

Application of Polymer-Natural Clay Composite in Water Treatment

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Abstract— A number of water sources contain contaminants which are hazardous to health and environment. Several treatment technologies have been employed for the remediation of contaminated water sources, with adsorption as the favored method based on its effectiveness, ease of operation and efficiency. This study evaluates the performance of polymer-natural clay composites as robust materials for multi-contaminants removal from water. More specifically, a detailed analysis of polypyrrole-montmorillonite composite performance in hexavalent chromium removal is provided. A number of water quality parameters and process variables such as flow rate and bed depth are considered. Results indicate that water quality parameters and flow dynamics have profound effect on performance. Indications are that polymer-natural clay composites are competitive materials for water quality improvement.

Keywords—contaminants, natural clay, water quality, treatment technologies.

I. INTRODUCTION

Industrial operations handle large volumes of process water, which are contaminated with organic chemicals, metal ions, oils and other materials. Aqueous streams containing heavy metals are frequently encountered in industrial effluents and sources of copper, lead, zinc and cadmium are very common in the electroplating facilities, electrolytic refining plants and acid mine waters, among others [1]. Dyes as organic chemicals are commonly found in waste streams from food and textile industries. Due to high level of industrial activities in South Africa, organic contaminants and heavy metals such as chromium, vanadium and dyes have been found to gain entry into receiving water streams and groundwater sources such as was the case with groundwater outside Bayer chemical factory in Durban [2].

Organics and heavy metals are toxic and environmentally harmful substances. Contaminants that accumulate within the living organisms as well as in human body are especially more

dangerous [3]. The presence of these contaminants in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. It is well known that heavy metals can damage nerves, liver and bone and block functional groups of essential enzymes [4].

The large volume of contaminated wastes exert enormous pressure to the existing wastewater handling mains. Moreover, to protect human health, groundwater sources and other receiving water bodies from contamination, industrial discharges must be treated sufficiently and where permitted, recycled. There are several treatment options that have been developed or show potential for remedying contaminated wastewaters. These techniques include: membrane bioreactor technology, electrodialysis, reverse osmosis, adsorption and hybrid processes combining two or more of the above techniques, among others. The choice of a treatment technique for a given utility depends on the nature and concentration of the ions, chemical species in source water, existing treatment processes, treatment costs, handling of residuals and versatility of a given technique [5]. Because of limitations in terms of cost, production of enormous waste and difficulty in end-use applications of some of the above treatment techniques, an environmentally benign, robust and low-cost a technique has to be implemented for remedying contaminated wastewater [6],[7]. Proponents of adsorption technology argue that the technique is economical, efficient and produces high quality water [8]. In the recent past, adsorption technique has been arguably one of the most versatile techniques in removing pollutants from water. Moreover, it attracts wider acceptance, is environmentally benign and is simple.

The algorithm of adsorption technology process development starts with selection of an appropriate media for a given process problem; in the foregoing water quality improvement. A number of established and potential media exist in open literature for ameliorating the quality of water. However, most of these media have poor capacity, show slow kinetics, have only been synthesized in the laboratory, are not regenerable and in some cases expensive and hence not desirable for water treatment applications.

This study proposes to explore the application of polymer-natural clay composites as robust materials for adsorptive treatment of waste streams. This line of thinking arises due to fact that (i) most adsorption materials have very low capacity for contaminants (ii) South Africa is a water scarce country and as such contaminated water resources should be treated

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sufficiently for re-use and (iii) a number of existing treatment technologies are expensive. We have previously shown the application of polymers in fluoride and chromium removal from water [9]-[10]. These new kind of materials exhibited superior quality compared to the conventional adsorbents. However, polymers have very low densities rendering them unsuitable for fixed bed operations. Adsorbent-based water treatment mostly occur in fixed-bed operations which produce high quality treated water. Dense media are required in fixed beds to avoid having extremely large (in volume terms) beds.

