CHARACTERIZATION AND APPLICATION OF BIOSORBENTS MODIFIED WITH TiO₂ FOR HEAVY METAL IONS REMOVAL†

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Abstract. Preparation, characterization and application of materials modified with TiO₂ nanoparticle have been reviewed. Chitosan, bacterial biomass and dendrimers were the starting material for modification. Sorbents characterization was performed by scanning electron microscopy (SEM). In order to investigate the sorption capabilities of sorbents, we used them for removal of heavy metal ions from aqueous solution. The effect of contact time on heavy metal ions sorption and maximum sorption capacities of biosorbents are shown. As a very important parameter of the sorption process, the effect of initial pH values on heavy metal removal was examined. This paper indicates that sorption using the material modified with TiO₂ is becoming a promising alternative to conventional adsorbents in removing heavy metal ions.

Key words: sorption, heavy metal ions, modification, TiO₂

1. INTRODUCTION

The contamination of aquatic systems with heavy metal ions is a problem of global concern (Chen et al., 2011). Heavy metals from industrial activities, such as plating and metallurgy, are a threat to humans and to the environment due to their toxicity and persistence after they are released into the natural environment (Aksu, Gonen, 2006).

Many traditional methods applied to remove heavy metal ions, such as electrochemical precipitation, ion exchange, reverse osmosis, are limited due to the poor heavy metal removal, high operational costs and limited adaptability to a wide range of effluents (Li
et al., 2011). Sorption has been recognized as one of the most popular and effective methods for the removal of the above-mentioned pollutants from wastewaters due to the flexibility in design and operation offered by the sorption process (Pang et al., 2011). However, this process is expensive, so low-cost biosorbents have been given increasing attention as they can significantly reduce the cost of a sorption system (Laus et al., 2010).

Biosorption can be defined as the removal of metal ions from solution by biological material (Wang, Chen, 2009). The biosorbent, unlike traditional sorbents (which have only one type of binding site), contains a variety of functional sites including carboxyl, imidazole, sulphydryl, amino, phosphate, sulphate, thioether, phenol, carbonyl, amido and hydroxyl moieties. These materials react with analytes resulting in a passive uptake from wastewater. Biosorption can be performed by metal binding functional groups of biosorbent. In addition, biosorbents are used either directly or after being loaded on a support material (Ahmad et al., 2010; Bag et al., 1998; Kratochvil, Volesky, 1998; Krishnani et al., 2008; Mendil et al., 2008; Tuzen et al., 2008). Biosorption provides a very effective preconcentration process, due to its simplicity, low cost, higher recoveries and environmental safety making the biosorbent just like a kind of ion exchange resin (Lemos et al., 2008; Baytak et al., 2007).

Numerous support materials have been proposed to modified biomaterials, e.g. modified silica, organics chelate resin, activated carbon, activated alumina, silica and zeolites (Copello et al., 2011; Krishna et al., 2005; Mendil et al., 2008; Soylak et al., 2006; Viswanathan and Meenakshi, 2010). Recently, different nanomaterials have been used as sorbent as well. Nanomaterial can sorb the metal ion selectively with quite high sorption capacity. However, in the column method, the nanoparticles are mostly removed passing through the filter from the bottom of the column and/or the filter is clogged so that the solution does not flow. In the batch method, the material may not be precipitated. These problems can be avoided by the loading of nanomaterials on different substrates. The modification of various sorbents with TiO$_2$ have been reported for the separation–preconcentration of metal ions in biological and environmental samples due to their functional groups (Kalfa et al., 2009; He et al., 2008; Liang et al. 2006).

2. PREPARATION OF BIOSORBENTS

In this paper, chitosan, bacterial biomass and dendrimers as a starting material for modification with TiO$_2$ have been reviewed. These materials have different structures and different functional groups on their surfaces. Because of that, the preparation of biosorbents for each starting material was different.

2.1. Crosslinked chitosan/TiO$_2$ biosorbent

In Padala et al. (2014) research, the chitosan was dissolved in a 3% acetic acid (v/v) solution. To this solution, TiO$_2$ was added with stirring. The mixture was sonicated followed by addition of epichlorohydrin (1 mL) with stirring. The resultant dispersion was added into a 0.25 M NaOH solution, under constant stirring, leading to formation of solid beads. The precipitated beads were left overnight. The beads were separated, washed with ultra-pure water and dried overnight in an air oven at 50°C. The dried beads were treated with 0.1 M HCl in order to remove any unreacted chitosan. The beads were
further washed with ultra-pure water to get neutral washings, and dried under vacuum. The purified dry beads thus obtained were used as the chitosan/TiO₂ sorbent for the studies.

