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RESEARCH ARTICLE

Treatment of Heavy Metals Contaminated industrial waste water by functionalized polymers

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Abstract

Two amine base polymer aniline formaldehyde condensate (AFC) prepared and coated on silica gel and polyanilne synthesized on jute fiber (PANI-jute) were used as an adsorbent for removal of copper [Cu2+], and hexavalent chromium [Cr(VI)] from industrial wastewater. Series of batch adsorption experiments were conducted to investigate the effect of pH, mechanism of metal ions adsorption along with kinetics. With the increase in reaction pH, adsorption of cationic ions Cu2+ increased with maximum removal of 71% at pH 6through tridentate and bidentate coordination bond formed between nitrogen atom in AFC and positively charged Cu2+ by sharing electron. Both AFC and PANI achieved maximum removal of Cr(VI) at pH 3. Adsorption of both Cu(II) and Cr(VI) by AFC and PANI-jute were observed to obeyed Lagergren's pseudo second order kinetic model suggesting chemiosorption. However, the efficiency of the adsorbent reduce by 10-15% when employed for actual industrial waste water due to presence of other co-ions.

1. INTRODUCTION

Heavy metals such as cadmium, nickel, copper, lead, zinc, mercury, arsenic, chromium etc. are generated largely from various industrial processes (Khezami et al, 2005; Singh et al 2015). Chromium exists in environment both as trivalent [Cr^{3+}] and hexavalent [Cr^{6+}] forms of which hexavalent form is five hundred times more toxic than the trivalent one. According to US Department of Health and Human Services, 1991, human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage**.** WHO (World Health Organization, 1993) and BIS (Bureau of Indian Standards, 1991) recommended guideline value for chromium (as total Chromium) in drinking water as 0.05 mg/L (desirable) with no relaxation on permissible limit. Industrial effluents are the major source of copper such as Electroplating, electricals (Aksu et al, 1991; Figueira et al, 2000). Adsorption is an effective and versatile method for removal of heavy metals when combined with appropriate desorption step solving the problem of sludge disposal (Bailey et al, 1999). During recent years, various low-cost and naturally available adsorbents like wool, saw dust, used tyres, seaweed, dead fungal biomass were used for removal of chromium (Dakiky et al, 2002; Tiwari et al 2014). The need for effective and economical adsorbents for removal of heavy metals from wastewater has directed attention to the development polyacrylonitrile fibers etc. due to their high affinity for metal ions, less equilibrium time, lower sludge generation and potential for metal (Neetu et al, 2014; Dhruv et al 2015). Aniline formaldehyde condensate (AFC) and polynailine (PANI) are functionalized polymer having amine ($-NH_2$) groups which can make coordination bond with cationic metals due to presence of lone pair of electrons in *sp3* hybridized amine nitrogen. Present study aims at investigating the feasibility of AFC and PANI for removal of toxic hexavalent chromium and copper from industrial waste water.

2. MATERIALS AND METHODS

Aniline formaldehyde condensate (AFC) was synthesized by reacting formaldehyde (HCHO) with aniline ($C_6H_5NH_2$) as per Liu and Freund, 1997 and the reaction scheme is shown in Fig. 1. Polyaniline was synthesized by oxidation of aniline in presence of 1,4-phenylenediamine, a chain terminator in acidic aqueous medium in presence of an oxidant, ammonium peroxydisulfate. The synthesis scheme of PANI is shown in Fig. 2.

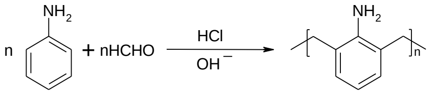

Fig 1. Synthesis scheme of Aniline formaldehyde condensate (AFC)

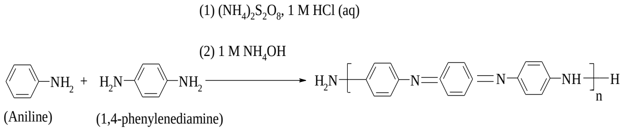

Fig 2. Synthesis scheme of short chain polyaniline

3. EXPERIMENTAL METHODOLOGY

All adsorption studies were carried out with 1000 mL of metal solution in two-liter beaker to prevent the spill off of the solution during mixing adsorbent. Predetermined quantities of adsorbent were added in the beaker and a paddle stirrer was also employed with speed adjusted at 1000 rpm. Solution pH ranges of 3 to 7 were well adjusted by 0.1 M NaOH and 0.1 N H_2SO_4. A blank solution experiment was run in each set and confirmed the inability of plastic reactor vessel to adsorb metal ions. The amount of metal ion adsorbed by adsorbent was calculated based on the difference of metal ion concentration in aqueous solution before and after adsorption according to the equation (1):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \text{..............} \; [1]$$

where, q_t is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at time t, C_0 and C_t are the concentrations of metal ions (mg/L) at initial time and at time t respectively, V is the initial volume of metal ions sample (L) and m is mass of adsorbent (g). When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of metal ions adsorbed at equilibrium, q_e was calculated using Eq. [1].

