

Adsorptive removal of trace thallium(I) from wastewater

A review and new perspectives

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1. Introduction

Thallium was initially discovered by William Crookes in 1861, and is a rare metal with high toxicity. The toxicity of thallium is even higher than that of mercury, lead, cadmium, and copper for mammals (Zitko, 1975). Human body has non-discriminatory uptake of Tl(I) over K(I) as the ionic radius of Tl(I) is similar to that of K(I), which will cause fatal result because it disrupts the proper functioning of the K(I) involved biochemical reactions such as pyruvate kinase, ATPase, and stabilization of ribosomes (Galván-Arzate and Santamaría, 1998). It has been also reported that thallium could cause acute and chronic poisoning with the effects of degenerative changes in the heart, liver and kidney (Birungi and Chirwa, 2015). Moreover, due to its properties of odorless and tasteless, and very low depilatory agent of 8–15 mg/kg (Galván-Arzate and Santamaría, 1998) to human, numerous tragic accidents as well as murders have been caused by thallium (Lennartson, 2015; Gunby, 1995).

Thallium is distributed with very low concentrations in nature (Węgiel et al., 2016). The average abundance of Tl is 0.75 mg/kg in continental crust, 0.001–0.25 µg/L in groundwater, and 0.012–0.016 µg/L in seawater (Xiao et al., 2012). Due to its chalcophilic and lithophilic properties, thallium is normally accompanied with potassium minerals like alkali feldspars and micas, and sulphide minerals such as galena (PbS), chalcopyrite (CuFeS₂), sphalerite (ZnS) and pyrite (FeS₂) (Tatsi and Turner, 2014). The way of thallium emission into environment typically includes coal combustion, cement plants, and nonferrous metals metallurgy (mainly lead and zinc) (Vaněk et al., 2010). The predominant contamination source of Tl is the wastewater from the mining, beneficiation and smelting of Tl-containing sulfide ores. Due to the high solubility and mobility of Tl(I) in water (Lupa et al., 2015), thallium can be readily transported into aqueous environment, resulting in the potential of causing adverse health effects to human through drink water or food chain (Antón et al., 2013; Wan et al., 2014).

Recent studies on thallium pollution indicate that thallium is an emerging pollutant and will become a common pollutant in aquatic environment in the future with the raising mining/smelting of thallium-containing ores. Hence, the removal of thallium from wastewater is an urgent task.

Thallium has two oxidation states of Tl(I) and Tl(III). Compared to Tl(I), Tl(III) has much stronger oxidizing properties that the standard electrode potential of Tl(III)/Tl(I) reaches as high as 1.25 V (Hanzel and Verstraeten, 2009), which is quite close to that of gold (1.50 V). Therefore, monovalent thallium is thermodynamically much more stable, making it the dominating Tl species in nature (Liu et al., 2014). In wastewater from metallurgical industry, thallium exists as Tl(I) also, which is normally accompanied by many other heavy metal species such as Zn(II), Pb(II), Cu(II), Cd(II). Many methods have been developed for the purification of metallurgical wastewater (Fu and Wang, 2011). In general, these methods are able to remove most of the heavy metal ions from wastewater but exhibit poor removal efficiency for Tl(I) mainly because of its extremely low concentration and high solubility in water. The concentration of thallium in wastewater after heavy metals removal is still far above its maximum discharge level. So far, there is no worldwide regulation for the allowable thallium content in wastewater. Hunan province of China established a standard for thallium discharge level of 0.005 ppm in industrial wastewater for the first time in 2014, representing that more and more attention will be paid to the removal of trace thallium from industrial wastewater in the future.

A number of methods such as precipitation (Dutrizac, 1997), flocculation (Hosseini et al., 2006), electrochemical deposition (Ussipbekova et al., 2015; Kozina, 2003), and solvent extraction (Escudero et al., 2013; Fang et al., 2009; Rajesh and Subramanian, 2006), have been developed to remove thallium from industrial wastewater. However, few of them appeared to hold promise for industrial application in thallium removal from wastewater because these methods generally

have the disadvantages of low removal efficiency, large waste amounts generation, and high energy consumption (Twidwell and Williams-Beam, 2002). In recent years, adsorption exhibits rapid development and great potential for application in industrial wastewater processing owing to the advantages of high purification efficiency, low energy consumption, and environmentally friendliness (Umit and Sahan, 2018; Dilara and Sahan, 2015; Yilmaz et al., 2019a). In particular, for the purpose of trace Tl(I) removal from wastewater, a number of novel adsorbents with high selectivity such as prussian blue analogues, biosorbents, and metal oxides have been synthesized, and their adsorption behavior towards Tl(I) has been systematically investigated. However, comprehensive review of the recently developed adsorptive removal technologies for thallium from aqueous media is very limited in open literature. In the present paper, various adsorptive technologies, particularly developed in recent years, for trace Tl(I) removal from wastewater are reviewed. Focuses are placed on the adsorption mechanisms of the various types of adsorbents towards Tl(I) in aqueous systems. Moreover, potential adsorbents with high selectivity and adsorption efficiency are proposed, and their prospects of applying in industrial wastewater processing for trace thallium removal in depth are discussed.

2. Adsorbents for Tl(I) removal from wastewater

2.1. Prussian blue analogues

Prussian blue (PB) is a hexacyanoferrate compound with the empirical formula of MFe₃(III)[Fe(II)(CN)₆]₃, where M = Fe, Li, Na, K, Rb, Cu, and Ni, which is usually used as a decomposition agent for internal radio cesium contamination or thallium poisoning since the 1960s (Faustino et al., 2008). Sangvanich et al. evaluated the removal of Tl(I) by insoluble PB (Fe₄(III)[Fe(II)(CN)₆]₃) and Cu(II) ferrocyanide ([Cu(II)[Fe(II)(CN)₆]²⁻) immobilized on mesoporous silica (FC-Cu-EDA-SAMMSTM) in varied aqueous systems (Sangvanich et al., 2010). Compared to PB, FC-Cu-EDA-SAMMSTM exhibited higher capability of capturing Tl(I) due to its greater adsorption affinity, better selectivity over competing cations, and broader working pH ranges. According to the experimental results, the distribution coefficient (K_d) of thallium on both sorbents increased with the increase of solution pH from 0.1 to 7.3, representing that cation ion exchange might be the major adsorption mechanism. The relatively low K_d at lower pH values is likely to be caused by the competition of hydrogen ions with Tl(I) for binding with the cyanides owing to its greater availability in an acidic environment. In addition, competing ions of Cu(II) and Zn(II) appeared to bind well with PB and FC-Cu-EDA-SAMMSTM at near neutral pH level. The Tl(I) concentration after adsorption under the optimal conditions was 0.075 ppm for FC-Cu-EDA-SAMMSTM, and 0.3 ppm for PB, which are much higher than wastewater discharge standard (0.005 ppm). Vincent et al. investigated the separation mechanisms of Tl(I) from slightly acidic solutions with a composite sorbent of Prussian blue immobilized in alginate capsules (Vincent et al., 2014). This sorbent has two types of sorption sites: PB for the “strong” sorption of Tl(I), and alginate encapsulating material which contributes to a marginal sorption. The binding mechanism of Tl(I) with PB was found to be the ion exchange of Tl(I) with hydrogen ions in the crystal lattice of PB, or with alkali metal impurities bound to PB during the synthesis process. Therefore, pH showed a significant effect on Tl(I) removal efficiency from 71 % to 94 % with increasing the pH value from 1.0 to 4.0. Moreover, as the sorption process follows a cation exchange mechanism, the ionic strength of the solution should be an important influencing factor. The distribution coefficients of the competing ions of Ca(II), K(I), and Na(I) generally remained at a high level of 10³ in a wide content range, indicating relatively strong affinities of the competing ions to the sorbent, which resulted in the decrease of thallium sorption capacity to a different extent in the presence of competing ions such as Ca(II), K(I), and Na(I).

