Removal of aqueous hexavalent chromium by polyaniline and nanocomposite)

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Abstract : A great challenge for this century lies in cleaning up the waste generated during industrial, do-mestic and agricultural activities. Water, an essential fluid on which all life depends, is heavily affected by such activities.Among the various contaminants found in water, heavy metals require special attention because of their toxic effect on humans and the environment, even at very dilute concentrations. Here, we report the synthesis of PANI/G composite containing graphene sheets (G), and polyaniline (PANI) via chemical route for removal of toxic Cr (VI) from water. TEM image shows the formation of uniformly distributed graphene/PANI composite. The functionalization of graphene sheets with polyaniline (PANI) was carried out in the aqueous medium via polymerizing aniline in the presence of graphene oxide and reducing it with sodium borohydride. The Cr(VI) removal capacity increases with graphene oxide loading and shows maximum for 12% loading (PANI-G12). The time dependent adsorption data shows maximum adsorption at 50min onto PANI-G12.

Keywords - **Polyaniline, Chromium, Graphene, Water, Adsorption**

I. INTRODUCTION

A great challenge for this century lies in cleaning up the waste generated during industrial, domestic and agricultural activities. In aquatic system, chromium metal exists mainly in the two oxidation states such as Cr (III) and Cr (VI). Cr (III) is an essential element needed to humans and less toxic and immobile than Cr (VI) [1]. Chromium (VI) exist in the water mainly as dichromate ($Cr_2O_7^{2-}$), chromate ($CrO4^{2-}$), and hydrogen chromate ($HCrO_4^-$ /H_2CrO_4) at pH equal to, less than, and above 6.8, respectively [2]. The US Environmental Protection Agency (EPA) and World Health Organization (WHO) recommended that a maximum allowable chromium concentration in drinking water should not be higher than 0.1 mg/L and 0.05 mg/L, respectively. On drinking water more than the permissible limit for prolonged period can lead to skin irritation, lung cancer, and damage to kidney, liver, and gastrointestinal track [3]. Hexavalent chromium concentration has to be reduced to permissible limit before discharging industrials effluents to aquatic environment [4].

Polyaniline (PANI) is a conducting polymer and has high removal capacity toward hexavalent chromium anions [5]. The conjugated PANI has three different structures, i.e., leucoemeraldine (LB), emeraldine (EB), and pernigraniline (PB) [6]. It has good reduction behaviors for Cr (VI) to Cr (III) with the electron transfer from the LB or EB states to PB state[7]. PANI in powder form is a good candidate for highly efficient Cr (VI) removal due to high adsorption capacity, low cost, and easily bulk production [8–10]. PANI is macroporous in nature and has small surface area and has been used for adsorption of Cr (VI). PANI doped with sulfuric acid shows maximum Cr (VI) removal 95.79 mg/g [11]. PANI has been functionalized with sawdust [12] silica gel, [13] ethyl cellulose, [14] and polyacrylonitrile [15] to enhance Cr (VI) removal capacity.

The most recent discovered synthetic allotrope of carbon, two dimensional graphene and its derivatives have been used in water treatment containing organic, inorganic, and biological pollutants[16–18]. Graphene-based magnetic adsorbents have been widely accepted for treatment of contaminated water due to low operation cost and do not need membrane and electrical/solar energy [19].

II. Experimental

2.1 Chemicals

Graphite (Alfa Aesar, Massachusetts United States), Sodium Nitrate (Merck, Mumbai India), Potassium Permanganate (Aldrich, Bangalore India), Hydrogen Peroxide (30 wt % Alfa Aesar, Heyshan England), Sulfuric Acid (Merck, Mumbai India), Hydrochloric Acid (Merck, Mumbai India), Liquor ammonia (Merck, Mumbai India), Aniline (Merck, Mumbai India), Ammonium Persulphate (Sigma Aldrich, Bangalore India) were obtained and used for synthesis of adsorbents and potassium dichromate (Merck, Mumbai India) in making chromium contaminated water.

