Removal of Aromatic Amines from Water by Cu^{2+}–impregnated Chitosan/alumina Bionanocomposite

Siamak Zavareh*[1], and Parizad Beiramyan[2]

Abstract**—** The pollution of natural waters with aromatic amines originating from wastewaters of many industries is of serious concern due to its negative impact on environment and living organisms. In this research work, Cu^{2+}–impregnated chitosan/alumina nanocomposite was prepared and employed as an adsorbent for removal of aromatic amines from water. The results showed that the adsorption capacity of the prepared adsorbent toward aromatic amines such as aniline is much higher than that of neat chitosan and chitosan/alumina nanocomposite. Adsorption behavior of the modified adsorbent was also studied using adsorption isotherms at room temperature. The adsorption data for the modified adsorbent were fitted well by Langmuir and Freundlich isotherm models. Chemical and morphological properties of the adsorbent were studied using FTIR and SEM. A much higher surface area of the modified adsorbent compared to neat chitosan and the presence of Cu(II) bonded to the adsorbent surface are main causes of the higher adsorption capacity for the prepared adsorbent compared to neat chitosan and chitosan/alumina nanocomposit. According to the obtained results, the introduced bionanocomposite can be applied for effective removal of aromatic amines from water.

Keywords**—**Adsorption, Aromatic amines, Bionanocomposite, Chitosan

I. Introduction

POLLUTION of natural waters with organic materials is of serious environmental concern because they have significant harmful effect on human health and environment [1]. A class of organic materials named as aromatic amines can be introduced into water bodies through many chemical, petrochemical and pharmaceutical industries [2]. Therefore, effective removal of aromatic amines from water is of significant importance.

Many methods such as coagulation [3], reverse osmosis [4], dialysis [5], photo-catalytic degradation [6], biological treatment [7] and adsorption [8] are used commonly for removal of aromatic amines from water.

Siamak Zavareh[1] is with the Department of Applied Chemistry, Faculty of Science, University of Maragheh, Iran.

Parizad Beiramyan[2] is with the Department of Material Engineering, Faculty of Science, University of Maragheh, Iran.

Among these methods, adsorption has attracted much interest due to its simplicity, easy operation and low cost. Various adsorbents have been developed for removal of aromatic amines from water. Activated carbon [9], magnetic iron oxide nanoparticles [10], surfaced modified and functionalized carbon nanotubes [11], silica gel [12] and montmorillonite [13] are samples of adsorbents studied for removal of aromatic amines.

Chitosan based biosorbents are used widely for removal of many pollutants (such as heavy metal ions, dyes and pesticides) from water due to the presence of many amino and hydroxyl functional groups in its structure and its biodegradability [14]. Many studies have been performed to increase the adsorption capacity of the chitosan by preparing the nanocomposites with metal oxides nanoparticles [15], clays [16], carbon nanotube [17], graphene oxide [18] and other nano-scaled inorganic materials.

The objective of the present study was to remove aromatic amines from water using a chitosan based adsorbent. It is also aimed to increase the adsorption capacity and selectivity of the chitosan toward aniline as a typical aromatic amine. For this purpose, Cu–chitosan/nano-alumina was prepared and employed for removal of aromatic amines from water. Structural, morphological and adsorption properties of the modified adsorbent were studied and compared with those of neat chitosan bead and chitosan/nano-alumina adsorbents.

II. Experimental

A. Materials

Medium molecular weight chitosan with deacetylation degree of 85–95% was purchased from Sigma-Aldrich Chemicals. γ-Al_2O_3 with average particle size of 20-30 nm supplied by TECNAN Nanoproducts was employed as nano-filler.

B. Preparation of Adsorbents

In order to prepare chitosan/nano-alumina beads, γ-Al_2O_3 nanoparticles were dried in an oven for 6 h at 100 °C. The dried nano-filler was mixed with oxalic acid solution for 5 h at room temperature. The acid-treated nano-filler was then filtered, washed with water and dried in an oven at 80 °C. About 10 g of medium molecular weight chitosan was slowly

mixed with 200 mL of 10 wt% oxalic acid solution to form a viscous mixture. The mixture, then, was diluted with 200 mL distilled water and heated to 50 °C to facilitate mixing. About 0.4 g of acid treated nano-alumina was added to the mixture and stirred for 24 h. Excess oxalic acid in the mixture was neutralized with NaOH solution to settle chitosan/nano-alumina beads. The chitosan/nano-alumina beads were filtered, washed with water completely and dried in an oven at 60 °C for 3 days.