To extend the knowledge gained in the previous works, we evaluate the feasibility of using low-cost locally available natural clay as a matrix to hold polymers in removing chromium as an example of a pollutant from wastewater. Natural clays have sufficient density and are suited for fixed bed operation. The study focuses on exploring the effect of several water quality parameters and process variables on chromium removal efficiency in both batch and column modes of operation.

II. POLYMER-NATURAL CLAY COMPOSITES FOR WASTEWATER TREATMENT

Clays are aluminosilicates and their performance properties are related to their weak silica-alumina bond. Examples of clays widely used in water and wastewater treatment are kaolinite and bentonite. Charge development on silicate clays is mainly due to isomorphous substitution. This is the substitution of one element for another in ionic crystals without change of the structure. It takes place only between ions differing by less than about 10% to 15% in crystal radii. In tetrahedral coordination, Al^{3+} for Si^{4+} and in octahedral coordination Mg^{2+} , Fe^{2+} , Fe^{3+} for Al^{3+} . Charges developed as a result of isomorphous substitution are permanent, responsible for sorption features of the clays and not pH-dependent.

Clays in the natural form have very low capacity for (waste) water contaminants. On the other hand, polymeric resins have a wide range of pore structures, good surface areas, and a good selectivity toward aromatic solutes and little or no adsorbent loss on regeneration [11]. However, their performance is dependent on the type of resin used (extent of chemical activation and modifications, nature and degree of functionality grafted on the polymeric surface), physicochemical characteristics (i.e. porosity, specific surface area and particle size of adsorbents) and they are not effective for all organic solutes [11]. Another drawback is their pH-dependence, poor water wettability and sensitivity to particle size [11]. Furthermore, they are very expensive which have rendered them unattractive for use by many industries and water treatment plants especially in the developing world.

Consequently, they have been modified with various polymers to improve their performance in inorganic and organic contaminants removal from aqueous stream. For instance, Unuabonah et al [12] showed the potential of a polymer-clay based composite adsorbent prepared from locally obtained kaolinite clay and polyvinyl alcohol for the removal of $Pb(II)$ ions from aqueous solution. However, the material showed

significant capacity reduction during regeneration and therefore from economic point of view not suitable for water treatment operations. In another study, acrylic acid and 2-hydroxyethyl methacrylate were supported into loess clay in situ polymerization, which afforded loess clay based copolymer (LC/PAAHM), a new kind of polymer adsorbent for removing $Pb(II)$ ions from aqueous solution [13]. Very high capacity of 356.9 mg/g was observed. No information on regeneration was provided though, which could further shed light on the economic feasibility of the material. Anirudhan & Suchithra [14] explored the feasibility of utilizing a novel adsorbent, humic acid-immobilized-amine modified polyacrylamide/bentonite composite (HA-Am-PAA-B) for the adsorption of $Cu(II)$, $Zn(II)$ and $Co(II)$ ions from aqueous solutions. The new adsorbent had significant capacity for the heavy metals and in particular the following capacities were achieved: 106.2, 96.1 and 52.9 mg g^{-1} for $Cu(II)$, $Zn(II)$ and $Co(II)$ ions, respectively, at 30 °C. Moreover, regeneration was possible and 97.7 for $Cu(II)$, 98.5 for $Zn(II)$ and 99.2% for $Co(II)$ were achieved using 0.1 M HCl. A critical evaluation of the synthesis process of HA-Am-PAA-B indicates that the process is not simple; involves several steps that may pose control and cost limitations. A good adsorbent should preferably be synthesized in a one-pot synthesis route.