2.2 Synthesis of Graphene Oxide

GO was synthesized via chemical oxidation of graphite as reported earlier [20] Approximately 5 g graphite and 5 g $NaNO_3$ were added in 125 mL of H_2SO_4 (95%) in a 1000-mL flask at ice temperature. The mixture was stirred for 30 min at this temperature. Approximately 15 g potassium permanganate was added to the suspension very slowly and temperature was maintained below 15^0C. After this, ice bath was removed and the mixture was stirred at 35^0C until it became brownish paste and

then diluted with slow addition of 250 mL water. Further, this solution was diluted by adding 500 mL water and 10 mL H_2O_2 (30 wt %). The solution mixture was washed with 10% HCl many times to remove metal impurities of graphite and finally washed with the deionized (DI) water several times. After filtration and drying under vacuum and at room temperature, the GO was obtained as a powder.

2.3 Synthesis of Graphene-Polyaniline Composite

About 200 mg of GO and 2 mL aniline were dispersed in 100 mL of 1 M HCl aqueous solution at 0^0C. About 5 g ammonium persulfate was dissolved in 100 mL of 1 M HCl and cooled down to 0^0C. Polymerization of aniline was carried out by addition of ammonium persulfate in the aniline solution with continuous stirring at ice temperature and resulting solution was allowed to stand at room temperature for overnight. The product was washed with copious amount of water and redispersed into 100 mL water. The reduction of GO was carried out using 10 mL of 0.5 M sodium borohydride solution. The product was washed with water and finally with ethanol and dried at 100^0C for 10 h.

2.4 Cr (VI) Adsorption Experiments

A stock solution of initial concentration (C_o) 35 ppm was prepared in distilled water by dissolving 100 mg of potassium dichromate ($K_2Cr_2O_7$, F.W. 294.19) in 1L and pH 6.5. The pH of solution was maintained using HCl and NaOH solution. The required amount of adsorbent was added to Cr (VI) solution and mechanically stirred for different time interval. At the end of adsorption experiment, the adsorbent was separated from solution using hand held magnet. The Cr (VI) concentration in the solution after (C) adsorption was measured using UV–vis spectrophotometer by monitoring the absorbance change at maximum wavelength (λmax = 372 nm). The equilibrium adsorption capacity was calculated q (mg /g) =(Co – C) x V/w, where w is adsorbent dose (mg) and V (mL) volume of Cr (VI) solution. The adsorption capacity of G/PANI (12%) was found to be 42.30 mg/g of 35 ppm Cr (VI) in 50 minutes.

2.5 Analysis Instruments

The powder X-ray diffraction patterns (XRD) were recorded on a Bruker with Cu-Kα irradiation (λ = 1.5406 A ˚) [21]. The microscopic features of the samples were characterized by transmission and high resolution transmission electron microscopy (TEM and HRTEM) using FEI Tecnai G2F30 S-Twin with an accelerating voltage of 200 kV. UV-visible spectra of the samples were obtained using a Systronics spectrometer in the wavelength region between 200 and 800 nm.

III.

Result and Discussion

The TEM observation of G/PANI shows the formation of PANI on the surface of graphene sheets due to p–p interaction and adopts morphology similar to the graphene sheet [20]. The powder X-ray diffraction patterns of graphite shows a sharp diffraction peak at 26.58 corresponding to (002) plane. On oxidation of graphite using oxidizing agents, the inter-planer distance between (002) planes increases due to intercalations of different functional groups and peak shifted to lower angle 2Ө = 14.68. (JCPDS No. 75-0033), The crystallite size calculated from Debye Scherrer formula shows 12 nm. The broad peak at 2Ө = 25 is due to the formation of amorphous G/PANI [20].
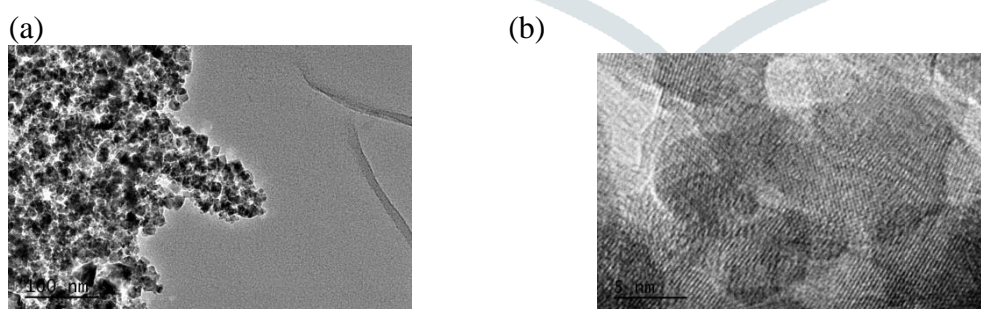
(a)

