REUSING wastewater as an additional resource of water in Egypt always be facing by high load of contaminants, especially potentially toxic elements (PTEs). Sorption of PTEs is one of the technologies used for treatment wastewater. Cellulose derived materials, like microcrystalline cellulose, can be used for removal of PTEs. In this study, microcrystalline cellulose prepared from rice straw with an eco-friendly method and tested for Pb, Cd, and Cu removal from artificial contaminated water. Factors affecting metal ions removal were also investigated. Obtained results showed that the removal efficiency of the PTEs was 94, 72, and 89% for Pb, Cd, and Cu, respectively at 10 mg L\(^{-1}\) of microcrystalline cellulose. Removal of Cd and Cu decreased with increasing of initial concentration up to 200 mg L\(^{-1}\), however, for Pb the removal efficiency was near 90% till initial concentration 150 mg L\(^{-1}\). In summary, the prepared microcrystalline cellulose were shown as promising adsorbents can assist PTEs from contaminated wastewater.

**Keywords:** Potentially toxic elements (PTEs); Microcrystalline cellulose (MCC); Contamination removal; Lead; Cadmium; Copper

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**Introduction**

Over the years, deterioration of the water quality observed due to anthropogenic activities, fast industrial progress and inexpert application of water resources (De Gisiet al. 2016; Bassouny and Abbas, 2020 and Bassouny et al. 2020). Choukr-Allah (2010) and Elbanaet al. 2017 reviewed that Egypt had 68.30 B m\(^3\)/year total water withdrawal, the great River Nile is the main water provider in Egypt is limited to 55.5 B m\(^3\)/year. Whereas, 3.76 B m\(^3\)/year wastewater production, and 2.97 B m\(^3\)/year treated wastewater in the first years of this century were reported. In addition, the most of the treated wastewater is reused to irrigate edible and non-edible crops, especially wood trees. Attia (2004) reported that the largest consumer of water in Egypt is the agricultural sector, (more than 80% of water demand). The agricultural sector consumed 62.4 B m\(^3\), while the drinking and healthy uses consumed 10.4 B m\(^3\). Wastewater recycling provided 1.3 B m\(^3\). As reviewed by Ahmad et al.(2020) and Asano et al.(2018), wastewater can be categorized into two categories based upon its derivation: domestic and industrial wastewaters. Industrial liquid wastes being drained which generate industrial wastewater having various components like FOG (fat, oil and grease), pharmaceutical wastes, chemicals, and other hazardous materials.

Potentially toxic elements (PTEs) are among the most enduring contaminant in water (Elshazly et al. 2019). In contrary other pollutants, they are incapable of being chemically degraded, thus, accumulate through the food chain (Hashim et al. 2017and Mohamed et al. 2018), causing potential hazard on human health and environmentally troubles (Abdelhafzet al. 2012 & 2015). PTEs reached to water bodies may be due to discharges
from urban towns; some industrial discharge especially chemical industries like fertilizers, pharmaceutical, textile and pesticides (El. Nonoet al. 2015 and Mosa et al. 2017). Abdel-Sabour et al. (1996), Hassan et al. (2013), Ali et al. (2016), Ibrahim et al. (2016), El-Ramady et al. (2017) and Farid et al. (2019) reported that sewage effluent has been used for crop irrigation for many years and its use is increasing particularly in water-short areas. Sewage effluent can be a useable water resource if suitable precautions are taken.

Therefore, searching for sustainable materials that can decontaminate PTEs from water became a necessity. One of these materials is cellulosic materials. Cellulose is a crystallization material with abundance of hydroxyl groups (Fathy et al. 2015). Thakur et al. (2020) reported that rice straw is usually of less importance because of its very low nutritive value and its combustion for removing its residue from agricultural lands, produces a enormous amount of ash and other hazardous materials. The major constitute of rice straw includes cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%), and silica (18.3%). Thakur et al.(2020) added that there are several adverse effects on the environment due to the open burning of rice straw. For instance, the burning of rice straw conducting to loss of important soil nutrients and can causes a scarcity in soil microbes. Another effect of straw burning is the smokescreen which leads to high risk on mankind life.