Meanwhile polymer-clays have also been used to remove organic contaminants from aqueous solution. El-Zahhar et al. [15] used composite material prepared by incorporating the clay (Kaolinite (Kao)) into a poly(acrylamide co-acrylic acid) (P(AAm-AA)) through the in situ polymerization method with cross-linker to remove bromophenol blue dye from industrial waste water. Another study explored the use of a new polyacrylamide-bentonite composite with amine functionality (Am-PAA-B) [16]. The Am-PAA-B was modified by immobilizing humic acid and tested as an adsorbent to remove basic dyes (Malachite Green, Methylene Blue and Crystal Violet) from aqueous solutions in a process where film diffusion was rate limiting. Further, desorption of dyes was achieved by treatment with 0.1 M HNO_3 and four adsorption-desorption cycles were performed without significant decrease in adsorption capacity. Earlier, Anirudhan and Su [17] used humic acid-immobilized amine modified polyacrylamide/bentonite composite (HA-Am-PAA-B) as an adsorbent for the adsorption of the same cationic dyes (Malachite Green (MG), Methylene Blue (MB) and Crystal Violet (CV)) from aqueous solution and showed 99% removal of these dyes in a process involving ion exchange. Gámiz et al [18] prepared and characterized a novel functional material by modifying montmorillonite with the cationic polymer hexadimethrine, and explored the potential use of this nanocomposite as a pesticide adsorbent. The characterization and adsorption experiments showed that the extent of pesticide adsorption was markedly subjected to the structure and features of the surface of each organo-clay and also to the nature of the considered pesticide. The material displayed a high affinity for anionic pesticides which, presumably, were adsorbed by electrostatic attraction on positively-charged ammonium groups of the polymer not directly interacting with

the clay.

III. PERFORMANCE EVALUATION OF POLYPYRROLE-MONTMORILLONITE IN CHROMIUM REMOVAL

A. Polypyrrole- Montmorillonite Characterization

This study considers polymer-natural clay of the type polypyrrole-montmorillonite. Polypyrrole was chosen because of its key features: very stable in the environment, has ion exchange capability and shows adsorption capability of a number of contaminants. Montmorillonite on the other hand is a major constituent of bentonite. Bentonite is low cost and abundantly available in South Africa. Coating of montmorillonite (OMMT) with polypyrrole (Ppy) produces a nanocomposite material (Ppy-OMMT NC) capable of water treatment for a number of contaminants.

The Ppy-OMMT NC was synthesized via in situ chemical oxidative polymerization technique. Based on chromium removal it was found that 33 % clay loading produced the best performance and hereafter the material containing 33% clay is referred to as Ppy-OMMT NC3. The surface area of the Ppy-OMMT NC3 was measured and found to be 16.1 m²/g while that of OMMT clay was 9.8 m²/g. This suggest that insertion of polypyrrole between the OMMT clay sheets increased the clay's surface area. Results from small angle x-ray diffraction pattern suggested that the material formed was an exfoliated Ppy-OMMT clay nanocomposite.

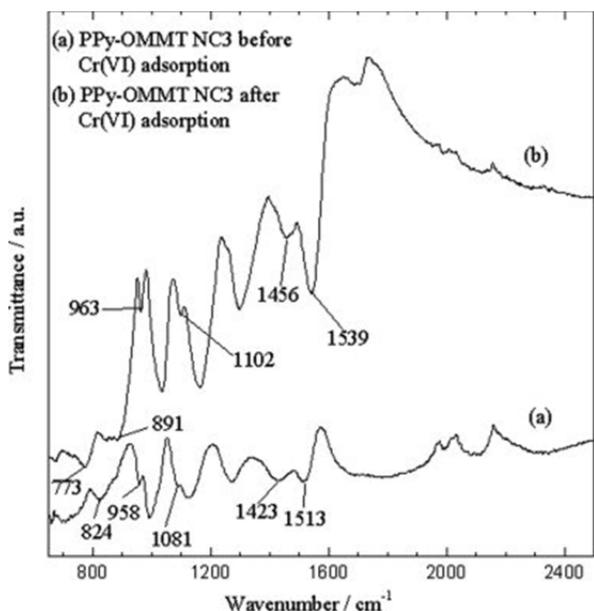


Fig. 1 FTIR spectra of the Ppy-OMMT NC3 (a) before and (b) after adsorption with Cr(VI)

