Role of Nanotechnology and Functionalization in the Remediation of Toxic Metals from Water System: Environmental Sustainability and Development

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***Abstract*- The development of technologies for water purification is decisive to meet the global challenges of inadequate access of water supply. Among all remediation methods, sorption is globally recognized as the most promising method because of versatility, reversibility and economic feasibility. The present communication describes the fabrication, characterization and application of paraben modified nanocellulose (PNC) enriched with COO^- functional groups for the removal of chromium and lead toxic metals. The fabricated nanobiomaterial has thoroughly characterized with recent microscopic and spectroscopic techniques. Paraben modified nanocellulose (PNC) is found to possess excellent removal efficiency for chromium (96.27%) and lead (80.85%) and it can be reused five times. The findings open up new avenues for the commercial preparation of a cost effective environmental friendly biosorbent and development of a pre-treatment green method prior to high-tech chemical treatments for decontamination of toxic metals particularly in rural and suburban areas of the developing countries.**

***Keywords*- Nanotechnology; toxic metals; removal efficiency; environmental sustainability development**

I. INTRODUCTION

In our planet, there is no shortage of water as our globe is rich of vast oceans and bodies of fresh water. If we consider the water's distribution on earth, we found that 97% of water is brackish in nature and remaining 3% is available as freshwater, out of 3% available to us only 0.3% is surface water. Out of 0.3% surface water but only 0.01% is easily accessible for drinking purpose [1]-[2]. Unfortunately, mankind has deployed this little amount of water become contaminated which is the outcome of the rapid growth in urbanization, industrialization, technological advancement and agricultural development [3].

Among the various contaminants encountered in the water system, Toxic metals are global epidemic because of their environmental toxicity, long biological life and non biodegradable nature which cause them to accumulate in soil, air and water and results into lethal effects to the organisms [4]-[6]. According to Agency of toxic substances and disease registry (ASTDR), the majority toxic metals are: arsenic, mercury, cadmium, nickel, lead and chromium. The ingestion or bio-accumulation and bio-magnification of these toxic metals cause neurological and carcinogenic issues over relatively short time interval or causing death [7]. According World Health Organization (WHO), 26.3 million people are globally dying from unsafe water annually due to existence of inorganic toxic heavy metals (lead, arsenic, nickel, chromium and cadmium) and some organics which are intrude in water system. Till 2050, this troubling predicament is anticipated to get worse substantially by heavy metal pollution as according to the United Nation World Water Development Report [8]

Sustainable development is a process for fulfill the present human development goals with maintaining the ability of natural systems to continue to provide the natural resources. Among various natural resources, water is also a fundamental to human well-being. Today, water ecosystem is posing a serious challenge to sustainable development of developing countries as is not managed efficiently and equitably.

To prevent this catastrophe, a wide number of prevalent technologies have been employed in the removal of toxic metals such as electrochemical treatment, chemical precipitation, reverse osmosis, ion exchange and electro dialysis [9]-[10]. but, all these techniques are classified as classical techniques because of their several limitations like cost- prohibitive, in-effective in low metal concentration, generation of toxic sludge [11]-[12], and most important is the wastage of 80 to 85% water. Therefore, these techniques are not efficiently managed the needs of sustainable development. Fortunately, a new paradigm is emerging: Sorption is much talked about these days and it is defined as "The ability of most abundant plant oriented materials to sorb heavy metals from wastewater through metabolically meditated". It has gained credibility due to cost effectiveness, less wastage of water, eco-friendly and low energy requirements [13]-[14].

Nanomaterials are used as novel ones to solve heavy metal pollution in water system. Material which has 1-100 nm dimensions is known as nanomaterials. Nanocellulose has recently an epitome of nanobiomaterials inheriting with unique chemical and surface properties which making them highly lucrative as nanosorbent. It is sustainable biocompatible green nanobiomaterial with the large surface area, high crystallinity, economic and large number of hydroxyl groups which are highly liable for chemical functionalization [15]-[17].

In the present communication, we explored a novel method for the removal of toxic metal from water system by using paraben functionalized nanocellulose. The fabricated nanobiomaterial is characterized with analytical techniques. The effect of nano biomaterial dose, metal concentration and removal time is observed and optimized. The removal efficiency of toxic metals is quantified with using batch experiments. For economic point of view, the reusability of fabricated nano biomaterial is determined with sodium hydroxide (NaOH).