2.2. Impregnated chitosan/TiO₂ biosorbent

In Miller and Zimmerman (2010) research chitosan beads were prepared from a solution of chitosan and 0.1 M HCl that was stirred with a magnetic stir bar. Impregnated chitosan/TiO₂ beads were prepared by adding TiO₂ to the chitosan. The beads were formulated by dispensing the chitosan-TiO₂ solution into 0.1 M NaOH and were then filtered through a Buchner funnel and rinsed with deionized water until the filtrate was of neutral pH and dry. The purified dry beads thus obtained were used as the chitosan/titania sorbent for the studies.

2.3. Filamentous fungal/TiO₂ biosorbent

Bakircioglua et al. (2010) prepared the biosorbent using bacterial cells as a starting biomaterial, which were separated from the sludge media using centrifugation. The isolated biomass was washed with a 0.1 mol/L HCl, and rinsed with distilled water and dried (Lemos et al., 2008; Tuzen et al., 2007). Dead bacteria powder was mixed with TiO₂, then the mixture was wetted with deionized water and thoroughly mixed and centrifuged. The precipitate was dried in at about 105°C to be used as a biosorbent.

2.4. Dendrimers/TiO₂ biosorbent

Barakat et al. (2013) diluted the as-received G4-OH dendrimer-methanol solution in a large excess of deionized water. TiO₂ was slowly added to the dendrimer containing aqueous solution to arrive at a slurry mixture. After sonication for 2 h, the composite material was dried (T = 60°C) to remove the solvent and then in a drying oven (T = 90°C) to remove all excess moisture and used as a sorbent.

3. CHARACTERISATION OF THE BIOSORBENTS

The prepared material specimens were examined with a scanning electron microscope (SEM).

3.1. Impregnated chitosan/TiO₂ biosorbent

In Miller and Zimmerman (2010) research, SEM measurement on the bulk bead surface provided quantitative elemental content for 1-2 µm of surface depth. This analysis confirmed the presence of Ti in chitosan/TiO₂ biosorbent (Fig. 1). Neat TiO₂ nanopowder used in chitosan/TiO₂ biosorbent preparation has a reported surface area of 55 m²/g (Sigma Aldrich). The surface area of chitosan/TiO₂ biosorbent was determined to be 0.5578 ± 0.0067 m²/g, as measured through BET surface area analysis.
3.2. Filamentous fungal/TiO$_2$ biosorbent

From Bakircioglua et al. (2010) research, a SEM photograph of biomass loaded on TiO$_2$ nanoparticles is given in Fig. 2. As shown from the figure, the bacteria bonded TiO$_2$ particles have much bigger sizes compared to the untreated TiO$_2$ nanoparticles with no permeability from the filter pores.
3.3. Dendrimers/TiO$_2$ biosorbent

In Barakat et al. (2013) research, the dendrimer/TiO$_2$ biosorbent has a porous surface with regions not covered by TiO$_2$ and a large aggregation of nanoparticles forming larger structures (Fig. 3 (a,b)). The pore formation might be achieved via removal of the embedded dendrimer by taking advantage of the activated oxygen gas treatment. The TiO$_2$ framework was stable upon template removal, and the pores were replicated from the template dendrimer. Nanopores are not two-dimensional in that sense, since they are not connected with each other.

![Fig. 3 SEM images of the dendrimer/TiO$_2$ biosorbent (Barakat et al., 2013)](image)

4. Evaluation of the Sorption Properties

4.1. Effect of contact time

Sorption studies for Sb(V) removal by crosslinked chitosan/TiO$_2$ sorbent were carried out with 40 mg of the sorbent with 8 cm$^3$ of 1.0 mM Sb(V) solution, with initial pH of 5.2, in batch mode (Padala et al., 2014). Crosslinked chitosan/TiO$_2$ sorbent showed fast uptake of antimony with almost complete removal of antimony from the solution within 30 min.

Kinetic data for arsenic sorption by impregnated chitosan/TiO$_2$ shows that equilibrium is reached after 185 h for both arsenite and arsenate, where initial arsenic concentration for both As(III) and As(V) was 10,000 μg/dm$^3$ (Miller and Zimmerman, 2010).

The metal ion removal rate increased over a wide concentration range (up to 800 mg/dm$^3$ for each of the three metals independent) within an equilibration time of 1 h. The simultaneous removal of 50 mg/dm$^3$ Cu(II), Cr(III), and Ni(II) ions from solution by dendrimer/TiO$_2$ sorbent shows that the removal efficiency for Ni(II) is 56% after 1 h and the efficiency is 79.4% after 3 h at pH 7. Complete removal of the three metals ions by
the dendrimer/TiO₂ sorbent, was achieved after 30 min at pH 7 for both for Cu(II) and Cr(III), and pH 9 for Ni(II) ions (Barakat et al., 2013).