Figure 1a and 1b shows the Fourier transform infrared (FTIR) spectrum of the Ppy-OMMT NC3 before and after adsorption, respectively. The peaks at 824–958 cm⁻¹, 1081 cm⁻¹, 1423 cm⁻¹ and 1513 cm⁻¹ in Fig. 1a are considered to

arise from C–H deformation, C–H stretching vibration, conjugated C–N stretching and pyrrole ring stretching, respectively [19]. These findings substantiate the presence of the PPy moieties in the nanocomposite. However, all peaks shifted to increasing wavenumber after Cr(VI) adsorption, indicating a possible interaction between the Ppy-OMMT NC3 with the Cr(VI) ions, as shown in Fig. 1b.

B. Batch Adsorption Performance

Batch adsorption is used in the initial stages to screen adsorption media in terms of capacity, performance under different water quality conditions and to compare the media with others. Studies were conducted to determine the effect of pH, adsorbent dose and initial concentration. The Ppy-OMMT NC3 performed best at pH and was able to reduce the remove completely Cr(VI) from aqueous solution. Further, the effect of temperature was explored. Temperature is known to have a profound effect on various chemical processes. Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate. Data obtained is shown in Fig. 2a. It is observed that the adsorption of Cr(VI) increases with an increase in temperature, indicating the endothermic nature of the process. For all the studied temperatures, the isotherms display analogous features, that is, very high uptake values in the low concentration range followed by plateau. It is possible that increasing temperature could have increased the mobility and the driving force of the Cr(VI) ions towards the active sites of the Ppy-OMMT NC3, hence resulting in higher Cr(VI) uptake. Additionally, the isotherm data was modeled using the Langmuir and Freundlich isotherm models. The linearized Langmuir isotherm which is based on the monolayer sorption on the adsorbent surface with identical sorption sites is represented by the following equation (Eq. (1)):

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (1)$$

where q_0 (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. Meanwhile, the Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface and the linear form is expressed by (Eq. (2)):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