II. MATERIALS AND METHODOLOGY

2.1 Fabrication of paraben functionalized nanocellulose (PNC)

For the fabrication of PNC, nanocellulose (10 g) is mixed with dioxane (150 mL) and NaOH (1 M, 10 mL) and stirred for 15 min. After that, epichlorohydrin (4.5 mL) is added with stirring for 5 h at 50° C. The above obtained nanocellulose is further mixed with paraben (1 M, 100 mL). The obtained product is washed with water and finally dried at ambient temperature.

The yield of PNC is calculated as follows:

$$\textbf{Yield (\%)} = \frac{W_2}{W_1} \times 100$$

where W_1 is the dry weight of nanocellulose before functionalization and W_2 is the dry weight of nanocellulose after functionalization. The yield of obtained PNC is determined to be 92%.

2.2 Characterization of PNC

The success of fabrication is determined with Fourier transform infrared (FTIR) analysis, energy dispersive X-ray spectroscopy (EDX) analysis, scanning electron microscopic (SEM) analysis and Atomic force microscopic (AFM) analysis.

2.3 Synthetic wáter preparation

Biosorption tests are performed with synthetic solutions for each heavy metal. Chromium solutions are prepared by dissolving requisite amount of chromium chloride hexahydrate ($CrCl_3.6H_2O$), and lead solutions are prepared from lead nitrate ($Pb(NO_3)_2$) with environmentally relevant concentrations which are in the order of 5-30 mg/L.

2.4 Removal of chromium and lead: Batch experiments

The sorption potential of prepared PNC for the removal of chromium and lead is investigated according to our previous experiment [18]-[19]. Briefly, synthesized PNC for metal remediation is investigated in batch experiments as a function of sorption time (10-60 min), sorbent dosage (0.1-1.0 g) and metal concentration (5-30 mg L^{-1}) at constant sample volume (500 mL) and solution pH (6.5). After that, a known amount of PNC is added at 350 rpm stirring and filtered. Filtrate is projected for metal ions analyses using atomic absorption spectrophotometer (AAS analyst-100, Perkin–Elmer) at resonance wavelength 357.9 nm. Two control or blank were included in each experimental set. The blank consisted in the heavy metal solutions without PNC addition.
The sorption efficiency is calculated by using following equation:

$$\textbf{Sorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 and C_e (mg/L) are the initial and final metal concentration. Data shown here is the mean of triplicate trials with error <5% to improve the reliability of the results.

2.5 Investigation of reusability of PNC

In order to recover metal from PNC for its safe disposal as well as to restore the sorbent for an economic perspective, the used PNC is regenerated using NaOH (0.5 M, 50 mL) as a desorbing medium.

III. RESULTS AND DISCUSSION

3.1 Confirmation of fabricated PNC

The developed chemical groups in PNC are corroborated by FTIR. The FTIR spectrum of PNC is shown in Fig. 1a. From Fig. 1a, peaks at 3600-3200, 3100-3000, 1657, 1560-1490 and 2310 cm^{-1} are related to O-H, C-H (stretching), -C=O, -C=C and C-H (bending) vibration of aromatic nuclei [20]-[22]. The presence of these bands are successfully confirmed the fabrication of PNC.

Further confirmation is done with EDX analysis and shown in Fig. 1b. In the spectrum, the presence of peaks provides strong support for the presence COO^- ions onto PNC.

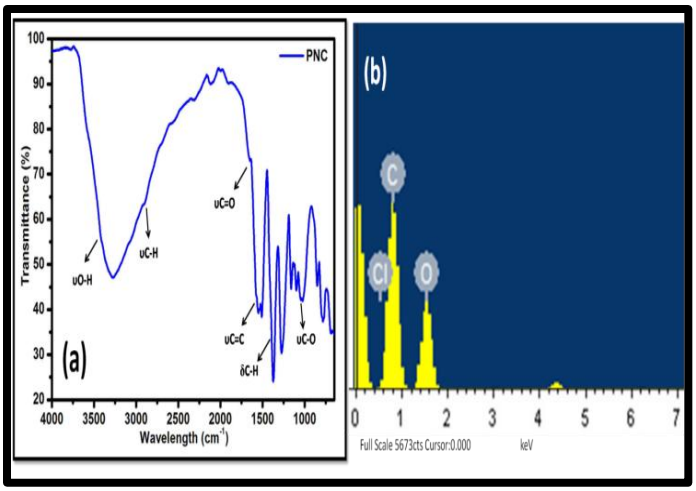

Fig. 1 FTIR (a) and EDX (b) spectrum of PNC

Nanosizing of materials plays an important role for the removal of metals because smaller the size, larger is the surface area which accommodates large number of functional groups which are responsible for the binding of metals. The particle size and shape of fabricated PNC are determined by SEM analysis (Fig. 2a) and found to be rod-like shape with 50 nm. From an AFM image (Fig. 2b) shows the average roughness of PNC and found to be 67.84 nm. From the analyses we conclude that PNC is in nano-range.

