



## Effective removal of metal ions from aqueous solution by silver and zinc nanoparticles functionalized cellulose: Isotherm, kinetics and statistical supposition of process

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### ABSTRACT

In present study we demonstrate the fabrication of nanoparticle (NPs) impregnated cellulose for the removal of metal ions from water. Co-precipitation method was employed to impregnate cotton fibers (cellulose) with silver and zinc oxide NPs. The NPs impregnated cellulose was characterised through FTIR, XRD and SEM techniques. To study adsorption kinetics, NPs impregnated cotton was exposed to water containing  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  at 25 °C (pH 5.5) for 400 min, separately. The results reveal that adsorption follows Langmuir Isotherm with regression coefficient ( $R^2 \sim 0.999$ ). The adsorption of metal ions on zinc NPs impregnated cotton (ZnCt) and silver NPs impregnated cotton (AgCt) follows the pseudo second-order kinetics in which higher  $K^2$  values indicate fast removal of  $\text{Hg}^{2+}$  and  $\text{Ni}^{2+}$  compared to  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Pb}^{2+}$ . Though concentration of adsorbents has no apparent difference on adsorption capability; however, a significant difference is observed among  $q_e$  values for metals ions. Among the tested metals ions, the  $\text{Hg}^{2+}$  exhibited maximum adsorption capacity on both NPs impregnated cottons. The intermetallic competitive adsorption indicates that the adsorption capacity follows the sequence of  $\text{Hg}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+} > \text{Pb}^{2+}$ , which roughly follow the same order of their hydration energies. The adsorption kinetics and competitive behavior of metals is further justified by Hotelling  $t^2$  and t-statistics. This cellulose-metal oxide NPs composite material can be efficiently used for the removal of heavy metal ions from wastewater.

### 1. Introduction

Heavy metal pollution is an aberrant issue that has been raised globally in water milieus owing to the severe threats it poses to human health and environment. The metals present in water do not have any propensity to degrade or destroy. This apprehension has led to stringent regulations regarding acceptable metals concentration in water (Adeleye and Keller, 2014). There is a portentous need to design a system for the protection of environment and human beings where the growing industrial activities lead to receive load of heavy metals in water bodies surpassing maximum permissible limit (Pereira et al., 2017). To enable water recycling, alternative remediation processes, i.e., filtration, chemical precipitation, solvent extraction, ion exchange, electrochemical deposition, electrolysis, and membrane process have been designed. However, these methods are either expensive or inefficient, particularly when lower concentration of the heavy metal ion

is dealt (Elkady et al., 2016). Among various methods, the adsorption process holds great promise to purify wastewater because of simplicity and relatively low cost technology (Ali and Gupta, 2016). A number of effective adsorbents have been prepared and tested for the removal of toxic metals from water. Generally, the conventional adsorbents such as clays, silica, zeolites, chitosan, polymers and activated carbons have weak binding affinity and truncated capacity for metals ions removal (Golie and Upadhyayula, 2016; Li et al., 2014; Song et al., 2009). On the other hand, use of organic molecules for metal removal suffer from instability and possess low adsorption and feeble affinity for heavy metals (Li et al., 2014; Uddin, 2017).

Metallic nanoparticles such as ZnO and Ag NPs have been studied due to inimitable behavior, ease of separation, enhanced catalytic activity, great biocompatibility, high adsorption capacity, high relation of surface-area to volume, reusability, greater dispersion degree, surface modifiability, and comparatively low cost (Ali et al., 2016a; Vélez et al.,

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2016; Giraldo et al., 2012). However, the use of NPs in wastewater treatment may cause harmful effects when exposed to the environment due to flaws in recovery and disposal issue (Zhou et al., 2015; Nel et al., 2006). Therefore, mechanical support such as polymers are employed to hold NPs for possible applications of wastewater treatment. Cotton cellulose fiber is regarded as the most abundant, renewable and environmental friendly biopolymer with good hydrophilicity, and is one of the promising raw material (Zhou et al., 2004). It is a linear homopolymer of ( $\beta$  1,4) linked  $\beta$ -D-glucopyranose units aggregated to form a highly ordered structure and spatial conformation (Song et al., 2014). Cellulose has great surface area and renders high affinity for metals controllable adsorption kinetics (Li et al., 2014). Recently few studies have been carried out about surface modification with different nanomaterials to enhance its adsorption capacity for heavy metals (Song et al., 2014; Hokkanen et al., 2013) but they are limited to singly metal adsorption or binding of organic nanomaterials.

We have designed metallic nano-trap cellulose by binding zinc and silver nanoparticles to enhance adsorption capability of cellulose and to minimize release of NPs in the treated water. The zinc and silver NPs impregnated cellulose was explored for removal of  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  ions from water. The parameters influencing adsorption and desorption capacity of adsorbents were also studied to regenerate the adsorbents. Based on this study, the Langmuir and Freundlich isotherm models as well as Pseudo first and second order reaction kinetics were used to fit the equilibrium data. Finally, the adsorption kinetics was supported by statistical variations.

## 2. Experiments

### 2.1. Material and methodology

All the reagents used were of analytical grade. Deionized water was used in all experiments. Laboratory glasswares were kept overnight in a 10% (v/v)  $\text{HNO}_3$  solution and then rinsed with deionized water.

The nitrate salts of  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  of analytical grade (Merck) and cotton wool (commercial grade) were used. Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), toluene (HPLC grade), ethanol were purchased from Aldrich.