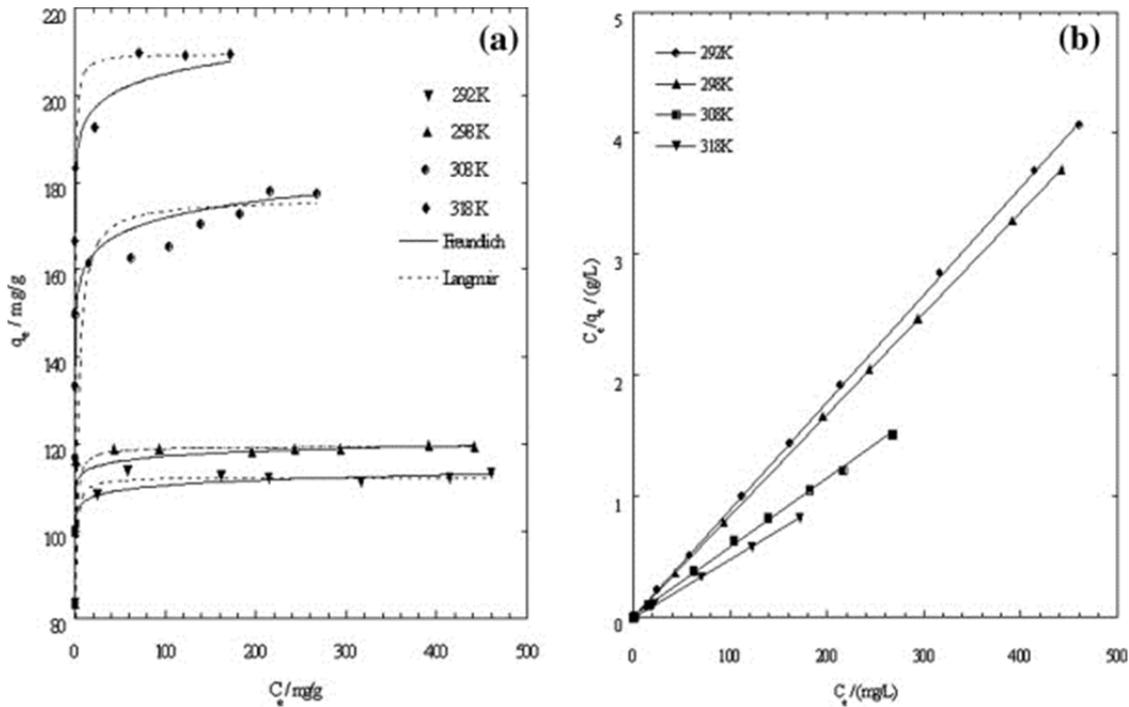


Fig 2. . Effect of temperature (a) and the linearized Langmuir isotherm (b) for Cr(VI) adsorption onto Ppy-OMMT NC3.

TABLE I
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR ADSORPTION OF Cr(VI) ONTO Ppy-OMMT NC3

Temperature (K)	Langmuir constants				Freundlich constants			
	q ₀ (mg/g)	b (L/mg)	R ²	SSE	K _F (mg/g)	1/n	R ²	SSE
292	112.3	3.37	0.999	2.67	102.9	0.0148	0.987	4.87
298	119.3	2.45	0.999	11.97	116.8	0.0042	0.987	19.83
308	176.2	0.63	0.999	7.96	148.8	0.0313	0.987	44.44
318	209.6	4.42	0.999	32.89	182.9	0.0257	0.973	56.82

where K_F(mg/g) and 1/n constants are related to the adsorption capacity and intensity of adsorption, respectively. The Langmuir isotherm provided a better fit to the experimental data based on SEE (Eq. 3) and linear plots of C_e/q_e versus C_e at 292, 298, 308 and 318 K are shown in Fig. 2b. The Langmuir and Freundlich isotherm parameters are given in

Table 1. The maximum adsorption capacities of the Langmuir isotherm increased from 112.35 to 209.6 mg/g as the temperature increased from 292 K to 318 K.

$$SSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,calc})^2}{N}} \quad (3)$$

TABLE II
COMPARISON OF ADSORPTION CAPACITY OF THE Ppy-OMMT NC3 WITH OTHER LOW COST ADSORBENTS FOR Cr(VI) AT ROOM TEMPERATURE.

Adsorbent	q ₀ (mg/g)	pH	References
Ppy-OMMT NC3	119.3	2	[19]
Aluminum magnesium mixed hydroxide	105	4	[20]
Polymeric Fe/Zr pillared montmorillonite	22.35	3	[21]
Bentonite based Arquad® 2HT-75 organoclays	14.64	4.7	[22]
Montmorillonite modified with hydroxyaluminum and cetyltrimethylammonium bromide	11.9	4	[23]
Surfactant-modified zeolite	5.07	6	[24]
Spent activated clay	0.957	2	[25]
Brazilian smectite (organically modified)	90.72	4	[26]
Surfactant-modified montmorillonite	41.5	1	[27]
Kaolinite clay	1.51	1	[28]
Magnetic natural zeolite-polypyrrole (MZ-PPy)	344.8	2	[29]

TABLE III
SUMMARY OF THE FIXED BED PARAMETERS AT BREAKTHROUGH AND EXHAUSTION POINTS FOR Cr(VI) ADSORPTION ONTO PPy-OMMT NC

Varied parameters	ECBT (min)	Service time t _b (min)	Capacity at breakthrough point (mg/g)	Capacity at exhaustion point (mg/g)	Bed volumes processed	AER (g/L)
Sorbent dosage (g)						
3	7.850	90	8.990	138.000	11.460	11.100
5	13.080	240	14.380	198.000	18.340	6.900
7	17.270	720	30.820	208.000	41.690	3.240
Initial conc. (mg/L)						
50	13.080	1080	31.390	139.500	81.500	1.560
100	13.080	240	14.380	198.000	18.340	6.900
150	13.080	60	5.390	226.800	4.560	27.770
Flow rate (mL/min)						
3	13.080	240	14.380	198.000	18.340	6.900
4	9.810	165	13.180	177.600	15.280	7.570
5	7.850	120	11.990	126.000	11.530	8.330