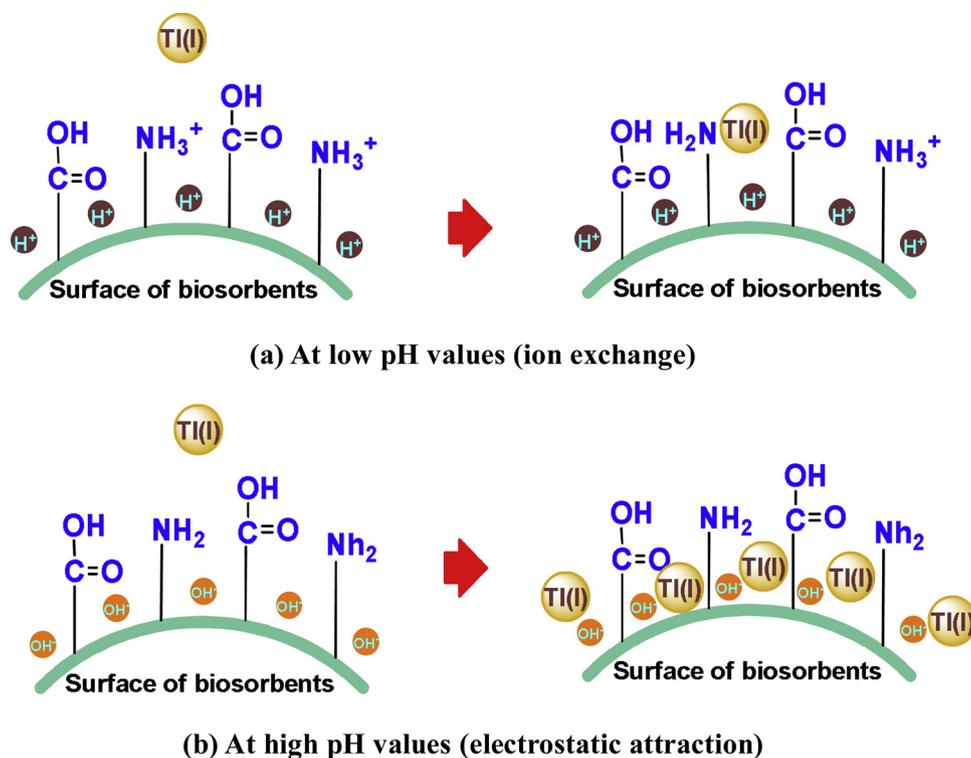


Fig. 1. Schematic diagram of Tl(I) adsorption onto biosorbents: (a) at low pH values; (b) at high pH values.

2.2. Biosorbents

Biosorption is a promising technology for heavy metal pollution control in wastewater particularly at low ionic concentration levels, which has the advantages of high cost-effectiveness, inexhaustibility, simplicity in operation and high process efficiency (Salman et al., 2015). It has been widely investigated for removing heavy metal ions such as Cu(II) (Peng et al., 2010), Pb(II) (Yuvaraja et al., 2014), Zn(II) (Mishra et al., 2012), Cd(II) (Rajesh et al., 2014), Ni(II) (T. et al., 2013), Cr(VI) (Miretzky and Cirelli, 2010) from wastewater.

Memon et al. investigated the removal of Tl(I) from aqueous solution by a NaOH treated waste material from furniture production, sawdust (Memon et al., 2008). The adsorption process was found to be proceeded rapidly that the adsorption rate reached about 98 % within 8 min with the initial thallium concentration of 10 ppm. The adsorption process was found to be strongly affected by the solution pH due to the protonation of the carboxylic groups at low pH values which are not able to attract Tl(I) from aqueous phase. When the pH is over 4.0, the carboxyl groups are negatively charged because of the de-protonation process, and thus can bind the positively charged Tl(I), in the meantime, the adsorption of competing metal ions such as Ag(I), Al(III), Ca (II), Cr(VI), Fe(II), Li(I) and Mg(II), was effectively limited.

After treated with H₂SO₄, NaOH, cetyl, silane, polyethylamine or coated with iron oxide, fungal biomass of *Aspergillus niger* can be also used to remove thallium from aqueous solutions (Peter and Viraraghavan, 2008). Little or no adsorption was observed when the solution pH was less than 3.0 owing to the competition between protons and Tl(I) for binding sites on the cell walls. The adsorption of Tl(I) was enhanced by the increase of the solution pH, and a pH value of 4.0–5.0 could deliver high thallium adsorption (up to 70 % removal efficiency, at an initial thallium concentration of 10 ppm) for almost all the biomass.

Dashti et al. studied the adsorption of Tl(I) from aqueous solutions by eucalyptus leaves powder (Dashti Khavidaki and Aghaie, 2013). The results showed that the basic modified adsorbent is more efficient for Tl (I) adsorption than the unmodified or acidic modified adsorbents. In the

case of NaOH modification, OH⁻ could associate with the adsorbent sites which is preferred to attach to positive Tl(I) on the adsorbent surface through electrostatic attraction. The adsorption of Tl(I) by eucalyptus leaves powder is a strong pH-dependent process. The adsorption efficiency is greatly increased with the increase of the solution pH within the relatively low pH region, and the optimal Tl(I) sorption efficiency can be obtained at pH 8.5. A waste-product of sugar beet pulp from sugar-refining factories, was also proposed to be an effective adsorbent for the removal of Tl(I) from aqueous solutions (Zolgharnein et al., 2011a). After pretreatment with NaOH, sugar beet pulp could remove 95 % of Tl(I) within 10 min from a 1000 ppm thallium containing solution. Similar to the other biosorbents mentioned above, the adsorption process with NaOH treated sugar beet pulp was also significantly affected by the solution pH. The highest Tl(I) removal efficiency was reached at the pH of approximately 7.0.

Moreover, dry biofilm biomass collected from eutrophic lakes (Yin et al., 2009) and modified *ulmus carpinifolia* tree leaves (Zolgharnein et al., 2011b) were also used to remove thallium ions from wastewater. Adsorption processes with both adsorbents could proceed rapidly and the results were well fitted to the Langmuir model. Effective removal of Tl(I) could generally be achieved when the solution pH was higher than 7.0.

In summary, biosorbents usually consist of functional groups such as hydroxyl, carboxyl, amine, esters, alcohols, carbonyl, and acetamide, which could provide strong attraction forces for the binding of target metal ions by the ion exchange with hydrogen ions, adsorption, or donation of electron pairs (complex formation) (Salman et al., 2015). By the treatment with modifiers, particularly with NaOH, biosorbents can be used to remove most of Tl(I) (70–98 %) from aqueous solutions. The Tl(I) adsorption process is highly pH dependent, because the surface charge of the adsorbents is significantly affected by the solution pH (Mathialagan et al., 2003), which further affects the uptake of Tl(I) through electrostatic repulsion or attraction. At low pH values, the negatively charged surface sites treated with modifier of NaOH, are neutralized by hydrogen ions, resulting in no attraction of positively charged Tl(I). Meanwhile, the functional groups (carboxylic, amine

etc.) of the adsorbents become protonated, which will lead to two consequences: on one hand, the functional groups are not available to attract Tl(I) due to electrostatic repulsion and, on the other hand, the protonated functional groups are able to adsorb a certain amount of thallium by ion exchange, as illustrated in Fig. 1(a). However, the hydrogen ions around the adsorbent surface will hinder the ion exchange process, resulting in poor adsorption efficiency of Tl(I) (< 20 %). When the solution pH is over 4.0, the functional groups will be deprotonated and the number of negatively charged surface sites will be increased, therefore, the positively charged Tl(I) can be readily bound and adsorbed, as explained in Fig. 1(b). In general, Tl(I) adsorption in aqueous solutions by biosorbents normally follows the mechanism of electrostatic attraction, and thus the selectivity of the biosorbents towards Tl(I) is limited. Therefore, Tl(I) removal from wastewater through biosorption is inevitably affected by the presence of co-existing cations such as K(I), Na(I), Cu(II), Pb(II), and Ni(II).

2.3. Metal oxides

2.3.1. Iron oxides

Electrochemically generated iron hydroxide plus hydrogen peroxide were utilized by Brewster et al. to remove multiple ions of heavy metals from contaminated groundwater (Brewster and Passmore, 1994). Almost all the ions including arsenic, copper, lead, mercury, and thallium could be effectively removed with their concentrations being below the applicable discharge limits. In particular, the content of remaining Tl(I) in the solution was decreased to below 0.005 ppm, from an initial concentration of 0.032 ppm. The target metal ions were tightly bound with the iron matrix through the mechanisms of surface complexation and precipitation. However, the adsorbent of iron hydroxide after heavy metal ions removal is colloidal form, which is difficult to separate from the aqueous phase. Yantasee et al. reported that magnetite (Fe_3O_4) nanoparticles functionalized dimercaptosuccinic acid (DMSA) is an effective adsorbent for softer heavy metal ions such as Pb(II), Ag(I), Hg(II), Cd(II), and Tl(I) (Yantasee et al., 2007). The distribution coefficient of DMSA- Fe_3O_4 for Tl is 13,000 mL/g in river water at pH 7.2, indicating an excellent adsorption efficiency for thallium. The binding affinity of DMSA- Fe_3O_4 to Tl is higher at neutral pH than that at acidic levels. This is because the DMSA groups will be protonated at low pH values, thereby reducing the affinity to Tl. Dutrizac proposed that jarosite precipitation is an effective approach to eliminate thallium from zinc processing circuits (Dutrizac, 1997). During the thallium precipitation process, the removal extent was virtually independent on the initial thallium concentration in the range of 0–3000 mg/L and was not significantly affected by the presence of Zn(II) in the solution (about 75 g/L). The removal of Tl(I) was achieved by the substitution of alkali ions with Tl(I) in the jarosite structure, forming a stable precipitate for thallium immobilization. This process can proceed rapidly with a high Tl(I) removal extent, however, the thallium content in the precipitate is generally low, being about 30 %, leading to large amount of hazardous solid waste generation which needs further harmless treatment.