### 4.2. Effect of initial pH

The initial pH value is a critical parameter in the sorption of heavy metal ions by a biosorbent modified with TiO₂, due to changing the surface charge of the sorbent and heavy metal speciation (Lee and Saunders, 2003; Ma and Tobin, 2004; Schiewer and Patil, 2008). pH values, when the maximal sorption of heavy metal ions by a modified biosorbent is achieved, are listed in Table 1.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Heavy metal</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinked citosan/TiO₂</td>
<td>Sb(V)</td>
<td>1-2</td>
<td>Padala et al., 2014</td>
</tr>
<tr>
<td>Impregnated citosan/TiO₂</td>
<td>As</td>
<td>6-7.25</td>
<td>Miller and Zimmerman, 2010</td>
</tr>
<tr>
<td>Filamentous fungal/TiO₂</td>
<td>Pb(II)</td>
<td>4-8</td>
<td>Bakircioglu et al., 2010</td>
</tr>
<tr>
<td>Dendrimers/TiO₂</td>
<td>Cu(II)</td>
<td>8-9</td>
<td>Barakat et al., 2013</td>
</tr>
<tr>
<td></td>
<td>Ni(II)</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr(III)</td>
<td>7-9</td>
<td></td>
</tr>
</tbody>
</table>

Crosslinked chitosan/TiO₂ biosorbent sorbed Sb(V) (as Sb(OH)₆⁻) only in acidic conditions. This is expected as the functional groups of the chitosan/TiO₂ biosorbent are protonated under acidic conditions (Navarro et al., 2003) and bind the anionic Sb(OH)₆⁻ species. As shown in Eq. (1), which depicts the pH dependent surface charge on TiO₂, at low pH, the surface is predominantly positively charged, leading to the sorption of hydroxyl and other anionic species. The hydroxyl ion sorption leads to reduction in the solution pH when the sorbent is equilibrated with alkaline solution. As the pH increases, the surface tends towards the negative charge there by leading to the reduced pick up of Sb(OH)₆ anions, as reflected by the drastic reduction in Sb(V) sorption at pH beyond 5.0.

\[
\text{Ti(IV)} – \text{OH}_2^+ \rightleftharpoons \text{Ti(IV)} – \text{OH} \rightleftharpoons \text{Ti(IV)} – \text{O}^- \quad \text{(with increasing pH)} \tag{1}
\]

Impregnated chitosan/TiO₂ sorbed both arsenite and arsenate from aqueous solution. It is an effective arsenic sorbent at pHs lower than its point of zero charge (pHₚₒzc = 7.25), where electrostatic attraction exists between the positively charged biosorbent surface and negatively charged arsenic oxyanions (H₂AsO₄⁻ and HAsO₄²⁻) (Nabi et al., 2009).

The sorption of lead ions on the Filamentous fungal/TiO₂ biosorbent was studied as a function of pH in a wide range between 1.0 and 10.0. Maximum (quantitative) retention was maintained within the pH of 4.0-10.0, which is quite a wide range.

The removal of Cu(II), Cr(III), and Ni(II) ions (independently) from aqueous solution with dendrimer/TiO₂ sorbent is highly dependent on pH. This dependency results from the fact that pH can affect the surface charge of the sorbent and the degree of ionization of the sorbate (Belgin, 2002). Metal ion removal increased with increasing pH from 3 to 11, because tertiary amines are able to efficiently complex metal ions from aqueous solutions at higher pHs (Mankbadi et al., 2011; Yamamoto et al., 2010).
It can be concluded that sorption of heavy metal ions by sorbents modified with TiO$_2$ is strongly dependent of the initial pH value of the solution. This effect is pretty much different for each material, because sorbents have different functional groups on their surface, as well as the form in which heavy metal occurs in the solution.

### 4.3. Sorption capacity of biosorbents

A sorbing system has a sorption capacity defined as the ratio of the mass of sorbate to the unit mass of sorbent (Langmuir, 1989). Maximum sorption capacities of biosorbents modified with TiO$_2$ for heavy metal ions are listed in Table 2.

**Table 2. Maximum sorption capacity of sorbents modified with TiO$_2$ for heavy metal ions**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Heavy metal</th>
<th>$Q_{\text{max}}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinked chitosan/TiO$_2$</td>
<td>Sb(V)</td>
<td>60.88</td>
<td>Padala et al., 2014</td>
</tr>
<tr>
<td>Impregnated chitosan/TiO$_2$</td>
<td>As(III)</td>
<td>2.198</td>
<td>Miller and Zimmerman, 2010</td>
</tr>
<tr>
<td></td>
<td>As(V)</td>
<td>2.050</td>
<td></td>
</tr>
<tr>
<td>Dendrimers/TiO$_2$</td>
<td>Pb(II)</td>
<td></td>
<td>Bakircioglua et al., 2010</td>
</tr>
<tr>
<td>Filamentous fungal/TiO$_2$</td>
<td>Pb(II)</td>
<td></td>
<td>Barakat et al., 2013</td>
</tr>
<tr>
<td></td>
<td>Ni(II)</td>
<td>798</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr(III)</td>
<td>703</td>
<td></td>
</tr>
</tbody>
</table>