4. ANALYTICAL PROCEDURE

Concentration of Cr(VI) was measured by diphenyl carbazide colorimetric method at 540 nm wavelength using U.V. Spectrophotometer (Varian, model Cary 50) according to APHA. Concentration of Cu^{2+} were estimated using atomic absorption spectrophotometer using air-acetylene flame at wavelength of 218.2nm at slit width of 0.2 nm and working condition of lamp at 4 mA.

5. RESULTS AND DISCUSSION

5.1 Effect of pH

Solution pH is one of the most important factors during adsorption since it reflects the nature of the physico-chemical interaction of the species in solution and the adsorptive sites of adsorbent (Aksu et al, 2003; Alla et al 2012). Effect of reaction pH on Cu^{2+} and Cr(VI) by AFC coated silica gel and PANI-jute was studied varying solution pH form 1 to 11. Since Cu^{2+} precipitates above pH 6, experiments were conducted till pH 6. From Fig. 3, it can be seen that Cu^{2+} uptake increased steadily with increase in pH. Negligible removal of Cu^{2+} ion was observed at solution pH 3 and at pH of 3.5 with less than uptake of 20%. With increase in pH, equilibrium Cu^{2+} uptakes increased to 30% at pH 5 to 55 at pH 5.4. When pH was further increased to 6, equilibrium Cu^{2+} uptakes increased to 71%. Copper ion (Cu^{2+}) exists in aqueous medium as square pyramidal form coordinated by water molecules. Nitrogen atom in amine can make coordinate bond with positively charged metal ions due to presence of lone pair of electrons in *sp3* hybridized amine nitrogen. In acidic medium amine exists as protonated ammonium ($-NH_3^+$) and affinity towards Cu^{2+} ion was negligible due to charge repulsion (Tiwari et. al). Hence very low removal of Cu^{2+} ion was achieved in acidic pH. With increase in solution pH, amine group was deprotonated ($-NH_2$ form) and it replaced one or more of water molecules from the coordination sphere of Cu^{2+}.

For adsorption of Cr(VI) by AFC and PANI-jute, the results are incorporated at Fig. 3. Optimum removal for both AFC and PANI-jute were observed at pH 3 with platue formation. At reaction pH of 1, Cr(VI) removal by AFC was 6% which increased significantly to 58% at reaction pH of 3. However Cr(VI) adsorption decreased drastically to 36% at pH 4 to insignificant removal of Cr(VI) at pH 7. Similarly for PANI-jute, Cr(VI) removal increase from 35 to 48% as pH increased from pH 1 to pH 3 and further drops in removal with further increased in pH. Similar pH trend with platue formation on removal of chromium were also observed by various adsorbents like wool, olive cake, sawdust, pine needles, almond, coal and cactus with optimum pH 2 as well as by modified PVP-coated silica gel at pH 5.5 (Garg et al , 2000). Within the studied pH range (2-6) used in the present work, the predominating form of Cr(VI) in solution is acid chromate ion ($HCrO_4^-$) **(**Benefield et al, 1982; Singh 2015). In acidic medium, amine group ($-NH_2$) of AFC and PANI-jute exists as protonated ammonium ($-NH_3^+$) form and electrostatic attraction between protonated ammonium ion and negatively charged $HCrO_4^-$ ion is expected for removal of Cr(VI) from solution. However reduction of Cr(VI) to Cr(III) at higher acidic pH decrease the binding of Cr(VI) to protonated amine as explained above With increase in pH, this electrostatic attraction is decrease due to deprotonation of amine group.