2.3.2. Alumina

Zhang et al. employed nano- Al_2O_3 particles as adsorbent for removing thallium from aqueous solutions (Zhang et al., 2008). The results showed that the removal efficiency increased with the increase of pH from 1.0 to 5.0, and the highest Tl(I) removal efficiency was reached in the pH range of 4.0–5.5. This can be attributed to the significant influence of pH on the distribution of active sites on nano- Al_2O_3 surface. At higher pH, the OH^- on the nano- Al_2O_3 surface provides the ability of binding with cations, whereas the decrease of pH results in the neutralization of the surface charge, losing the affinity to thallium cations.

2.3.3. Titania

Kajitvichyanukul et al. investigated the adsorption of Tl(I) on a

titania surface in the presence of additives such as oxalate, formate, acetate and phosphate anions in aqueous solutions (Kajitvichyanukul et al., 2003). According to the experimental data, the point of zero charge (PZC) of TiO_2 surface is at the pH 6.04, indicating a net positive and negative charge on the titania surface at lower and higher pH over 6.04, respectively. At pH 11, the initially added Tl(I) (~40 ppm) was effectively adsorbed following the mechanism of electrostatic attraction. The adsorption of Tl(I) was significantly enhanced by the addition of oxalate, formate, acetate and phosphate anions. This phenomenon is mainly due to the formation of the inner-sphere complexes by the additives with the titania surface, which could act as anchors to bind thallium ions, enhancing the adsorption process.

Liu et al. reported that the hydrothermally synthesized titanate nanotubes (TNTs) could effectively remove thallium ions from aqueous solutions (Liu et al., 2014). The adsorption efficiency of Tl(I) increased with the increase of pH, which can also be explained by the forementioned surface charge theory. The PZC of TNTs is 2.56. The positive surface charge at low pH could inhibit the adsorption of Tl(I) due to electrostatic repulsion, whereas the surface charge of the TNTs turned to be negative at the pH higher than 2.56, benefiting the adsorption process of Tl(I) onto TNTs surface through electrostatic attraction. Thereafter, ion exchange between Tl(I) and sodium/hydrogen ions in the interlayers took place, leading to the improvement in adsorption capacity. As a result, nearly 100 % removal efficiency was reached when pH was above 5.

Zhang et al. synthesized titanium peroxide via a facile oxidation coupled with a precipitation method at ambient temperature and investigated its adsorption performance towards Tl(I) (Zhang et al., 2018). Similar phenomena were observed that Tl(I) adsorption was a pH-dependent process which can be effectively enhanced by the increase of solution pH. The Tl(I) adsorption mechanism is considered to be the cation-exchange reaction of thallium ions with hydroxyl groups on the peroxide surface. However, the Tl(I) adsorption process was significantly affected by the co-existing ions of copper and zinc, resulting in a decrease of Tl(I) adsorption efficiency by 10–25 %.

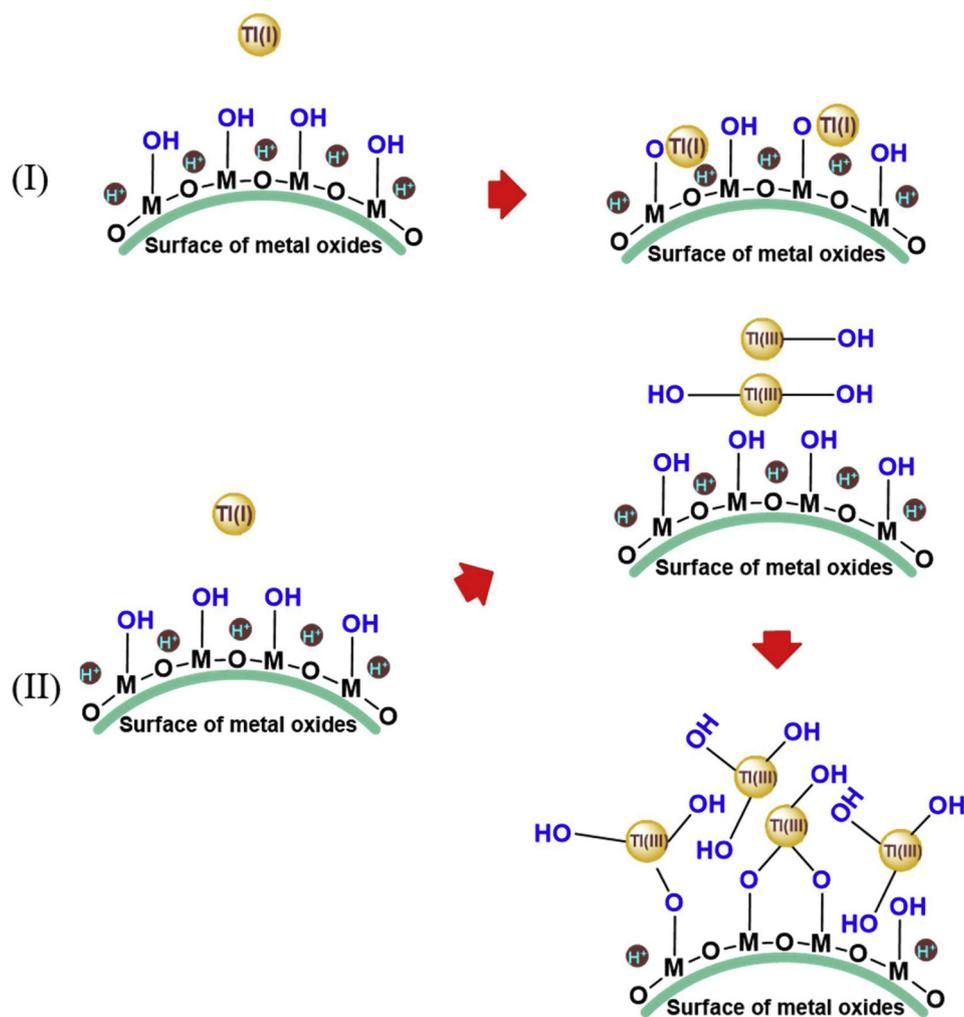
Zhang et al. investigated the adsorption mechanism of Tl(I) by rutile nano-titanium dioxide (RNTD), of which the average particle size is 20–50 nm in diameter, offering sufficiently large surface area for Tl(I) adsorption (Zhang et al., 2019). The effects of various parameters such as ion strength, temperature, and solution pH on the adsorption process were studied. The maximum adsorption capacity was calculated to be 51.2 mg/g by Langmuir model at room temperature. The Tl(I) adsorption kinetics fit the pseudo-second-order equation well, and Tl(I) was found to be adsorbed by the monolayer adsorption sites on the adsorbent surface.

Tang et al. synthesized a nano-sized titanium iron magnetic adsorbent for thallium removal from wastewater (Tang et al., 2019). The Tl(I) adsorption was investigated to be a highly pH-dependent process, and the maximum Tl(I) adsorption capacity of 111.3 mg/g was obtained at pH 7.0. The adsorption process was proceeded rapidly that an equilibrium adsorption capacity of approximately 83 % could be achieved in the beginning 30 min. The mechanism of the Tl(I) adsorption process was explained to be the binding of Tl(I) to the deprotonated sites on the hydroxyl groups of the nano-sized adsorbent surface. Although this novel adsorbent shows excellent removal capacity for thallium ions from aqueous solutions, the adsorption process was affected by the co-existing ions of sodium, calcium, and copper to a different extent.

2.3.4. Manganese dioxide

Amorphous hydrous manganese dioxide (HMO) is an effective adsorbent for heavy metals retention. Heavy metal ions like Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) can be efficiently removed from aqueous solutions with HMO by the formation of inner-sphere complexes and electrostatic forces (Tripathy and Kanungo, 2005; Wan et al., 2010).