The maximum adsorption capacities (q₀) obtained in this study were compared to some of the other adsorbents reported in literature as shown in Table 2. Ppy-OMMT NC3 is quite competitive as its capacity for Cr(VI) is higher than the capacities of most clay materials. It should be noted, however, that the values given in Table 2 originate from different

studies in which the experimental conditions might not match those applied in the current study and, as such, that the comparison made here aims at showing the high uptake potential of Ppy-OMMT NC3 medium rather than establishing a quantitative scale of efficiency among different adsorbents.

A. Column Dynamic Performance

To produce high quality treated (waste)water, fixed beds are the preferred mode of operation. Consequently we studied chromium removal using lab scale column designed to vary bed mass, flow rate and initial concentration. These process variables are important for obtaining data to design fixed beds. Figure 3 shows breakthrough performance of PPy-OMMT NC3 for various initial concentrations. The initial concentration values were not chosen to reflect the usual concentrations present in most industrial and groundwater worldwide, instead, to show the behavior and performance of the PPy-OMMT NC3 for Cr(VI) sorption in a continuous fixed packed bed column. The influent flow rate and bed mass were kept constant at 3 mL/min and 5 g, respectively. It is observed that the breakthrough time decreases with an increase in the initial Cr(VI) concentration. This results from the fact that active sites are consumed at a faster rate at higher concentration. The bed volumes processed and adsorbent exhaustion rate (in parenthesis) were computed and found to be 81.530 (1.560), 18.340 (6.900) and 4.560 (27.770) for 50, 100 and 150 mg/L, respectively. The AER values decreased significantly with an increase in initial concentration suggesting that PPy-OMMT NC3 would be best suited to polish wastewater containing low concentration of chromium. In deed a test run at an initial concentration of 5 mg/L (Fig. 3a) gave an AER value of 0.67 g/L further confirming that the material would be best applied for low concentration chromium, which matches also the typical concentration found in many industrial wastewaters.

Further, we explored the effect of the bed mass on breakthrough performance. Bed mass relates with number of active sites available for adsorption. Three masses were used: 3, 5 and 7 g. The resulting number of BV [AER (g/L) values in parenthesis] are 11.460 (11.100), 18.340 (6.900) and 41.690 (3.240) for 3, 5 and 7 g, respectively. An increase in the number of bed volumes and a decrease in the AER values with an increase in bed mass further show that the bed efficiency increases with increasing bed mass. This may also imply that contact time played a role in adsorption and may suggest that either reaction or diffusion played a limiting role in overall uptake of chromium. This is further shown when flowrate was varied. Table 3 summarises the results obtained. It is shown that increased flowrate results in reduced performance again suggesting that diffusion played a limiting role in adsorption.

IV. CONCLUSION

Polymer-clay composite is a robust adsorption media for water treatment applications. The composite combines both the features of clay and polymer to give a material expected to have a lot of applications in water treatment. It has been shown by various researches that the composite is suited for both organic and inorganic contaminants in water. For our study the focus was inclined towards hexavalent chromium removal using polypyrrole modified montmorillonite (PPy-OMMT NC3).