In order to prepare Cu–bonded chitosan/alumina nanocomposite, the chitosan/alumina beads were mixed with $CuSO_4$ solution for 2 h. The concentration of $CuSO_4$ and chitosan/alumina beads in the mixture was selected based on maximum adsorption capacity of the prepared adsorbent. In the optimum condition, the molar ratio of Cu^{2+} to glucosamine groups of the adsorbent was 1.3. Then, the modified adsorbent was filtered, washed with water and dried.

C. Characterization of Adsorbents

Surface morphology of adsorbents was studied using scanning electron microscopy (SEM). A Vega Tescan SEM (Czech Republic) was employed to take micrographs of adsorbents. In order to obtain clear picture, the surfaces of adsorbents were gold sputter-coated before observation.

Fourier transform infrared (FTIR) spectra of adsorbents were recorded on Bruker Tensor 27 spectrometer (Germany).

D. Batch Adsorption Experiments

All batch adsorption studies were performed with aqueous solutions of Aniline with certain concentrations prepared by consecutive dilution of the stock solution. All solutions had the pH values in the range of pH=7-8. Equilibrium isotherm measurements were carried out by constant solution volume of 100 mL and adsorbent amount of 0.2 g, and varying amounts of Aniline concentrations at room temperature. Aniline solutions in the presence of adsorbents were allowed to attain equilibrium by stirring at 100 rpm in a water bath for 4 h. After equilibration, adsorbents were filtered from solutions and filtrates were analyzed.

The amount of As (III) adsorbed (mg) per unit mass of the adsorbent (g), q_e, was obtained by using the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

where C_i and C_e are initial and equilibrium concentrations in mg/L, m is the dry mass of adsorbent in gram and V is volume of solution in liters.

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbents

SEM images of chitosan, chitosan/nano-alumina and cu-chitosan/nano-alumina beads are shown in Fig. 1.

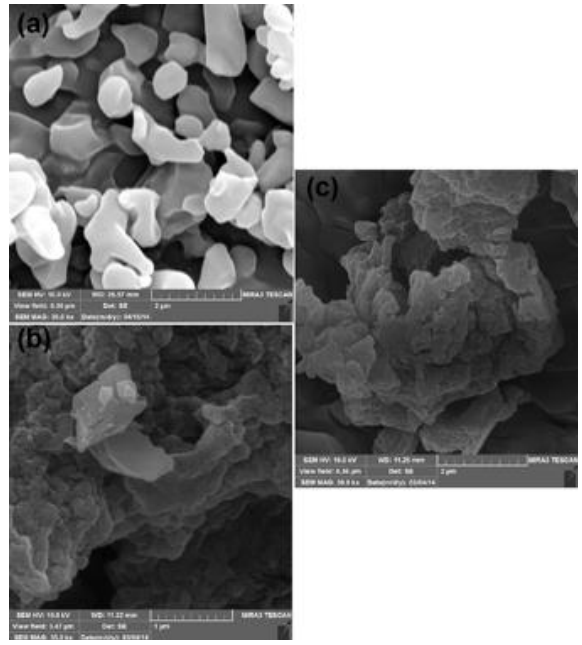

Fig. 1 SEM image of (a) neat chitosan, (b) chitosan/nano-alumina and (c) Cu-chitosan/nano-alumina

More porous surface morphology was observed for Cu-chitosan/nano-alumina and chitosan/nano-alumina adsorbents compared to neat chitosan. This implies that the incorporation of nano-alumina into chitosan matrix increases surface porosity of the resultant nanocomposite. To confirm the results observed by SEM imaging, the BET surface area of the adsorbents were determined to be 10, 35 and 29 m^2/g, respectively. The surface area for cu-chitosan/nano-alumina was slightly lower than that of chitosan/nano-alumina. Impregnation of chitosan/nano-alumina adsorbent by Cu^{2+} solution to prepare Cu-chitosan/nano-alumina with Cu(II)-bonded on the adsorbent surface may reduce the surface area.

Chemical properties of the adsorbent surfaces were evaluated by FTIR spectroscopy as presented in Fig. 2.