The first report on the removal of thallium from aqueous solutions



(a) At low pH values ((I) ion exchange, or/and (II) redox reaction)



(b) At high pH values (electrostatic attraction and ion exchange)

Fig. 2. Schematic diagram of Tl(I) adsorption onto metal oxides: (a) at low pH values; (b) at high pH values.

using manganese dioxide was published by Bidoglio et al. (1993). The adsorption behavior of Tl(I) onto δ -MnO₂ synthesized by oxidizing MnCl₂ with KMnO₄ in the basic pH region was investigated. For a wide Tl(I) content range from 24 to 40,000 ppm, nearly complete adsorption was achieved even at a low pH value of 4.7. This might be related to the acidic character of δ -MnO₂, which has a PZC of 2.2. However, considering the general lower stability of Tl(I) bonds with oxygen electron donors, the marked displacement of the adsorption edge towards the low pH region can be explained neither by coulombic attraction, nor by the much greater negative charge of δ -MnO₂. Further studies with X-ray absorption spectroscopy showed that the adsorbed thallium on manganese oxide mainly existed as Tl₂O₃, indicating that the removal mechanism involves the oxidation of thallium ions from the valence state

of +1 to +3 followed by the surface precipitation of sparingly soluble oxides. Differently, the patent of Jibiki et al. in 1995 proposed a method for removing thallium ions from ZnSO₄ or CdSO₄ solutions using manganese dioxide sludge produced from the zinc electrolysis process, in which the uptake of thallium ions by MnO₂ was considered to be an ion exchange mechanism, as explained in Eq. (1) (Jibiki, 1995). For an industrial zinc sulphate solution containing 150 g/L of Zn(II), 423 mg/L of Cd(II), 903 mg/L of Cu(II), 17 gm/L of Co(II), 7 g/L of Mn(II), and 13 mg/L of Tl(I), thallium ions were effectively removed by the manganese dioxide sludge with the remaining Tl(I) concentration being 0.5 mg/L in the solution after adsorption at pH 4.0.

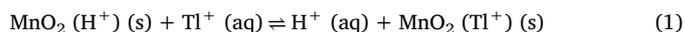
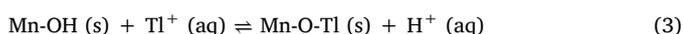
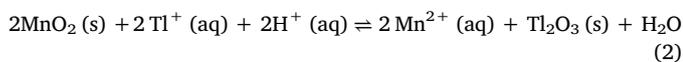


Table 1
Adsorption capacity of different adsorbents for Tl(I).

Adsorbents	Adsorption capacity (mg/g)	Source	
Prussian blue analogues	Prussian Blue	5.82	(Sangvanich et al., 2010)
	FC-Cu-EDA-SAMMS	28.3	(Sangvanich et al., 2010)
Biosorbents	Prussian blue immobilized in alginate capsules	54.7	(Vincent et al., 2014)
	Sawdust	13.18	(Memon et al., 2008)
	Aspergillus niger biomass	6.27	(Peter and Viraraghavan, 2008)
	Eucalyptus leaves powder	80.65	(Dashti Khavidaki and Aghaie, 2013)
	Sugar beet pulp	185	(Zolgharnein et al., 2011a)
Metal oxides	Ulmus carpinifolia tree leaves	54.6	(Zolgharnein et al., 2011b)
	Nano-Al ₂ O ₃	6.28	(Zhang et al., 2008)
	Titanate nanotubes	709.2	(Liu et al., 2014)
	Titanium peroxide	412.0	(Zhang et al., 2018)
	HMO	352.9	(Wan et al., 2014)
	HMO-001	448.8	(Pan et al., 2014)
	Fe-Mn binary oxides	236.4	(Li et al., 2017a)

In 2014, Wan et al. synthesized HMO by oxidation of MnSO₄ with NaOCl-NaOH solution and subsequent chemical precipitation, for the purpose of removing Tl(I) from wastewater (Wan et al., 2014). Similar to the other adsorbents, the adsorption of Tl(I) by HMO is also a pH-dependent process. Tl(I) could be effectively adsorbed by HMO in a relatively large pH range. For a solution containing 100 ppm of thallium, Tl(I) removal efficiency of 80–88 % was reached in a low pH range of 2.0–4.0, and it can be rapidly promoted to 98 % by increasing the solution pH to 8.0. XPS analysis results of the HMO after Tl(I) adsorption showed that about 54.5 % of the adsorbed Tl(I) was oxidized to Tl(III) at pH 2.02, while that for the experiment at pH 5.83 was only 9.7 %. The XPS results indicate that the interaction between Tl(I) and manganese dioxide follows a redox mechanism in the low pH region, that the presence of hydrogen ions motivates the removal of thallium from the aqueous solution, as described in Eq. (2). On the other hand, at high pH values the adsorption mechanism should be attributed to the ion exchange between Mn-OH groups and Tl(I), as illustrated in Eq. (3).



Pan et al. proved the H⁺-motivated oxidation of Tl(I) by HMO at pH 2.2 through XPS analysis when they synthesized a polymer-supported nanocomposite (HMO-001) for removing Tl(I) from wastewater (Pan et al., 2014). Similar phenomena were also found by Li et al. when they investigated the thallium removal process from aqueous solutions with Fe-Mn binary oxides (Li et al., 2017a). The removal efficiency of thallium reached over 95 % within a wide pH range of 3.0–12.0 with an initial Tl(I) content of 10 mg/L. Based on the fact that 64.5 % of the Tl was oxidized and efficient removal of Tl was achieved at high pH values, the authors concluded that the thallium removal mechanism was not only the oxidation and precipitation of Tl(III), but also the inner sphere complexation of Tl(I).

In conclusion, the removal of thallium by metal oxides in aqueous solutions mainly follows three kinds of mechanisms: electrostatic attraction, ion exchange and redox reaction. Similar to other types of adsorbents, the surface charge of metal oxides is also significantly affected by solution pH. At the pH values lower than PZC, the adsorbent surface is positively charged with hydrogen ions which hinder the adsorption of positive Tl(I) through electrostatic repulsion. On the other hand, ion exchange between the protonated adsorbents and Tl(I) can occur, contributing to the removal of thallium from aqueous solutions, as explained in Fig. 2(a, d). However, large amount of co-existing hydrogen ions will compete with Tl(I) during the ion exchange process, hindering the removal of Tl(I) from the solution. As a result, most of metal oxides are not able to completely remove thallium from aqueous solutions at low pH values with a relatively low removal efficiency of

10–40 % (Zhang et al., 2008; Kajitvichyanukul et al., 2003). By increasing the solution pH, the positive surface charge of the metal oxide adsorbents will be neutralized by OH⁻. When pH is higher than PZC, the adsorbent surface will become negatively charged, thereby having high affinity for Tl(I) through electrostatic attraction, as illustrated in Fig. 2(b). Meanwhile, if monovalent cations such as Na(I) and K(I) enter the interlayers of the metal oxide adsorbents during the preparation procedure, ion exchange can also take place enhancing the adsorption process of Tl(I). Metal oxides with high oxidation ability such as iron oxide and HMO, are able to efficiently remove Tl(I) even at the pH values below PZC, mainly due to the oxidation of Tl(I) to Tl(III) by H⁺-motivated redox reaction and subsequent precipitation of Tl(OH)₃ on the adsorbent surface, as described in Fig. 2(a, d).

However, the Tl(I) removal from wastewater by metal oxide adsorbents always encounter several problems. For instance, the metal oxide adsorbents normally show a good adsorption capacity for Tl(I), but the selectivity to thallium is generally poor, resulting in low Tl(I) adsorption efficiency in the presence of co-existing cations due to their severe competition during the electrostatic attraction or ion exchange process. Experimental results showed that the co-existing calcium ions could decrease the adsorption of Tl(I) by more than 10 % (Wan et al., 2014). Another important problem is the difficulty in desorption and regeneration after the Tl(I) adsorption process. Particularly for the cases using HMO as the adsorbents, when Tl(I) was oxidized to Tl(III) and further precipitated as Tl(OH)₃, thallium could be hardly desorbed from the adsorbents and most of the adsorbed thallium remained in the adsorbent. The remaining thallium will further affect the microstructure and adsorption capacity of HMO, resulting in inefficient adsorbent regeneration.

The adsorption capacities of different adsorbents for Tl(I) are exhibited in Table 1, and the effects of varied co-existing cations on Tl(I) adsorption capacity are summarized in Fig. 3.