### 2.2. Synthesis and characterization of ZnO and Ag NPs impregnated cotton

The bulk cotton cluster was first cut into small pieces followed by thorough washing with sterile distilled water, ethanol and sonicated for 15–20 min (three times) in ice cold water. The cotton samples were dried overnight in oven at 50 °C and used for synthesis of composites of zinc and silver NPs via method reported by Ali et al. (2016a,b).

Briefly, one gram dried cotton wool (cellulose) was immersed in 500 ml of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (1 mM) or  $\text{AgNO}_3$  (1 mM) solution for 1 h with constant stirring at 200 rpm. The mixture was sonicated for 20 min in a water bath, followed by treating with 10 mM NaOH or sodium borohydride ( $\text{NaBH}_4$ ) solutions to reduce zinc and silver into nanoparticles, respectively. Afterwards, the NPs impregnated cellulose was thoroughly washed with ethanol and deionized water to remove excessive unbound ions/NPs. The synthesized nano-composite material was overnight vacuum-dried at 30 °C.

An infrared spectrum (400–4000  $\text{cm}^{-1}$ ) was obtained with Fourier transform infrared spectrometer (FTIR, Perkin-Elmer,) to identify the functional groups and chemical bonding of the coated materials. The morphology, particle size and aggregation state of cotton material impregnated with nanoparticles was analysed by scanning electron micrograph (JEOL-JSM-6490LA SEM; JEOL, Tokyo, Japan) operating at 20 kV with a counting rate of 2838 cps. Successful deposition of silver and zinc oxide NPs on cotton, and also the crystallinity of as-prepared AgCt and ZnCt was studied by XRD analysis using X'Pert<sup>3</sup> Powder (PANalytical) with nickel monochromator having theta ranges from 20°

to 80°. Wavelength of radiation source (Cu K $\alpha$ ) was 1.5406 Å. A voltage of 40 kV with 30 mA of current at room temperature was the working conditions of XRD.

#### 2.2.1. Batch experiment for heavy metal ion removal from wastewater

The adsorption of cations by ZnCt and AgCt (nanocomposite adsorbents) was studied by a batch operation at room temperature. The batch mode adsorption was selected due to its simplicity (Mahdavi et al., 2012). The 0.5 and 1 g of adsorbent dose was suspended separately in 1000 mL solutions of metallic salts. The experiment was conducted at optimum pH 5.5 with initial concentrations of cations ( $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$ ) ranging from 2 to 8  $\text{mg L}^{-1}$ . The solutions were not buffered to mimic potential industrial practice. The samples were stirred at 150 rpm for 400 min and after every 10 min, 5 ml supernatant from suspensions was collected and analyzed for cations concentration by atomic absorption spectrometer on flame mode. A Shimadzu model AA-670/g V-7 atomic absorption spectrometer with deuterium lamp background correction and hollow cathode lamps at respective wavelengths (resonance line) as radiation sources, was used throughout the measurements. An air-acetylene flame was used for the determination of the metals ions.

The adsorption capacity was investigated as percent removal, isotherm kinetics, pseudo order reaction and competitive adsorption and desorption. The percent removal of metal ions from solution by the adsorbents is calculated by the following equation:

$$R (\%) = (C_0 - C_t)/C_0 \times 100 \quad (1)$$

where R is the removal efficiency of the metals ions,  $C_0$  is the initial concentration of the metal ions in  $\text{mg L}^{-1}$ , and  $C_t$  is the concentration of the metal ions at any time in  $\text{mg L}^{-1}$ . All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the repeatability and the relative deviation of the order of  $\pm 1.5\%$ .

The concentration of metal ions remaining in the solution is calculated by taking the difference of initial and final metal ion concentrations. The adsorption capacities are then obtained by mass balance equation.

$$q_e = (C_0 - C_e)V/W \quad (2)$$

where  $C_0$  and  $C_e$  are initial and equilibrium metal ion concentrations in solution, respectively. V (in L) is the solution volume and W (in g) is the amount of dry adsorbent used.

## 3. Results and discussion

Cotton fibers have been successfully modified by ZnO and Ag NPs by co-precipitation method. The cotton initially treated with metal salt that resulted in covalently bonding of metal ion with hydroxy (-OH) group of glucose molecule of cotton. Followed by treatment with alkali reduced the metal ions into nanoparticle. It can be presumed that the NPs interlinks with different cellulose fibers or with other monomers of single fibers (Fig. 1).

### 3.1. Characterization of adsorbents

Fig. 2 shows the morphology of the cotton surface before and after deposition of Ag and ZnO NPs is studied by SEM. The plain symmetry is observed in case of pure cellulose, while deposition of Ag and ZnO NPs can be seen in SEM images after NPs synthesis methodology. The SEM image also showed that ZnO NPs are nm in range and evenly distributed on the surface of cotton fiber while in case of Ag NPs; they are also attached on the surface but in cluster form. These results are consistent with reported findings (Shaban et al., 2016; Ravindra et al., 2010).

Characteristics peaks of cotton, in case of FTIR analysis, appeared at 3400  $\text{cm}^{-1}$  and 2926  $\text{cm}^{-1}$  due to O–H stretching and C–H stretching (Chung et al., 2004), while 1749–1579  $\text{cm}^{-1}$  are due to C=O stretching

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