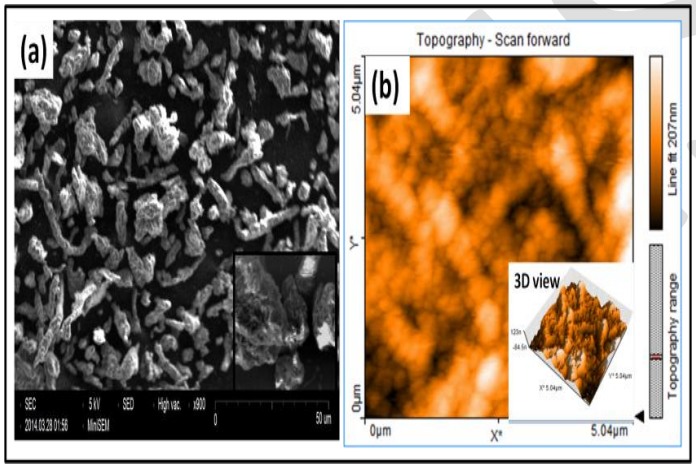

Fig. 2 SEM (a) and AFM (b) image of PNC

3.2 Optimization of the sorption experimental conditions

3.2.1 Effect of nanosorbent dose

The rate of removal of metal ions is considered to be an imperative factor which depends upon the nature and amount of sorbent. Fig. 3 shows that the removal efficiency increases with increasing fabricated nanosorbent dose upto 0.5 g. This trend is because the presence of number of active sites (COO^- functional groups) is increased proportionally with the addition of nanosorbent dose [23]-[24]. After 0.5 g nanosorbent dose, equilibrium is established. This might be due to the all activated sites are filled with metal ions. Therefore, optimum nanosorbent dose is 0.5 g.

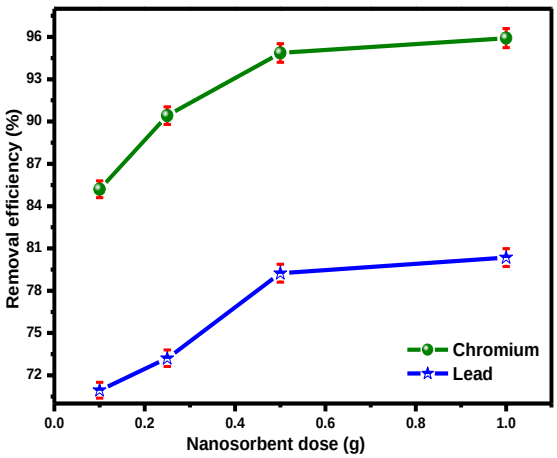

Fig. 3 Effect of nanosorbent dose

3.2.2 Effect of time

Fig. 4 shows the effect of time on the removal of lead and chromium. It is noteworthy that the chromium and lead rapidly attained equilibrium at 40 min and maximum uptake of chromium and lead are 95.67% and 80.85%, respectively. This might be endorsed to the fact that, at the beginning, the larger number of reactive sites on the surface of nanosorbent [25]-[26]. As time went by, the availability of reactive sites is saturated. Therefore, removal efficiency of chromium and lead are slowed down and attained a plateau. After equilibrium is attained, the time no longer has influenced on the removal efficiency of metals. Therefore, 40 min is taken as optimum time for this study.