3. New perspectives for removal of thallium from wastewater

3.1. Macrocyclic compounds

Macrocyclic compound is defined as a cyclic compound with nine or more members of atoms (including all hetero atoms) and with three or more donor (ligating) atoms (Gordon, 2012). It is uncharged and contains a cavity in which a cation is able to be encapsulated (Koltoff, 1979). With the development of supramolecular chemistry, the synthesis of different types of macrocyclic compounds and the modification of their conformations can be readily achieved to gain excellent selectivity towards certain ions. Consequently, macrocyclic compounds are widely applied in various fields such as chemical sensor, extractive metallurgy, and analytical chemistry.

In recent years, considerable interests on the determination of

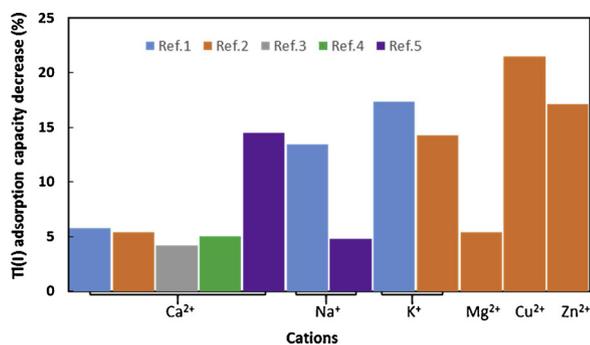


Fig. 3. Effects of varied co-existing cations on Tl(I) adsorption capacity.

Ref. 1 (Vincent et al., 2014): initial Tl(I) concentration 80 mg/L, pH 4.0, M^{n+}/Tl^+ ratio (mol/mol) = 250; Ref. 2 (Zhang et al., 2018): initial Tl(I) concentration 18 mg/L, pH 4.0, M^{n+}/Tl^+ ratio (mol/mol) = 10; Ref. 3 (Wan et al., 2014): initial Tl(I) concentration 50 mg/L, pH 5.0, M^{n+}/Tl^+ ratio (mol/mol) = 10; Ref. 4 (Pan et al., 2014): initial Tl(I) concentration 51 mg/L, pH 5.8, M^{n+}/Tl^+ ratio (mol/mol) = 10; Ref. 5 (Liu et al., 2014): initial Tl(I) concentration 100 mg/L, pH 5.0, M^{n+}/Tl^+ ratio (mol/mol) = 2.

thallium in aqueous environments have come up in the research field due to the increasing awareness of environmental pollution and high toxicity of thallium. However, the determination of Tl is difficult because the content of the thallium-containing species in nature is extremely low at ng/L level or even less. Therefore, the application of analytical methods with efficient pre-concentration procedure or highly sensitive ion sensor is required. Recently, a variety of new adsorbents or ion sensors for the pre-concentration and accurate determination of trace thallium have been developed. These new achievements can provide us with useful information for seeking effective adsorbents to remove trace thallium more efficiently from industrial wastewater.

3.1.1. Determination of trace thallium with macrocyclic compounds

Katsu et al. constructed a selective membrane electrode which could recognize Tl(I) with high selectivity by using calix[6]arene-hexaacetic acid hexaethyl ester as ionophore (Katsu et al., 2002). The electrode markedly avoided the disturbances from Na(I), K(I), and Ag(I) and showed a near-Nernstian response to Tl(I) within the content range from 10^{-6} to 10^{-2} mol/L. Further studies demonstrated that calix[5]arene-hexaacetic acid hexaethyl ester also showed excellent selectivity to thallium ions.

Dong et al. described a glassy carbon electrode (GCE) which is coated with a Langmuir-Blodgett (LB) film of p-allylcalix[4]arene for the determination of trace amount of thallium in ground water (Dong et al., 2006). The coated p-allylcalix[4]arene film was used to pre-concentrate Tl(I) by complexation based on the high selectivity and affinity of p-allylcalix[4]arene towards thallium. The pre-concentration process was not affected by alkali and alkaline-earth metal ions, and most of the other metal cations such as Co(II), Zn(II), Bi(II), Mn(II), Pb(II), Fe(II), Ni(II), and Ag(I) generally gave errors lower than 5%. As a result, the detection limit of thallium(I) is estimated to be as low as 1.0 μ g/L.

Cheraghi et al. investigated the selective pre-concentration and detection of Tl(I) by the use of carbon paste electrode modified with dicyclohexyl-18-crown-6 (Cheraghi et al., 2013). The response of the developed sensor to Tl(I) followed a linear relationship within the content range of 3.0–250 μ g/L, and the detection limit was found to be 0.86 μ g/L. Interference study showed that the Tl(I) recovery was quantitative in the presence of 500-fold interference metal cations of zinc, manganese, copper, nickel, sodium, and potassium.

Chester et al. utilized three modified calix[4]arene as ionophores to build ion-selective electrodes for the determination of Tl(I) in the content range of 10^{-2} – 10^{-6} mol/L (Chester et al., 2014). The electrodes displayed a Nernstian response, representing that the process is dominated by the complexation of calix[4]arene with Tl(I). Furthermore, the

ionophores showed great selectivity against the cations of calcium, zinc, barium, cadmium, copper, and aluminum, and moderate selectivity against the interference ions of lithium, lead, sodium, hydrogen, potassium, and cesium.

Talanova et al. designed a fluorescent chemosensor, dansyl group-containing derivative of 1,3-alternate calix[4]arene-bis (crown-6-ether) for the detection of thallium (Talanova et al., 2005). The detection limit of this chemosensor for thallium was 14 μ g/L under the given experimental conditions. The fluorescence spectrum of the ionophore was not evidently affected by the additions of sodium, potassium, silver, calcium, lead, mercury, and some of the transition metal ions into the solution.

Asadoulahi et al. synthesized an adsorbent by physical immobilization of a crown ether dibenzo-18-crown-6 onto surfactant coated alumina for pre-concentration of thallium before determination with electrothermal atomic absorption spectrometry (Asadoulahi et al., 2007). The experimental results indicated that the immobilized DB18C6 adsorbent could efficiently recover thallium within the pH range of 6.0–10.0 from the aqueous solution with the initial Tl(I) content of 5 μ g/L. The sensitivity and utility of the adsorbent towards thallium in the presence of potential disturbing species like magnesium, calcium, sodium, potassium, copper, zinc, lead, nickel, and cobalt ions in water, and environmental samples at an initial interfering ion to Tl(I) mole ratio of 1000 were investigated. It was observed that the determination of thallium at trace levels was not interfered significantly by the co-existing ions.

Chamsaz et al. developed a single drop liquid-phase microextraction (SDME) technique adopting dicyclohexano-18-crown-6 as the complexing agent for the pre-concentration of Tl(I) in the aqueous solution (Chamsaz et al., 2009). The results indicated that dicyclohexano-18-crown-6 exhibited high extraction efficiency for Tl(I) even at a very low Tl(I) content level of 0.02 ppm. Furthermore, by the use of EDTA (0.005 M) for masking the metal ions, the extraction of Tl(I) by dicyclohexano-18-crown-6 became relatively free from 100-fold of interfering ions of potassium, sodium, copper, nickel, and mercury.

In summary, the macrocyclic compounds of crown ethers and calixarenes generally exhibit high affinity and selectivity to thallium even in the presence of relatively high concentrations of co-existing ions, achieving accurate determination of trace Tl(I) in varied types of aqueous solutions. Accordingly, the macrocyclic compounds based adsorbents should have great potential for application in complete thallium removal from wastewater, which is considered to be an important future direction of research and development for industrial wastewater treatment.

3.1.2. Complexation properties of thallium with macrocyclic compounds

The complexation of macrocyclic compounds, especially crown ether, towards metal ions including Tl(I) has been investigated for several decades. Crown ether was firstly synthesized by Pedersen in 1967 (Pedersen, 1967), since then its excellent complexing affinity towards metal ions has been widely recognized. Crown ether can form complexes with salts of most metallic elements. These compounds appear to be salt-polyether complexes formed by ion-dipole interaction between the negatively charged oxygen atoms and the cation symmetrically positioned in the crown ether ring. In general, the selectivity and stability of the resulting complexes are affected significantly by the relative size of the cation to crown ether cavity (Izatt et al., 1985, 1991). Thallium is a metallic element in group IIIA of the periodic table and the ionic diameters of Tl(I) is 3.0 Å (Izatt et al., 1985). According to the cavity of different crown ethers, Tl(I) matches best the cavity size of 18-crown-6 (18C6, 2.6–3.2 Å). Therefore, Tl(I) is expected to be able to form stable complexes with 18-crown-6 and its derivatives.