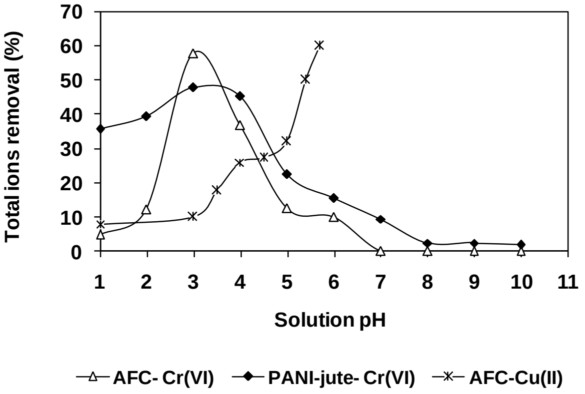

Fig. 3. Effect of pH on Cu(II) and Cr(VI) removal; initial Cr(VI) 50 mg/L

5.2 Adsorption Kinetics

Adsorption kinetics is one of the important parameters during the interaction of adsorbate and adsorbent since it reflects the requirement of volume of reactor. The adsorbent-Cu^{2+} ion interaction reached equilibrium within 120-150 min [Fig. 4]. The shape of the curve representing Cu^{2+} uptake versus time suggests that a two-step process involved. The first portion indicates rapid adsorption during initial 20-30 min after which equilibrium was achieved slowly in 120-150 min. Along with, to know the effect of time on Cr(VI) removal by AFC and PANI-jute, initial Cr(VI) of 50 mg/L were contacted separately with 4 g/L AFC dose and 2 g/L PANI-jute. Adsorption equilibrium for Cr(VI) were almost achieved within 90- 120 min of agitation time by AFC and 40- 120 min by PANI-jute. Such rapid adsorption suggests a readily available, large surface area and smaller diffusion path for both AFC and PANI-jute on chromium ions adsorption. As compared to 2 h equilibrium time of AFC and PANI-jute, seaweed biomass *Ecklonia* pre-treated with HNO_3 required 9 h for complete removal of Cr(VI) from initial concentration of 200 mg/L (Park et al, 2005).

The kinetics data of all the three adsorption of Cu(II) by AFC and Cr(VI) by AFC & PANI-jute were treated with Lagergren's linear pseudo first order kinetics model [Eq. 2 & Eq. 3 respectively].

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303}t \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ [2]$$

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ [3]$$

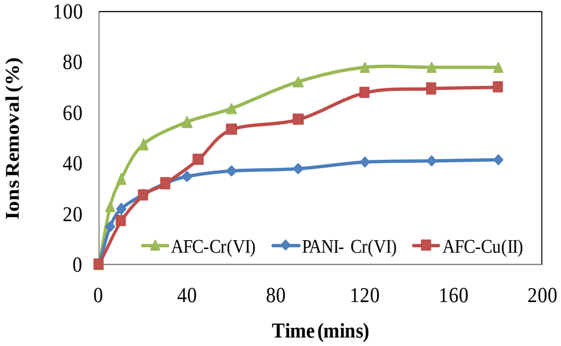

Fig. 4. Effect of time on Cu(II) & Cr(VI) removal: dose: 2 g/L PANI-jute, 8 g/L AFC

Second order kinetics showed better regression with R^2 value of above 0.99 as compared to lower value for first order model as shown in Table I. These suggest the adsorption kinetics obeying second order model indicating the chemical adsorption behavior. In order to confirm this hypothesis, error analyses were conducted through Chi square method. From Table 1, its clear that with error of less than unity for all adsorption of Cu(II) and Cr(VI) by both AFC and PANI-jute against high error of first order, chemical adsorption behavior of second order is thus confirmed.

In order to evaluate the actual performance of the adsorbents, industrial waste water was collected from electroplating unit from Okhla industrial area of Delhi. The concentration of the metal ions was diluted and make similar concentration of 50 mg/L to the synthetic samples. However on adsorption experiments, the uptake of all Cu(II), Cr(VI) were decreased by 15%. The reason was studied by assessing the sample and observed other co-ions Ni(II) and Zn(II) of similar concentrations. Along with Cu(II) and Cr(VI), both Ni(II) and Zn(II) were also absorbed by the adsorbents by about 20- 30% thus occupying the active sites of Cu(II) and Cr(VI).

TABLE I: REGRESSION & ERROR ANALYSIS OF LAGERGREN'S FIRST AND SECOND ORDER KINETIC MODELS.

	1st Order		2nd Order	
	R^2	λ^2	R^2	λ^2
AFC-Cr(VI)	0.977	9.87	0.999	0.071
PANI-Cr(VI)	0.6	2725	0.999	0.046
AFC-Cu(II)	0.955	10.35	0.991	0.375

6. CONCLUSION

Two functionalized polymer with abundance of amine were prepared and employed as adsorbent for removal of Cu^{2+} and Cr(VI). With the increase in reaction pH, adsorption of Cu^{2+} increased with maximum removal of 71% at pH 6. At acidic pH, amine group in AFC gets protonated and repulsed the positively charged Cu^{2+} ions. With increase in solution pH, protonation on amine in AFC decreased and thus tridentate and bidentate coordination bond was formed between nitrogen atom in AFC and positively charged Cu^{2+} ions by sharing electron. Maximum removal of Cr(VI) by both AFC and PANI-jute were observed to be at pH 3 with maximum reduction to Cr(III) at acidic pH. Removal mechanism of Cr(VI) by AFC and PANI-jute were observed similar and can be explained as electrostatic attraction of negative chromate ions $[HCO_4^-]$and protonated amine (NH_3^+) sites of polymers along with reduction of Cr(VI) to Cr(III). On employment of adsorbents to actual industrial waste water, the efficiency reduced by almost 10-15%. The presence of other metal ions such a s Ni(II) and Zn(II) were the probable reasons.

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