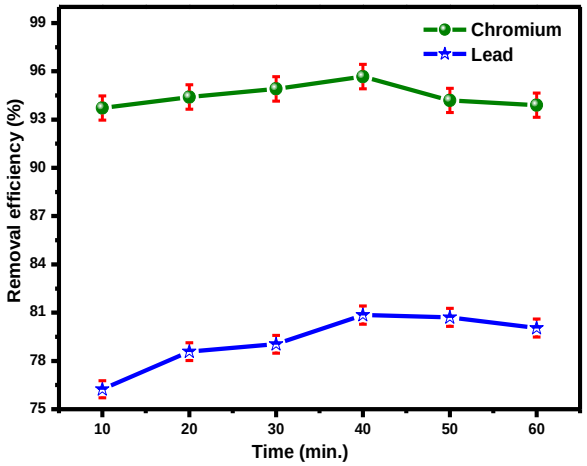

Fig. 4 Effect of time

3.2.3 Effect of chromium and lead concentration

The effect of chromium and lead concentration is studied by varying the concentration from 5 to 30 mg/L. As displayed in Fig. 5, removal efficiency is increased with increase of metal concentration and gradually attained equilibrium at 25 mg/L. This can be explained by the fact that at low metal concentration, the ratio of available reactive sites to the total metal is high [27] and all the ions of metal are bound to be the reactive sites of PNC, whereas metal concentration is further increased, the ratio is lessened. Therefore, 25 mg/L is opting as optimum metal concentration for this study.

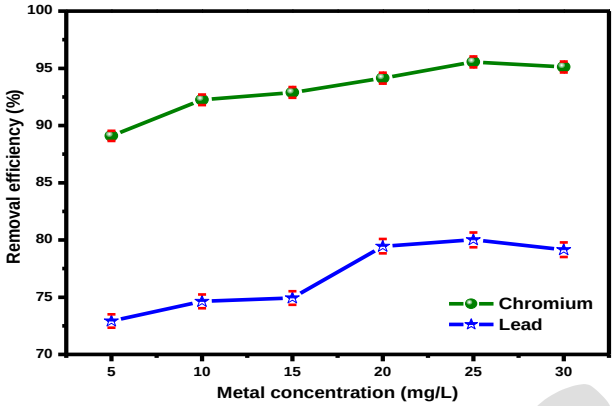

Fig. 5 Effect of metal concentration

3.3 Removal efficiency of PNC for lead and chromium

A series of the experiments has been handled and displayed in the Table. 1. Nanocellulose shows 62% removal efficiency for lead and 72% for chromium. This efficiency presumes to the attendance of OH groups and larger surface area. The chemical functionalization with paraben, the removal efficiency increases upto 25% for metal ions. This increment relates to the introduction of COO^- functionalities out of the result of chemical modification which act as binding sites for metal removal.

Table 1 shows the %removal efficiency of PNC for lead and chromium

Metal ions	Nanocellulose	**PNC**	% increase wrt of nanocellulose
	Removal efficiency (%)	Removal efficiency (%)	
Lead	62.41±0.26	80.85±0.40	19
Chromium	71.82±0.75	96.27±0.17	25
Nanosorbent dose:0.5 g; time:40 min; metal conc. 25 mg/L; sample volume: 500 mL			

3.4 Reusability of PNC

For reusability of nanobiomaterial, sodium hydroxide (50 mL) is used for recovery of metal ions under optimized conditions. The result is displayed in Fig. 6. The removal efficiency of lead and chromium is almost constant for five cycles. This results show the reusability of fabricated nanobiomaterial. The lead and chromium recovered from reusability experiments is crystallize in the form of salts for further use.

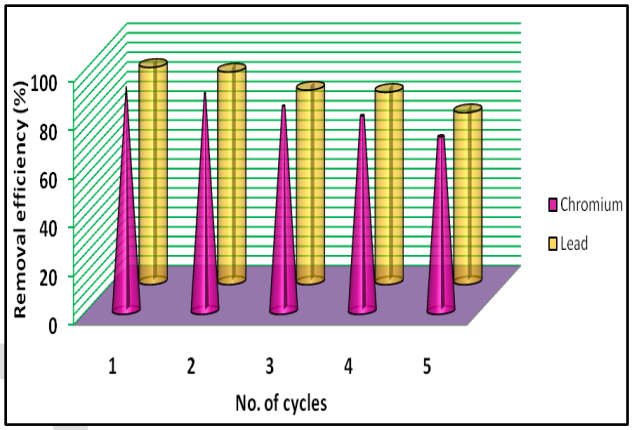

Fig. 6 Regeneration of PNC

IV. CONCLUSIONS

In summary, PNC nanobiomaterial has been synthesized from low cost cellulose for the removal of chromium and lead metal from water system. PNC has endowed excellent removal efficiency for metal ions is owing to large surface area and electrostatic force of interactions between metal ions and COO^- centres. The PNC is reused for the recovery of chromium and lead for 5 cycles. The proposed fabricated nanobiomaterial has significant removal efficiency, reusability and environmental friendliness, and ensures its potential for environmental wastewater treatment at least as a pre treatment step before large scale chemical treatment.

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