Therefore, the utilization of extracted cellulose and its derivatives from rice straw and other agricultural wastes represented an important subject for researchers. Microcrystalline cellulose (MCC), as described by Järvenpää (2019) is almost white and odorless purified cellulose produced from different lignocellulose sources by various techniques such as acid hydrolysis. Ibrahim et al. (2013) used rice straw and banana plant waste to prepare MCC. Microcrystalline cellulose usage for water and wastewater treatment was discussed in some studies. For example, Garba et al. (2019) reviewed that cellulosic materials can form several complexes with PTEs. Therefore, this study aims at using rice straw as an agricultural waste to synthesize microcrystalline cellulose as a cheap adsorbent for removing Pb, Cd, and Cu from artificial contaminated waters.

**Materials and Methods**

Laboratory experiments were conducted in the Soil and Water Research Department, Nuclear Research Center, Atomic Energy Authority, Egypt. Rice (*Oryza sativa*) straw (RS) was brought from a local field at El-Sharquia government, Egypt. Straw was cleaned with tap water twice to remove dirt and once with distilled water, then dried at 70°C for 24hr, and preserved in a cool dry place. Chemical constituents of the straw are listed in Table 1.

**Table 1. Rice straw constituents**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>α-Cellulose</th>
<th>Lignin</th>
<th>Hemicelluloses</th>
<th>Ash</th>
<th>Silica in ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>70.1</td>
<td>1.34</td>
<td>17.8</td>
<td>13.8</td>
<td>72.1</td>
</tr>
</tbody>
</table>

**Chemicals**

Lead nitrate Pb(NO₃)₂ (assay 99.5%, MW: 331.21), cadmium chloride CdCl₂ (assay 99%, MW: 183.31) and copper sulfate CuSO₄·5H₂O (assay 98%, MW: 249.68) for preparation metal ion solutions. All these reagents were AR (Analytical Reagent) grade chemicals. Also, H₂SO₄, H₂O₂, which were used for synthesis experiments were AR grade. NaCl and NaOH are used as technical grade for synthesis of MCC.

**Synthesis of sorbent materials**

Twenty grams of washed and dried rice straw (RS) was added to 600 mL of 1% H₂SO₄ and boiled for 45 min then the straw was detached and washed with abundant water till pH turned to neutral and the filtrate was dumped. The acid-treated RS from the last step was added to 600 mL of 1.5M of NaOH (6% W/V) and 5% (V/V) H₂O₂ and boiled for 30 minutes, then filtered and washed with abundant water. This step was for silica and lignin removal with alkali treatment. Because of H₂O₂ addition, the filtrate color was yellow, the alkali treatment without oxidation agent (H₂O₂) always produces black liquor and the fibers produced with H₂O₂ addition were of a lighter color than those produced without it. To bleach fibers to synthesis white MCC, fibers from alkali treatment added to 0.5L of 0.5% NaClO and boiled for 30 min, then filtrate and washed with abundant water, dried in air and ambient laboratory temperature for two or three days depending on ambient temperature and moisture in MCC. Then, ground with a household grinder. This method is according to Nassar and El Shakankery (2014) with a slight modification.
Materials characterization

FTIR, XRD, EDX, SEM

Active groups in MCC were characterized using FT-IR spectroscopy (Fourier-transform infrared spectroscopy) using an FTIR – (Model: 8201 PC), Shimadzu, Japan. XRD (X-ray diffraction) was used to determine the crystallinity of the rice straw fiber and MCC was analyzed by Bruker (Model: D2 Phaser)-USA X-ray diffraction meter with a CuKα radiation source. The measurements were performed at a step size of 0.02° in a 2θ angle range of 10° to 40°. The crystallinity index (CrI) was calculated by using the peak area method. Also, to determine chemical composition and surface graphical imagining of the prepared material, MCC was analyzed by Philips (Model: XL 30)-USA Scanning Electron Microscope SEM with the attached EDX (Energy Dispersive X-Ray Analyzer) Unit.