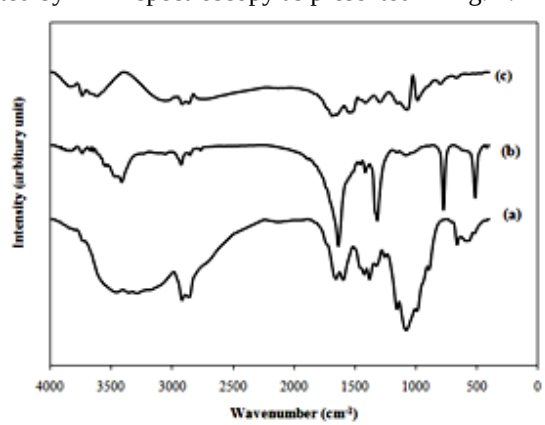

Fig. 2 FTIR spectrum of (a) neat chitosan, (b) chitosan/nano-alumina and (c) Cu-chitosan/nano-alumina

The characterization bands of the adsorbents are presented in Table I. The following results can be deduced from the table. One is that the presence of nano-alumina with low contents (maximum 4%) has no considerable effect on chitosan chemical properties because there is no significant

difference between the spectrum of the neat chitosan and chitosan/nano-alumina adsorbents. Second is the formation of a copper complex with amine and hydroxyl groups on the chitosan surface for Cu-chitosan/nano-alumina adsorbent because the broad band between 3400-3200 cm^{-1} observed in the spectrum of chitosan and chitosan/nano-alumina is not present in the spectrum of Cu-chitosan/nano-alumina nanocomposite.

TABLE I
CHARACTERIZATION BANDS OF ADSORBENTS

Adsorbent	Characterization bond	Band frequency (cm^{-1})
Neat chitosan	N–H and C–H (stretching)	3400-3200 (broad)
	Aliphatic C–H (stretching)	2920 and 2865
	–NH in the NH_2 (bending)	1659
	–NH in the NH_2 (deformation)	1382
	–CO in –COH (stretching)	1081
Chitosan/nano-Al_2O_3	N–H and C–H (stretching)	3400-3200 (broad)
	Aliphatic C–H (stretching)	2929 and 2856
	–NH in the NH_2 (bending)	1638
	–NH in the NH_2 (deformation)	1319
	–CO in –COH (stretching)	1088
	Al–O (stretching and bending)	755 and 515
Cu^{2+} impregnated chitosan/nano-Al_2O_3	Aliphatic C–H (stretching)	2920 and 2865
	–NH in the NH_2 (bending)	1687 (weak)
	–CO in –COH (stretching)	1073 (weak)

B. Adsorption Isotherms

Adsorption isotherms are commonly employed to describe the relationship between adsorption capacity of an adsorbent and equilibrium concentration of an adsorbate. The data obtained from isotherm studies provide important information about surface properties of an adsorbent and its affinity to an adsorbate. The adsorption data for three types of adsorbents toward aniline are shown in Fig. 3.

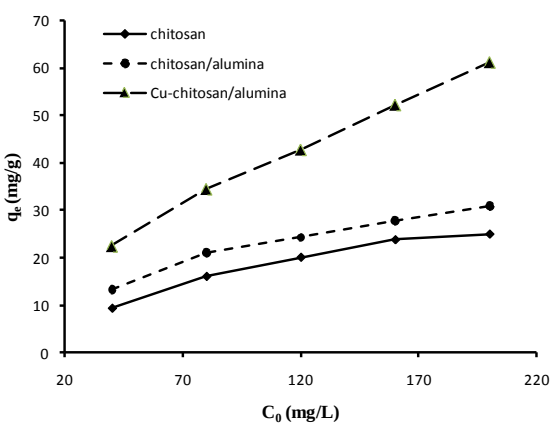

Fig. 3 Adsorption data for three types of adsorbents

In the present study, the data of aniline adsorption on chitosan, chitosan/nano-alumina and Cu-chitosan/nano-alumina were fitted to Langmuir and Freundlich isotherm models. The following equation shows Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e(mg/g) is the amount of aniline adsorbed per unit mass of adsorbent, C_e(mg/L) is the equilibrium concentration of aniline, and q_m(mg/g) and K_L(L/mg) are the Langmuir constants. The parameter q_m is the maximum adsorption capacity corresponding to monolayer coverage and K_L is the Langmuir constant related to the free energy of adsorption. The values of the parameters for adsorbents were obtained by nonlinear fitting of adsorption data to the isotherm.