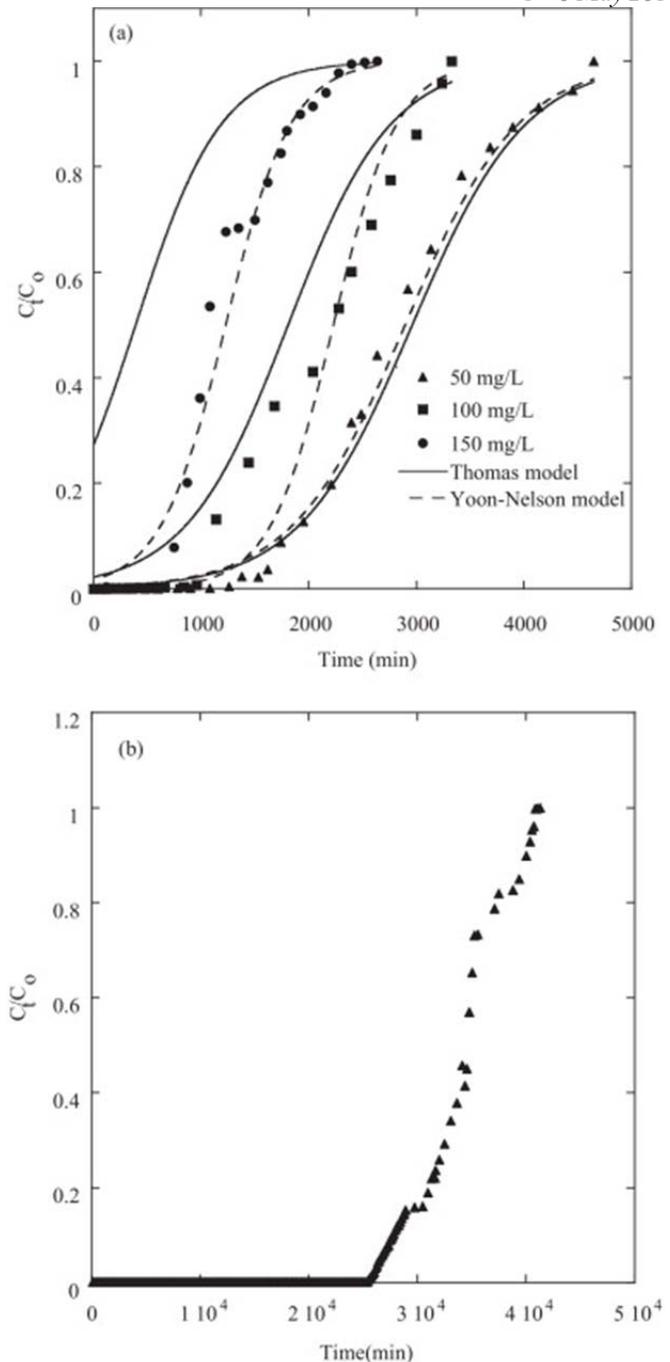


Fig. 7. (a) Breakthrough curves for adsorption of Cr(VI) onto PPy-OMMT NC3 at different initial concentration of Cr(VI) (flow rate – 3 mL/min and bed mass – 5 g) and (b) breakthrough curves for adsorption of Cr(VI) onto PPy-OMMT NC3 at lower initial concentration (10 mg/L) of Cr(VI) (flow rate = 3 mL/min and bed mass = 5 g)

Higher Cr(VI) uptake by the Ppy-OMMT NC3 was achieved compared to various low cost adsorbents reported in literature. The removal efficiency was controlled by water quality parameters. Adsorption data fitted well to the Langmuir model, from which the maximum adsorption capacity was determined as 119.34 mg/g at 298 K. The application of the PPy-OMMT NC3 as an adsorbent was also evaluated in a

fixed bed column. Process parameters such as initial Cr(VI) concentration, bed mass and flow rate were considered. The column sorption process was found to perform better at lower flow rate and initial Cr(VI) concentration and high bed mass. At breakthrough point, high bed volumes and low AER values were attained at lower flow rate, lower initial Cr(VI) concentration and higher bed mass, implying a good bed performance. We are now considering building a pilot scale production unit for PPy-OMMT NC3. From this, we will be able to evaluate the cost of the current process. Moreover, further research on desorption and regeneration of the PPy-OMMT NC3 should be considered as this also has a bearing on the cost of the material.

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