Poonia et al. and Farago prepared complexes of Tl(I) salts with 18C6 and showed that they are stable 1:1 anhydrous complexes (Poonia and Truter, 1973; Farago, 1977). Jabbari reported a conductometric study of the complexation reactions of Tl(I) and Ag(I) with several crown

ethers in acetonitrile, acetone and dimethylformamide solutions at 25°C (Jabbari et al., 1993). The conductance behavior showed that in the metal ion-ligand systems of Tl^+ -18C6, Tl^+ -DC18C6 (dicyclohexyl-18-crown-6) and Tl^+ -DB18C6 (dibenzo-18-crown-6), a fairly stable 1:1 complex was formed. $Tl(I)$ generates more stable complexes with these ligands than $Ag(I)$ ion (2.3 Å) since it better fits the cavity of 18-crowns. On the other hand, the cavities of 12C4 and B15C5 (benzo-15-crown-5) are too small for thallium(I) so that much less stable complexes were formed compared to that with 18-crowns. Izatt et al. determined the equilibrium constants of Tl^+ -18C6 derivatives and the results turned out to be $\log K_e = 2.27-7.40$ (Izatt et al., 1985). Maeda et al. investigated the solvent extraction of thallium picrate by benzo-18C6 and also confirmed the formation of 1:1 ion-pair complexes between $Tl(I)$ and benzo-18C6 (Maeda et al., 1979). Domasevitch et al. prepared $[Tl(18\text{-crown-6})(H(BTCO)_2)](HBTCO = 2\text{-isonitroso-2-(benzothiazolyl-2)-acetonitrile})$ complex and determined its crystal and molecular structure by X-ray diffraction (Domasevitch et al., 1996). The results showed that the centrosymmetric cations $Tl(18\text{-crown-6})^+$ and $[H(BTCO)_2]^-$ anions played a role of bridges between neighboring cations, which delivered a one-dimensional polymeric structure. The Tl atom was coordinated in a slightly distorted hexagonal bipyramid (coordination number 8) and positioned exactly in the mean plane of the six oxygen atoms of 18-crown-6.

Besides 18C6, some other crown ethers are also able to form stable complexes with $Tl(I)$. For example, 15C5 and $Tl(I)$ could form 2:1 sandwich conformation complex though the size of $Tl(I)$ is considered to be too large for 15C5. Farago reported the preparations of complexes of $Tl(I)$ with benzo-15crown-5, 4,5dibromo-benzo 15-crown-5, and methylbenzo-15-crown-5 (Farago, 1977). Similar to potassium, thallium(I) can react with benzo-15-crown-5 and yield 1:2 complexes. The infrared spectrum of the coordinated ligand in $TlSCN(\text{benzo-15C5})_2$ was practically the same as those of $KBPh_4(\text{benzo-15C5})_2$ and $KI(\text{benzo-15C5})$. The potassium iodide complex has a sandwich microstructure in which the macrocycle allows the oxygen atoms to be close to the metal ion, whereas all the methylene groups on the side away from the metal ion. The similar infrared spectra of the three types of benzo-15-crown-5 thallium complexes indicate that they are sandwich-structured also. Maeda et al. demonstrated that benzo-15-crown-5 could form 2:1 crown ether unit-cation complexes with $Tl(I)$ during the thallium solvent extraction process. The extraction equilibrium constant $\log K_e$ reached as high as 7.56 in the chloroform phase at 25°C (Maeda et al., 1979).

Differently, some researchers found the formation of 1:1 complex between $Tl(I)$ and 15-crown-5 rather than 1:2 complex formation. Poonia et al. reported that the Tl :benzo-15-crown-5 ratio was 1:1 in their prepared Tl^+ -15C5 complexes, and the reason was explained to be

the stereochemically active lone pair of electrons in $Tl(I)$ which could prevent the sandwich-structured complex formation (Poonia and Truter, 1973). Poonia's another report also stated that thallous (2,4-dinitrophenolate) could form a dehydrated 1:1 complex with benzo-15-crown-5 (Poonia, 1974). Although there are contradictory conclusions about the complexation mechanisms of Tl^+ -15C5, one thing is certain that complexes with high stability can be formed by the interactions between $Tl(I)$ and 15C5.

Furthermore, large crown ethers such as 21C7, 24C8, 30C10, and even 60C20 could also form complexes with $Tl(I)$. The formation constants of DB21C7 (dibenzo-21-crown-7) and DB24C8 (dibenzo-24-crown-8) complexes with sodium, cesium, and thallium ions in several nonaqueous solvents were determined by Shamsipur et al. through multinuclear NMR measurements (Shamsipur et al., 1980). The results indicated that the complex formed by DB21C7 with $Tl(I)$ is more stable than that with sodium or cesium ions. This is because the $Tl(I)$ -crown ether bonding associates with some covalent contribution. DB24C8 is likely to have a more suitable size for $Tl(I)$, compared to sodium and cesium ions, due to the formation of a stable three-dimensional wrapped-around complex. Cesium ion is not able to form a 'wrap around' complex because it is much too big to fit the cavity size of DB24C8. Sodium ions can also form a three-dimensional complex with DB24C8 but the stability of the complex is quite low compared to that with thallium. Jabbari reported the stability of large crown complexes with $Tl(I)$ is in the order of $DB30C10 > DB21C7 > DB24C8$. $Tl(I)$ could readily form a stable 'wrap around' complex with the large flexible DB30C10 because all of the ten oxygen atoms in DB30C10 can be involved in the bond formation with the central cation (Jabbari et al., 1993). The stability of Tl^+ -DB30C10 complex was found to be even higher than that of Tl^+ -18C6 in acetonitrile and acetone solutions. Moreover, the selectivities to $Tl(I)$ of the ring-enlarged DB20C6 and DB22C6 were investigated to be higher than that of DB18C6 in the solvent extraction experiments of Weber et al. (1990) and the polymer membrane thallium(I)-selective electrodes experiments of Yamashoji et al. (1991).

Izatt et al. also reported the formation of remarkably stable complexes of DB30C10 and DB60C20 with $Tl(I)$ (Izatt et al., 1985). These larger polyethers are able to wrap around the cation to form a three-dimensional cavity, in which all the oxygen atoms are coordinated to the cation, stabilizing the structures of the complexes.

3.1.3. Design of thallium(I)-selective crown ether

As reviewed above, many crown ethers exhibit excellent affinity for $Tl(I)$ and are able to form stable complexes with it. Therefore, it is considered to have high potential of developing an efficient and highly

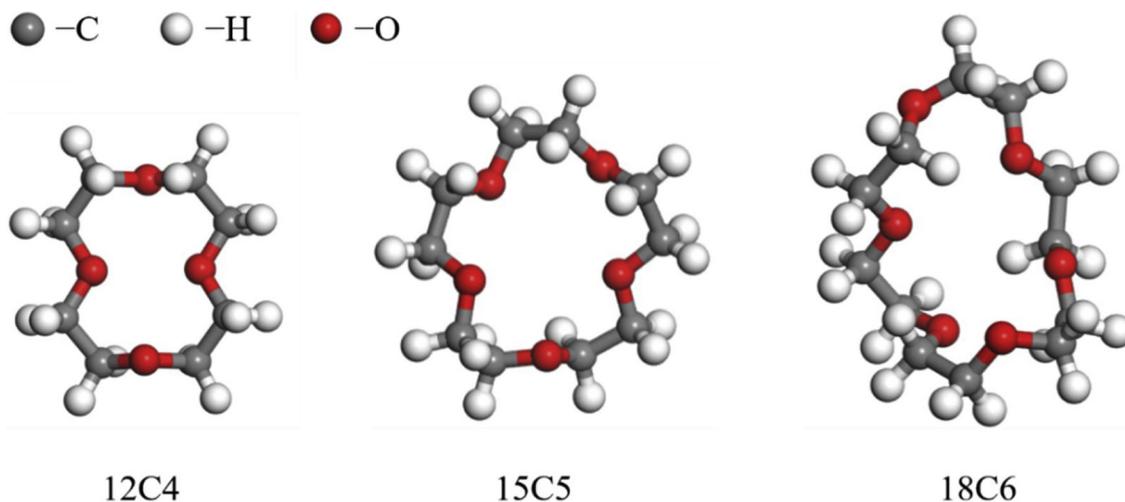


Fig. 4. Molecular structures of several crown ethers.