The Freundlich adsorption isotherm is expressed as follow:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F[(mg/g)/(mg/L)$^{1/n}$] and n are the Freundlich constants indicating the relative adsorption capacity and the adsorption intensity, respectively. The adsorption data were fitted to the isotherm to obtain the Freundlich constants.

TABLE II
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS AND RELATED FITTING PARAMETERS FOR ADSORPTION OF ANILINE ON CHITOSAN, CHITOSAN/NANO-AL_2O_3 AND CU–CHITOSAN/NANO-AL_2O_3

Isotherm	Isotherm constants and fitting parameters		
	chitosan	Chitosan/nano-Al_2O_3	Cu-chitosan/nano-Al_2O_3
Langmuir	q_m=38.88 K_L=0.05267 R^2=0.9954 SSE=0.7391 RMSE=0.4964	q_m=35 K_L=0.02524 R^2=0.9483 SSE=9.972 RMSE=1.823	q_m=55 K_L=0.05264 R^2=0.7465 SSE=230.7 RMSE=7.595
Freundlich	n=1.842 K_F=1.615 R^2=0.9923 SSE=6.99 RMSE=1.526	n=1.123 K_F=2.231 R^2=0.9981 SSE=0.3596 RMSE=0.3462	n=5.143 K_F=2.01 R^2=0.9933 SSE=5.99 RMSE=1.645

SSE: Sum square errors
RMSE: Root mean square errors

The isotherm constants and fitting parameters for both models are presented in Table II. According to the data in Table 2, both models successfully describe adsorption data. Considering fitting parameters, Freundlich equation is better fitted to the experimental data, especially for the modified adsorbent. The maximum adsorption capacity obtained from Langmuir model for three types of adsorbents is in the order Cu-chitosan/nano-alumina>chitosan/nano-alumina>chitosan.
The incorporation of nano-alumina into chitosan bead increases the surface morphology of chitosan/nano-alumina and Cu-chitosan/nano-alumina considerably as indicated by SEM and BET studies. Furthermore, the presence of Cu(II) bonded on surface of the modified adsorbent provides more favorable condition for chemical adsorption through chelating of aniline. Accordingly, it can be said that Cu(II) can form a stable complex with aniline and it may be an explanation for higher that adsorption capacity of the modified adsorbents compared to the others.

C. Interfering Effect of Common Anions

The adsorption capacity of the modified adsorbent toward aniline was examined in the presence of natural waters

common anions with the concentration 10 times higher than aniline. Initial concentration of aniline and adsorbent was 50 mg/L and 2g/L, respectively.

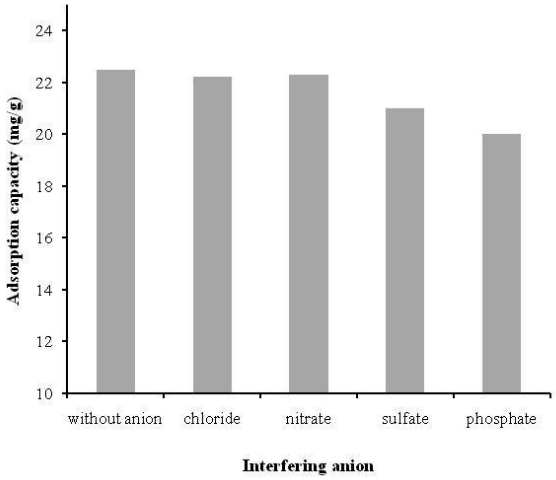

Fig. 4 Aniline adsorption capacity in the presence of interfering anions (500 mg/L). The experiments conditions: aniline concentration of 50 mg/L and the adsorbent amount of 2 g/L

As shown in Fig. 4, the presence of chloride and nitrate had no considerable effect on the adsorption capacity. In the presence of sulfate and phosphate inions, the adsorption capacity of the adsorbent decreased somewhat. The interfering effect of phosphate ions was higher than that of sulfate ions. It may be as a result of possible complex formation between these anions and Cu(II) on the adsorbent surface. The interfering effect of phosphate was higher that sulfate because phosphate can form more strong complex with Cu(II)-bonded to the adsorbent surface. However, the modified adsorbent shows relatively a high selectivity toward aniline in the presence of interfering anions because of formation very strong complex between aniline and Cu(II) on the adsorbent surface.