Adsorption experiments

Factors affecting removal of PTEs using MCC were studied by conducting of batch techniques. Batch experiments were carried out in 100 mL Erlenmeyer flasks at 25°C and 300 rpm. A weighed amount (0.10 g) of adsorbent was added to 50 mL of metal solutions of varying concentrations which differ between 10 and 200 mg L⁻¹ (i.e.: 0, 10, 20, 30, 50, 70, 100, 150 and 200 mg L⁻¹) each time and shaken continuously for 3 hr to achieve equilibrium. The mixtures were centrifuged and the concentrations of metal ions (Pb, Cd, and Cu) were determined by AAS method using a atomic absorption spectrophotometer (AAS)- GBC, (Model: 902)-Australia. Then, experiment to determine effects of pH (differed between 3 to 7 with stepwise with 1). The applied pH values of the solutions were adjusted using a dilute solution of either NaOH or HCl of 0.01M. That was using 0.1g of MCC with 50 mL of 10 mg L⁻¹ of each studied PTEs for each studied equilibrium time. The contact time (10–360 min). For this experiment, 0.1g of MCC with 50 mL of 10 mg L⁻¹ of each studied PTEs for each studied equilibrium time was used. Adsorbent/solution ration experiment was conducted with 2.5–100 g L⁻¹. For this experiment, certain weights of MCC with 50 mL of 10 mg L⁻¹ of each studied PTEs for 180 minutes equilibrium time was used.

Calculation

In all experimental runs, the sorbed ion amounts were calculated as follows:

Removal percentage (R%)=..........................(1)

Where $C_0$ and $C_e$ are the concentrations (mg L⁻¹) of each ion before and after sorption, respectively.

Statistical analysis

Data of the current study were statistically analyzed using Statistical Software Program (PC-Mstat). Means of treatments were compared with the Least Significant Deference (L.S.D) at the 0.05 level.

Results and Discussion

Characterization of MCC as a sorbent material

The FT-IR spectrum of the MCC is given in Fig. 2. FT-IR spectrum of MCC materials have identified the presence of several surface functionalities such as the peak at wavenumber 1055 cm⁻¹ for hydroxyl groups. The peak at 1729 cm⁻¹ refers to the presence of carboxylic groups and 3352 cm⁻¹ which found for the vibration of phenols. These functional groups can help in the sorption of ion contaminants, including PTEs.
MCC crystallinity degree can be determined from the interpretation of XRD diffraction patterns of MCC shown in Fig. 3. The characteristic peaks occurred at 16.5° and 22.5° are expressed to cellulose crystal lattice structure. Calculated Crystallinity index (CI) was 40%. These results are similar to that found by Chin et al. (2013).

SEM images of the MCC are illustrated in Fig. 4. It can be seen that the morphology of the cellulose fibers and MCC. This is due to the success of the removal of the other untreated cellulose materials. Results of EDX analysis for MCC, showed that carbon and oxygen are the main components, however, silica and calcium were detected at lower levels. Similar results were reported by Chin et al. (2013) on MCC extracted from RS, Kunusa et al. and (2018) on MCC extracted from corn cobs with 6% NaOH alkaline treatment.