Table 2
Cavity diameters of different macrocycles and selectivity towards Tl(I) over other metal ions (M^{n+}).

Macrocycle	Cavity diameter (Å)	Source	Selectivity coefficient	Source
12-crown-4	1.2-1.5	(Pedersen, 1967)	Ag ⁺ , ∞ Pb ²⁺ , 0.49 Ca ²⁺ , 0.54 Mg ²⁺ , 1.29	(Jabbari et al., 1993) (Izatt et al., 1985)
15-crown-5	1.7-2.2	(Maeda et al., 1979)	Ag ⁺ , 0.25 Ag ⁺ , 1.95 Pb ²⁺ , 0.24 Hg ²⁺ , 0.35	(Jabbari et al., 1993) (Izatt et al., 1985)
thio-15-crown-5	1.7-2.2		Ag ⁺ , 0.02 Pb ²⁺ , 0.14	(Izatt et al., 1985)
Bis-15-crown-5	1.7-2.2		Ag ⁺ , 1585 Pb ²⁺ , 39811 Cd ²⁺ , 2.0×10^5 Ca ²⁺ , 10^5 Mg ²⁺ , 1.6×10^5	(Yamashoji et al., 1991)
18-crown-6	2.6-3.2	(Maeda et al., 1979)	Ag ⁺ , 1.58	(Jabbari et al., 1993)
dibenzo-18-crown-6	2.6-3.2		Ag ⁺ , 1.62 Ag ⁺ , 1.23 Pb ²⁺ , 0.41 Cu ²⁺ , 12589 Zn ²⁺ , 50118 Cd ²⁺ , 12589 Ca ²⁺ , 25118 Mg ²⁺ , 22387	(Jabbari et al., 1993) (Yamashoji et al., 1991)
dibenzo-18-crown-6 immobilized on surfactant coated alumina	2.6-3.2		Ag ⁺ , 83333 Cu ²⁺ , 10416 Pb ²⁺ , 8474 Zn ²⁺ , 9803 Cd ²⁺ , 27777 Ca ²⁺ , 26316 Mg ²⁺ , 10^5	(Asadoulahi et al., 2007)
dicyclohexano-18-crown-6	2.6-3.2		Ag ⁺ , 1538 Cu ²⁺ , ∞ Pb ²⁺ , 3384 Zn ²⁺ , 3452 Cd ²⁺ , 2205 Ca ²⁺ , 10710 Mg ²⁺ , ∞	(Chamsaz et al., 2009)
dicyclohexyl-18-crown-6	2.6-3.2		Ag ⁺ , 7 Cu ²⁺ , 53125 Pb ²⁺ , 1932 Zn ²⁺ , ∞ Ni ²⁺ , 1.9×10^5 Hg ²⁺ , 2428 Cd ²⁺ , 8511	(Jabbari et al., 1993) (Cheraghi et al., 2013)
dibenzo-21-crown-7	3.4-4.3	(Shamsipur et al., 1980)	Ag ⁺ , 83	(Jabbari et al., 1993)
p-allylcalix[4]arene	lower rim: 2.0 upper rim: 5.5	(Ohto, 2010)	Ag ⁺ , 47 Cu ²⁺ , 227 Pb ²⁺ , 156 Zn ²⁺ , 3487 Ni ²⁺ , 7684 Hg ²⁺ , 10	(Dong et al., 2006)
calix[5]arene-hexaacetic acid hexaethyl ester			Ag ⁺ , 794 Na ⁺ , 6309 K ⁺ , 316	(Katsu et al., 2002)
calix[6]arene-hexaacetic acid hexaethyl ester			Ag ⁺ , 3162 Na ⁺ , 10000 K ⁺ , 501	(Katsu et al., 2002)

selective adsorbent for Tl(I) removal from wastewater based on crown ether. The typical molecular structures of several crown ethers are exhibited in Fig. 4. For the design of Tl(I)-selective crown ether, several important factors should be taken into account to obtain active function group of the new developed adsorbents.

3.1.3.1. The cavity of the crown ethers. The relative size of the cation and the macrocyclic cavity is an important factor influencing the stability of the macrocyclic complexes. The cavity diameters of some macrocycles and their selectivity towards Tl(I) over other metal ions (M^{n+}) were summarized in Table 2. Generally, the cation-cavity size compatibility determines the selectivity of crown ether to the target

cation and the structure of the formed macrocyclic complexes. For instance, 18C6 and 21C7 show the highest selectivity to potassium and cesium ions, respectively (Bajaj and Poonia, 1988). The 2:1 complex will be formed when the macrocyclic ring size is smaller than that of the cation, for example, 15C5 with K(I) or Tl(I) (Tamura et al., 1980) and 18C6 with Cs(I) (Bajaj and Poonia, 1988). However, for such a complex, the stability is normally lower than that of the corresponding best-fitted system. For large crown ethers which contain seven or more oxygens in the polyether ring, two kinds of complexation behaviors were cleared: (a) Since the ligands are rather flexible in the free state, they wrap themselves around the metal ion to generate a three-dimensional 'wrap around' structure, in which all the oxygen atoms of the ring take part in

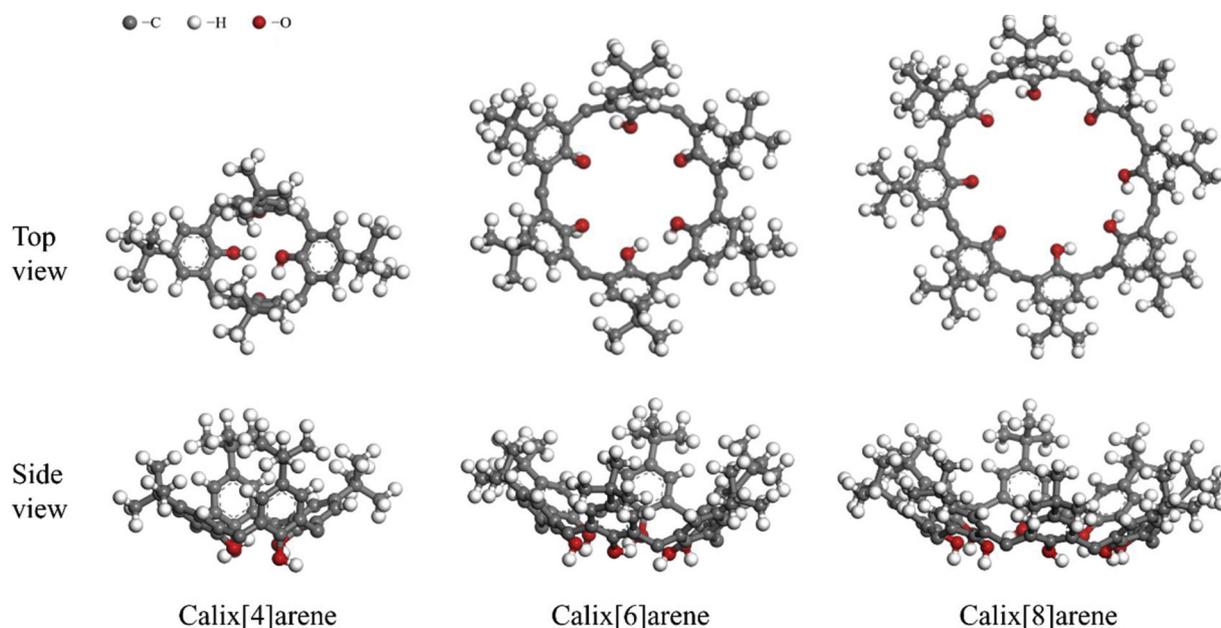


Fig. 5. Molecular structures of several calixarenes.

the bond formation process. For example, potassium ion can be completely enclosed by dibenzo-30-crown-10 according to the X-ray crystallographic data (Bush and Truter, 1970). It is interesting to note that, this type of complexes is even more stable than the corresponding best-fitted complexes since all the oxygens form bond with the central cation. For instance, the stability of Tl^+ -DB30C10 complex is higher than that of Tl^+ -18C6 (Jabbari et al., 1993). (b) In some cases, the large ligand rings are capable of accommodating more than one cations (Fenton et al., 1972). As mentioned previously, the diameter of $Tl(I)$ fits the cavity size of 18C6 best and could form stable complexes with 18C6 derivatives. However, for selective removal of $Tl(I)$ from wastewater, 18C6 may be not a good choice. Tl -containing wastewater usually consist of high concentrations of impurity ions such as $Zn(II)$, $Pb(II)$, $Cu(II)$, and $Cd(II)$ (Li et al., 2017b; Perotti et al., 2018). Although small ions like zinc (1.66 Å), copper (1.44 Å), and cadmium (1.66 Å) could not coordinate with 18C6, it has been found that lead ion (2.28 Å) could form stable complex with 18C6 (Takeda and Kat, 1979). Therefore, the presence of $Pb(II)$ would significantly influence the selective adsorption process of 18C6 towards $Tl(I)$. Moreover, if there are potassium ions present in the wastewater, they would also negatively affect the complexation between 18C6 and $Tl(I)$.