(b)

Figure 1. TEM image of (a) G/PANI, (b) HRTEM image of G/PANI

3.1 Hexavalent Chromium Adsorption

The Cr (VI) adsorption onto PANI, grapheme and G/PANI was studied at pH 6.5, temperature 308K, adsorbent dose 0.5 mg/mL, Cr (VI) concentration 35 ppm, and time of adsorption 2 hr [Figure (a)]. The G/PANI (12%) shows Cr (VI) adsorption capacity higher than the PANI. The increase in the Cr (VI) removal capacity originates from the presence of graphene sheets having   high   surface   area   and   electron   transport   and   enhances   adsorptive   sites
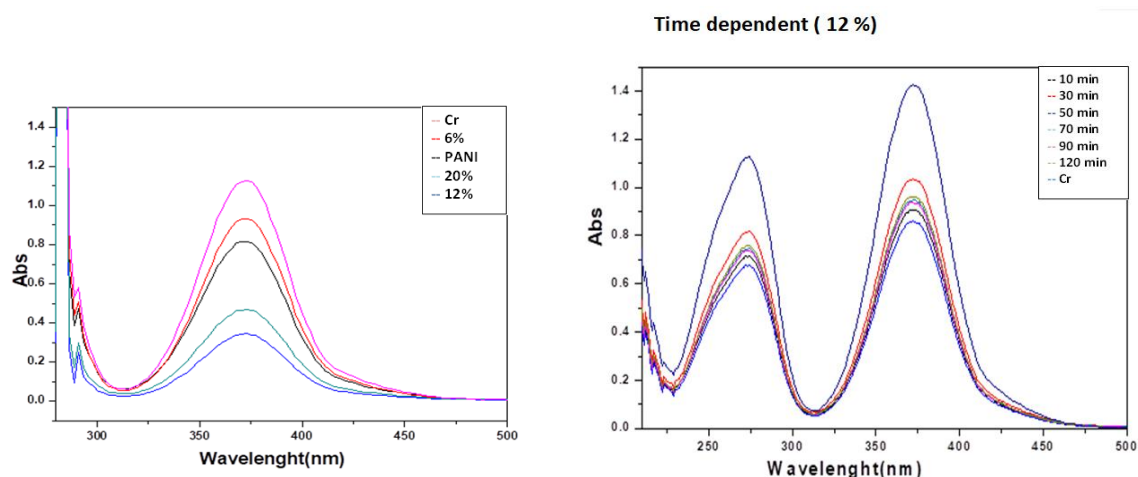
Figure (a)
Effect of Adsorption Time

Figure (b)

The time-dependent adsorption of Cr (VI) on to G/PANI (12%) was studied for 35 ppm Cr (VI) solution at pH 6.5 and 308K and adsorbent dose 0.5 mg/mL. The time dependent results showed that adsorption capacity increases with increase in contact time and attained equilibrium after 50 min [Figure (b)]. The adsorption capacity of G/PANI (12%) was found to be 42.30 mg/g of 35 ppm Cr (VI) in 50 minute**s.**

IV. Conclusion

The adsorbent (G/PANI) was synthesized via chemical route. The presence of G/PANI composite removed around 70% Cr (VI) within 50 min from 35 ppm solution at pH 6.5. The Cr (VI) removal is the combined effect of electrostatic interaction and electroreduction and comes from amino groups of PANI. More than 60% Cr (VI) ions can be easily desorbed from the adsorbent using basic solution of pH 12.

V. ACKNOWLEDGMENTS

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