**Factors affecting removal of heavy metals under investigation using MCC**

**Initial concentration**

Adsorption experiments were conducted with differed initial metal ion concentrations from 0 to 200 mg L\(^{-1}\) using 2 g MCC L\(^{-1}\). Results illustrated in Fig. 5 show that MCC was effective in the removal of Cu and Cd diluted concentrations (i.e. 10 and 20 mg PTEs L\(^{-1}\)) , however, lead removal percentages were the highest (ranged from 94 to 90%) until 150 mg L\(^{-1}\) of lead in the initial solution, thereafter decreased to 63% at 200 mg L\(^{-1}\). Cadmium and copper removal (expressed as a percentage of initial concentration) decreased sharply from 67 to 15% and 89 to 11% for 10 to 70 mg L\(^{-1}\) initial concentration for Cd and Cu, respectively. Removal percentages of Cd and Cu at initial metal ion concentrations from 100 to 200 mg L\(^{-1}\) didn’t have wide changes.
Resulted data is detailed in Table 2 which showed that significant effect of initial metal ion concentration on removal of PTEs using MCC. These results were similar to those reported by Garba et al. (2019) who reported that the sorption data showed that the removal percentages for Pb$^{2+}$, Cu$^{2+}$, and Cd$^{2+}$ with an initial metal ion concentration of 10 mg L$^{-1}$ were 93.2%, 87.5%, and 72.3%, respectively, and that was attained within 5 min.

Effect of pH on the adsorption of studied PTEs

Figure 6 shows the impact of pH on the removal of Pb$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$ at a pH ranging from 3–7. The percentage removal was found to increase progressively with increasing pH and reaches to the highest value at pH 7, 6 and 5 for Pb, Cd and Cu ions, respectively. After pH 5, each metal ion behaved differently. Lead removal increased with increasing pH value, until pH 7 while cadmium removal decreased till pH 7. Whereas copper removal increased until pH 6, then decreased. The solution pH may change the surface charge of the adsorbent material and the ionization degree as well as the surface functional groups (Anah and Astrini, 2017). Similar trends of metals removal were observed by Singha and Guleria (2014) for Pb, Cd, Cu, and Zn sorbed by cellulosic fibers. Deshmukh et al. (2017) described cadmium sorption on cellulosic materials as follows: In low pH values, Cd$^{2+}$ compete with H$^+$ for binding sites therefore. Increasing in the rate of metal removal was observed at a pH ranged from 4 to 7. Metal removal may not involve complete sorption in this pH range. Kaur et al. (2020) reported the same trend of lead removal which was found to depend on pH level using cellulosic material.

Fig. 4. SEM characterization of MCC

Fig. 5. Effect of solution initial metal ion concentration (mg L$^{-1}$) on removal of the PTEs lead, Cadmium and Copper from their aqueous solutions using Microcrystalline cellulose MCC.
Effect of contact time
The effect of time of contact on the sorption of Pb, Cd and Cu ions is shown in Fig. 7. The results show that increase in the contact time (from 10 to 360 minutes) increased of the metal ions removal and it persisted constantly after the equilibration time of 30 min. Therefore, the optimum agitation period of metal sorption was near to 30 minutes. Similar results were reported for modified MCC-Pb sorption by Fu and Xie (2020) found that equilibrium time was about 30 minutes under high concentration (100-200 mg L\(^{-1}\)). For cadmium, El-Naggar et al. (2018) reported similar results, where they found that 20 to 40 minutes was enough to reach equilibrium on MCC aerogel. For copper, Abdel-Halim, and Al-Deyab (2012) reported equilibrium time for sorption Cu on MCC was about 30 minutes.

Effect of sorbent dose
Results in Fig. 8, show that sorbed amounts of metal ions per the unit mass of sorbent reduced with increasing sorbent/solution ratio (g MCC L\(^{-1}\)) for all the PTEs under investigation. Some other studies indicated that, the removal percentages seemed to follow an opposite trend, where they found that sorption increased with increasing sorbent dose from 2.5 to 100 g L\(^{-1}\) (El-Naggaret al. 2018). The decrease occurred in sorbed metal ions per the unit mass of the sorbent is probably because more sorbent amounts mean more available sites for sorption of the metal ions whose initial concentration was constant. Therefore, a pronounced number of sorption sites is expected to be free of sorbed ions. While the increase of lead removal using MCC reached near 100% at a 100 g L\(^{-1}\) dose of sorbent, cadmium removal reached about 90% at the same dose of the sorbent i.e.100g L\(^{-1}\) dose. Copper removal did not reached more than 80% at the maximum studied sorbent dose. Similar trends were recorded by many researchers, for example, cadmium removal described as the same with Deshmukh et al. (2017).