The formation of 'wrap around' complexes is strongly influenced by the size of the cation. The complexation of a cation by ligand with a proper size leading to the formation of a stable 'wrap around' complex. If the cation size is much smaller than the ring, the ligand is still able to form the 'wrap around' structure, but the oxygen atoms of the ligand will be close to each other and the complex structure could be weakened by the resulting repulsive force (Shamsipur et al., 1980). If the size of the cation is too big, the three-dimensional structure is not able to be formed, and only a few oxygen atoms could participate in bond formation, resulting in a weak complex. Therefore, according to the ionic size of $Tl(I)$, large crown ethers of 24C8 and 30C10 could probably provide the most suitable cavity to form stable 'wrap around' complexes with $Tl(I)$ for effective $Tl(I)$ removal from wastewater.

3.1.3.2. The principle of hard and soft acid and base (HSAB principle). The complexation process of the crown ether with cation can be explained with the HSAB principle (Tamura et al., 1980), that hard-hard or soft-soft interaction between acceptor and donor causes strong interaction (Ohto, 2010; Pearson, 1963). According to the HSAB principle, an oxygen atom is a hard base, thus the complexation

between crown ether and hard ions, e.g. alkaline earth ions, takes place easily. Substitution of oxygen atoms by other atoms such as nitrogen and sulfur in the crown ether ring would significantly affect the complexation property of the crown ether. For instance, Jabbari et al. found that the stabilities of the Tl^+ -18C6 and Ag^+ -18C6 complexes can be enhanced significantly by substituting two oxygen atoms with two nitrogen atoms in the 18C6 (Jabbari et al., 1993). It can be explained that both $Tl(I)$ and $Ag(I)$ ions are soft acids, which are preferred to interact with the soft bases of nitrogen atoms in the ring. $Tl(I)$ is classified as a soft acid, so that the binding between $Tl(I)$ and oxygen atoms in the crown ether ring is relatively weak. If the oxygen atoms are substituted by the softer atoms of nitrogen and sulfur, the resulted crown ethers are expected to have an excellent extractability and selectivity for $Tl(I)$ in the wastewater.

3.1.3.3. Steric hindrance. $Tl(I)$ ion has a pair of electrons in the outer s orbital which will always be σ -antibonding (Lee, 1972), and thus shows little tendency to form complexes. In Tl_3PO_4 (Ganne and Tournoux, 1973), Tl_3BO_3 (Marchand et al., 1973), and TlH_2PO_3 (Kosterina et al., 2001), the thallium atom is located at the apex of a tetragonal pyramid formed by the oxygen atoms surrounding the cation and is separated by the shortest $Tl-O$ distances, because the stereochemically active lone electron pair points in the direction opposite to the axial vertex of the pyramid. Similarly, Tl atom has been observed at a distorted pentagonal pyramid apex in the thallium hydroxobenzoic acid complex with phenanthroline (Farago, 1977). Poonia et al. reported that the stereochemically active lone pair of electrons in $Tl(I)$ might prevent the formation of 'sandwich' conformation during the interactions between $Tl(I)$ and 15C5 (Poonia and Truter, 1973). Unfortunately, theoretical data relevant to the stereochemical activity of lone pair electron density of thallium can be hardly found from open literature. Therefore, the stereochemical influence of the lone pair of electrons in $Tl(I)$ needs to be further investigated in depth in order to provide fundamental data for the design of crown ethers-based adsorbents with high adsorption capacity and selectivity to thallium.

In addition, it is also important to note another type of macrocyclic compounds, calixarenes, which are the products of the base induced condensation of p -substituted phenols and formaldehyde, being very promising adsorbents for efficient $Tl(I)$ removal from wastewater. Fig. 5 shows the typical molecular structures of several calixarenes. Compared to crown ethers, calixarenes have many advantages as following: (1)

simplicity of the parent compounds synthesis (one-step process); (2) functionalization of both the lower and upper rim of these macrocycles, resulting in high selectivity towards target ions; (3) capability of being fixed at different conformations through the introduction of functional groups of suitable length (Ohto, 2010; Danil de Namor et al., 1998; Mokhtari et al., 2010). Nevertheless, scientific research in this field is very limited so far. Future research and development in calixarene based adsorbents towards Tl(I) are highly needed in order to achieve the goal of complete removal of trace thallium from industrial wastewater.

3.2. Other promising adsorbents

3.2.1. Surface-modified clays

Clay minerals generally have the advantages of abundant availability, inexpensiveness, high specific surface area and ion exchange capacity, making them preferred adsorbents for industrial wastewater processing (Hua, 2015). Surface modification of clay minerals by specific functional groups is an effective way to improve the adsorption capacity and selectivity towards the hazardous metal species in aqueous media (Hernandez-Hernandez et al., 2013). Bentonite clay has a clear negative charge due to its 2:1 crystal structure of two silicon-oxygen tetrahedral layers and one aluminum-oxygen-hydroxyl octahedral layer, exhibiting excellent affinity to heavy metal ions (Bandpei et al., 2017). It has been demonstrated that thiol-functionalized bentonite and mercapto-modified bentonite are efficient adsorbents for selective removal of As(III) and Cd(II), respectively (Yilmaz et al., 2018; Ecer et al., 2018). In addition, grafting of polymers onto clay surfaces shows also great potential of application in wastewater processing because the formed polymer/clay composites have a number of superior features such as good dispersibility in aqueous environments, fast adsorption kinetics, and high adsorption capacity (Ozkose et al., 2017). For instance, pumice grafted with polymer brush has been found to be an efficient adsorbent for the uptake of dyes like methylene blue from the wastewater in textile industry (Yilmaz et al., 2019b).

3.2.2. Activated carbon

Activated carbon is a carbonaceous material with large surface area and well-developed internal pore structures, which possesses many adsorption sites, being able to eliminate a wide range of soluble organic and inorganic contaminants from aqueous media (Liew et al., 2018). Activated carbon is normally produced through intense heating with activating agents at a high temperature in the absence of oxygen. Recently, a novel microwave pyrolysis method which combines carbonization and steam activation as a single-step has been proposed for the production of activated carbon with high porosity and surface area from biomass waste. The activated carbon produced by this approach shows excellent adsorption capability for various hazardous waste such as landfill leachate (Lam et al., 2020), herbicides (Lam et al., 2018), and methylene blue (Kong et al., 2019) in aqueous environments. Although the novel adsorbents summarized above have not been utilized in thallium uptake yet, they are considered to be promising directions of research and development of wastewater processing particularly for complete removal of trace Tl(I) from industrial wastewater.

4. Conclusions

Thallium is an emerging pollutant and will become a common pollutant in aqueous environment in future. Many adsorbents including Prussian blue analogues, biosorbents, metal oxides such as hydrous iron oxide, superparamagnetic Fe₃O₄, nano-Al₂O₃, TiO₂, titanate nanotubes, and hydrous manganese dioxide, have been developed. However, the removal of thallium by these adsorbents are readily affected by the co-existing cations due to their poor selectivity to Tl(I). Recently, the pre-concentration and accurate determination of trace thallium in aqueous solutions have made rapid progress and a variety of new adsorbents or

ion sensors for Tl(I) have been developed. The efficient determination of trace thallium by these methods is attributed to the high affinity and selectivity of the macrocyclic compounds like crown ethers and calixarenes towards Tl(I). Accordingly, macrocyclic compound based adsorbents show great potential for application in efficient removal of trace thallium from industrial wastewater in the presence of numerous co-existing cations.

According to the complexation properties between crown ethers and cations, three factors should be taken into account for the design of Tl(I)-selective crown ether: (1) The crown ethers cavity should be highly compatible with the ionic size of Tl(I) to form stable 'wrap around' complexes. (2) Substitution of the oxygen atoms in the crown ether ring by softer atoms such as nitrogen and sulfur to enhance the affinity and selectivity of the crown ether towards Tl(I). (3) Avoiding the stereochemical influence of the lone pair of electrons in Tl(I).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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