### 4.4 Desorption studies

Desorption and regeneration of sorbents are crucially important for keeping processing costs low, but also to understand the nature of sorbate-sorbent interaction (Gao et al., 2003; Hammami et al., 2007). Like the sorption process, the desorption process is also pH dependent, due to changing the surface charge of the sorbent and heavy metal speciation.

Complete desorption of the sorbed Sb(V) from the crosslinked chitosan/TiO$_2$ sorbent could not be achieved, indicating a strong binding by the sorbent. Maximum desorption attained was about 30–40% using 0.25 M NaOH by prolonged equilibration (about 70 h) (Padala et al., 2014). Apart from electrostatic attraction of the anionic species by the surface charges on the TiO$_2$, there is a possibility of strongly bound complex formation with the surface titanium dioxide sites (Gonçalves et al., 1999). The low rate of desorption indicates the possibility of such a strong binding of antimony by the sorbent.

Both acidic and alkaline solutions have been used for desorption of sorbed Pb(II) by *Filamentous fungal*/TiO$_2$ sorbent. Various concentrations of HCl and HNO$_3$ (0.5–2.0 mol/dm$^3$) were used for desorption of the lead ions from the biosorbent. The best results were obtained with 1.0 mol/dm$^3$ HCl (Bakircioglua et al., 2010).

### 5. Future Perspectives

The sorption of heavy metals by a material modified with TiO$_2$ have been compiled and reviewed in this paper. From the literature, sorption of heavy metals using a material modified with TiO$_2$ is expected to have improved performance in the future. However, the comparison between the sorbents is just a guideline. It is almost impossible to make a...
comparison between sorbents due to the different materials used during their formation. Different experimental conditions, scarcity of information provided and the inconsistencies in data presentation have also added to the difficulty in making the comparison. Here, we would like to highlight some points which might help future research. Some sorbents are economically feasible because they are easy to prepare and involve inexpensive chemical reagents.

Regeneration studies need to be performed in detail as it will enhance the economic feasibility. Based on the available literature, not many regeneration studies have been reported. The regeneration studies will determine the reusability of the sorbents, which contributes to its effectiveness. Regeneration could be done using several techniques but solvent extraction is the most common way found in the literature. The mechanism that is involved in the process is not well defined. Not many research studies have discussed the mechanism involved in the process. Assumptions were made based on the kinetic studies. Isotherm models were also insufficient to explain the mechanisms that were involved. Different techniques can provide various kinds of information on the sorbents. Therefore, combining different techniques will give a better picture in exploring the sorption mechanism.

5. CONCLUSION

This paper indicates that biosorbents modified with TiO$_2$ are becoming a promising alternative to conventional sorbents in removing heavy metal ions. Since there is a variety of TiO$_2$ based sorbents, arguments on which type of sorbent is better in sorption is still going on. There is no definite answer to this argument since each of the sorbents has its own advantages and disadvantages. A comparison between sorbents is almost impossible to make since the parameters and the sorbate used are different. This field of research has a great room for improvement in the hope that TiO$_2$ composites can be applied commercially instead of only at laboratory scale.

REFERENCES

KARAKTERIZACIJA MODIFIKOVANIH BIOSORBENTATA POMOĆU TiO₂ I NJIHOVA PRIMENA ZA UKLANJANJE JONA TEŠKIH METALA

U ovom radu je predstavljen pregled dobijanja, karakterizacije i primene materija modifikovanih pomoću TiO₂.ako početni material za modifikaciju korišćen citozan, bakterijska biomasa i dendrimeri. Karakterizacija dobijenih sorbentih je rađena primenom skenirajuće elektronske mikroskopske (SEM). Sorbeni su korišćeni za uklanjanje jona teških metala iz vodenih rastvora, u cilju ispitivanja njihovih sorpcione sposobnosti. Prikazan je uticaj kontaktnog vremena na uklanjanje jona teških metala i maksimalni sorpcioni kapacitet biosorbenata. Ispitivan je uticaj inicijalnog pH rastvora na uklanjanje jona teških metala, kao jedan od najbitnijih faktora koji utiče na sorpcioni proces. Rezultati pokazuju da se biosorbeni modifikovani sa TiO₂ mogu koristiti kao efikasno sredstvo za uklanjanje jona teških metala iz vode.

Ključne reči: sorpcija, teški metali, modifikacija, TiO₂