<table>
<thead>
<tr>
<th>Initial metal ion concentrations (mg L(^{-1})) (C)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>94.04</td>
<td>92.10</td>
<td>90.00</td>
<td>93.40</td>
<td>89.00</td>
<td>90.10</td>
<td>94.07</td>
<td>63.25</td>
<td>88.83</td>
</tr>
<tr>
<td>Cd</td>
<td>67.00</td>
<td>57.17</td>
<td>47.67</td>
<td>28.40</td>
<td>15.67</td>
<td>13.47</td>
<td>13.20</td>
<td>13.20</td>
<td>31.97</td>
</tr>
<tr>
<td>Cu</td>
<td>89.00</td>
<td>63.67</td>
<td>50.00</td>
<td>33.00</td>
<td>10.43</td>
<td>11.27</td>
<td>4.80</td>
<td>5.50</td>
<td>33.46</td>
</tr>
<tr>
<td>Mean</td>
<td>83.35</td>
<td>71.61</td>
<td>63.22</td>
<td>51.60</td>
<td>38.37</td>
<td>38.28</td>
<td>37.62</td>
<td>27.32</td>
<td>51.42</td>
</tr>
<tr>
<td>LSD C-Pb:</td>
<td>1.547</td>
<td>C-Cd:</td>
<td>0.6594</td>
<td>C-Cu:</td>
<td>0.7705</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

L.S.D: Least significant difference

Fig. 6. Effect of pH of solution on removal of the PTEs Pb, Cd, and Cu from their aqueous solutions using Microcrystalline cellulose MCC

Conclusion

Due to water scarcity in Egypt, reusing of treated wastewater comes to be necessary. Potentially toxic elements one of the most dangerous contaminants in wastewater, because of these nature. Adsorption one of the promising technique to remove PTEs from contaminated water. Cellulose one of the sustainable sources of sorbent materials. Microcrystalline cellulose MCC is one of the successive sorbents. In this study, synthesis of MCC from rice straw with the least amounts of chemicals and least consumed energy for synthesis. Characterization techniques were proved that successive synthesis of MCC using synthesis procedure. Factors affecting the removal of lead, cadmium, and copper was initial concentration with an inverse relationship with removal percentages for Cd and Cu, but not for Pb. The best pH for PTEs removal was 7, 6 and for Pb, Cd, and Cu, respectively. The optimum agitation period of metal sorption was about 30 minutes. An expulsive relationship was found between sorbent dose and removal of PTEs. These results concluded that MCC can be synthesis with eco-friendly methods and effective in usage of MCC, without further additions, for removal of PTEs.

![Fig. 7. Effect of contact time (minutes) on the removal of the PTEs (Pb, Cd, and Cu) from their aqueous Solutions by MCC](image)

Fig. 7. Effect of contact time (minutes) on the removal of the PTEs (Pb, Cd, and Cu) from their aqueous Solutions by MCC

![Fig. 8. Effect of contact time (minute) on the removal of the PTEs (Pb, Cd, and Cu) from their aqueous solutions using MCC](image)

Fig. 8. Effect of contact time (minute) on the removal of the PTEs (Pb, Cd, and Cu) from their aqueous solutions using MCC
Ethics approval and consent to participate

This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of interest

There is no conflict between the authors of this study.

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Consent for publication:

All authors declare their consent for publication.

Author contribution

All authors of this study shared in all stages from the beginning with idea, design and experimental work up to interpretation of data and edit of manuscript for publication.

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