REFERENCES

[1] Vörösmarty, Charles J., et al. "Global threats to human water security and river biodiversity." *Nature* 467.7315 (2010): 555-561. http://dx.doi.org/10.1038/nature09440

[2] Li, Junmin, and Zexin Jin. "Effect of hypersaline aniline-containing pharmaceutical wastewater on the structure of activated sludge-derived bacterial community." *Journal of hazardous materials* 172.1 (2009): 432-438. http://dx.doi.org/10.1016/j.jhazmat.2009.07.031

[3] Edzwald, J. K. "Coagulation in drinking water treatment: Particles, organics and coagulants." *Water Science and Technology* 27.11 (1993): 21-35.

[4] Hidalgo, Asuncion M., et al. "Modeling of aniline removal by reverse osmosis using different membranes." *Chemical Engineering & Technology* 34.10 (2011): 1753-1759. http://dx.doi.org/10.1002/ceat.201000510

[5] Klein, Elias, et al. "Solute Separations from Water by Dialysis. I. The Separation of Aniline." *Separation Science* 7.3 (1972): 285-292. http://dx.doi.org/10.1080/00372367208058989

[6] Kamble, Sanjay P., et al. "Photocatalytic and photochemical degradation of aniline using concentrated solar radiation." *Journal of Chemical Technology and Biotechnology* 78.8 (2003): 865-872. http://dx.doi.org/10.1002/jctb.867

[7] Zhang, Si, et al. "Performance of enhanced biological SBR process for aniline treatment by mycelial pellet as biomass carrier." *Bioresource technology* 102.6 (2011): 4360-4365. http://dx.doi.org/10.1016/j.biortech.2010.12.079

[8] Durán, Nelson, et al. "Applications of laccases and tyrosinases (phenoloxidases) immobilized on different supports: a review." *Enzyme and Microbial Technology* 31.7 (2002): 907-931. http://dx.doi.org/10.1016/S0141-0229(02)00214-4

[9] Laszlo, Krisztina. "Adsorption from aqueous phenol and aniline solutions on activated carbons with different surface chemistry." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 265.1 (2005): 32-39. http://dx.doi.org/10.1016/j.colsurfa.2004.11.051

[10] Kakavandi, Babak, et al. "Synthesis and properties of Fe3O4-activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies." *Iran J Environ Health Sci Eng* 10.1 (2013): 10-19. http://dx.doi.org/10.1186/1735-2746-10-19

[11] Xie, Xiaofeng, Lian Gao, and Jing Sun. "Thermodynamic study on aniline adsorption on chemical modified multi-walled carbon nanotubes." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 308.1 (2007): 54-59. http://dx.doi.org/10.1016/j.colsurfa.2007.05.028

[12] An, Fuqiang, Xiaoqin Feng, and Baojiao Gao. "Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO 2." *Chemical Engineering Journal* 151.1 (2009): 183-187. http://dx.doi.org/10.1016/j.cej.2009.02.011

[13] Essington, Michael E. "Adsorption of aniline and toluidines on montmorillonite." *Soil science* 158.3 (1994): 181-188. http://dx.doi.org/10.1097/00010694-199409000-00004

[14] Bhatnagar, Amit, and Mika Sillanpää. "Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater—a short review." *Advances in Colloid and Interface Science* 152.1 (2009): 26-38. http://dx.doi.org/10.1016/j.cis.2009.09.003

[15] Gandhi, Muniyappan Rajiv, Natrayasamy Viswanathan, and S. Meenakshi. "Preparation and application of alumina/chitosan biocomposite." *International journal of biological macromolecules* 47.2 (2010): 146-154. http://dx.doi.org/10.1016/j.ijbiomac.2010.05.008

[16] Wang, Li, and Aiqin Wang. "Adsorption characteristics of Congo Red onto the chitosan/montmorillonite nanocomposite." *Journal of Hazardous Materials* 147.3 (2007): 979-985. http://dx.doi.org/10.1016/j.jhazmat.2007.01.145

[17] Salam, Mohamed Abdel, Mohamad SI Makki, and Magdy YA Abdelaal. "Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution." *Journal of Alloys and Compounds* 509.5 (2011): 2582-2587. http://dx.doi.org/10.1016/j.jallcom.2010.11.094

[18] Fan, Lulu, et al. "Synthesis of magnetic β-cyclodextrin–chitosan/graphene oxide as nanoadsorbent and its application in dye adsorption and removal." *Colloids and Surfaces B: Biointerfaces* 103 (2013): 601-607. http://dx.doi.org/10.1016/j.colsurfb.2012.11.023