the nanocomposite is positively charged, hence giving a repulsive force to the approaching positively charged cations, and further adsorbing Cr(VI) without competition. In case of the Cr(VI)/NO_3^- binary system, the selectivity of Cr(VI) can be explained by the behaviour of NO_3^- in adsorption processes. Nitrates (NO_3^-) are of low affinity ligands which are well known to form outer-sphere complexes with binding surfaces. Their low affinity nature thus imply weaker adsorption mechanism via outer-sphere complexation, and consequently, their competitive influence during Cr(VI) adsorption is negligible [28].

CONCLUSION

PPy/O-CNT nanocomposite were successfully synthesized *in situ* polymerization technique, applied as a promising sorbent for Cr(VI) removal from aqueous solution. Results of adsorption experiment revealed that adsorption efficiency is strongly pH dependent. The removal efficiency was controlled by solution pH, contact time, temperature and initial concentration. Adsorption increased with an increase in PPy/O-CNT dosage and optimum removal of Cr(VI) was achieved at pH 2. Adsorption data fitted well to the Langmuir model, from which the maximum adsorption capacity was determined as 555mg/g at 298 K. Kinetically the adsorption process followed the Ho pseudo second order mechanism. Furthermore, PPy/O-CNT NCs proved to be selective for Cr(VI) adsorption. It can therefore be concluded that by oxidized CNTs with PPy successfully increased the uptake of the nanocomposite for Cr(VI).

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