Environmental remediation of heavy metal ions from aqueous solution through hydrogel adsorption: a critical review

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ABSTRACT

Heavy metal ions such as Cd^{2+}, Pb^{2+}, Cu^{2+}, Mg^{2+}, and Hg^{2+} from industrial waste water constitute a major cause of pollution for ground water sources. These ions are toxic to man and aquatic life as well, and should be removed from wastewater before disposal. Various treatment technologies have been reported to remediate the potential toxic elements from aqueous media, such as adsorption, precipitation and coagulation. Most of these technologies are associated with some shortcomings, and challenges in terms of applicability, effectiveness and cost. However, adsorption techniques have the capability of effectively removing heavy metals at very low concentration (1–100 mg/L). Various adsorbents have been reported in the literature for this purpose, including, to a lesser extent, the use of hydrogel adsorbents for heavy metal removal in aqueous phase. Here, we provide an in-depth perspective on the design, application and efficiency of hydrogel systems as adsorbents.

Key words | adsorbent, adsorptive capacity, biosorption, electrochemical sensor, heavy metals, hydrogel, toxicity

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NOMENCLATURE

C_0	initial dye concentration ($mg\ dm^{-3}$)	MAA	methacrylic acid
C_e	equilibrium sorbate (dye) concentration in solution ($g\ dm^{-3}$)	MBA	$N,N0$-methylenebisacrylamide
C_s	amount of the sorbed dye per dm^{-3} of the solution at the equilibrium ($mg\ dm^{-3}$)	m_{eq}	weight of equilibrium swollen hydrogel sample (g)
		m_s	sorbent (xerogel) weight (g)
C_t	dye concentration after certain sorption time t ($mg\ dm^{-3}$)	n	Freundlich parameter
		q_e	equilibrium sorption capacity ($mg\ g^{-1}$)
K	kinetic model rate constant (h^{-1})	$q_{e,cal}$	calculated value of maximum sorption capacity ($mg\ g^{-1}$)
k_0	Bangham parameter (g)		
K_d	distribution coefficient	$q_{e,exp}$	experimental value of maximum sorption capacity ($mg\ g^{-1}$)
K_F	Freundlich constant ($mg\ g^{-1}$)1/n		
k_f	pseudo-first order kinetic model rate constant (min^{-1})	q_m	maximum sorption capacity at complete monolayer coverage ($mg\ g^{-1}$)
k_{id}	diffusion rate constant ($mg\ g^{-1}\ h^{-0.5}$)	q_t	sorption capacity at time t ($mg\ g^{-1}$)
K_L	Langmuir sorption coefficient ($dm^3\ g^{-1}$)	R	universal gas constant (8.314 $J\ mol^{-1}\ K^1$)
K_s	pseudo-second order kinetic model rate constant (min^{-1})	R^2	linear correlation coefficient
		R_L	separation factor
		SD_{eq}	equilibrium swelling degree

DH	change of enthalpy (kJ mol^{-1})
DS	change of entropy (kJ mol^{-1} K^{-1})
AMPS/PVA	2-Acrylamido-2-methyl-1-propane sulfonicacid (AMPS) and polyvinyl alcohol (PVA) copolymer hydrogel
PVA/AAc	Polyvinyl alcohol/acrylic acid copolymer hydrogel
PMAA	Poly(methacrylic acid) based hydrogel
PAA	Poly acrylic acid (PAA) hydrogel beads
Poly(EGDMA–VIM)	Poly(ethylene glycol dimethacrylate-*n*-vinyl imidazole)

INTRODUCTION

In the last two decades there has been a remarkable increase of heavy metal pollution of ground water due to industrialization. This has posed many serious environmental problems due to the toxicity of heavy metals to many life forms. Ingestion of cadmium, vanadium and lead above the tolerance levels have been linked to cancer (Storr *et al.* 2006; Thompson *et al.* 2009; He *et al.* 2014; Wang & Chen 2014), brain damage (Storr *et al.* 2006; He *et al.* 2014), kidney, DNA damage (Shechter *et al.* 2003; Kammerer *et al.* 2004; Facchini *et al.* 2006; Thompson *et al.* 2009; Gad & Pham 2014), blocking of protein and oxidation of lipids, which is a preliminary step in the development of cardiovascular disease (Willsky *et al.* 2001; Kammerer *et al.* 2004; Bishayee *et al.* 2010). Heavy metal ions have the tendency to form complexes with biological matter (Storr *et al.* 2006; Holder 2010; He *et al.* 2014). These elements, along with amino and fatty acids and vitamins, are required for normal biochemical processes such as respiration, biosynthesis and metabolism (Lin 2014; Raimundo *et al.* 2014). Environmental monitoring agencies have set permissible limits (12 µg/L) for heavy metal levels in drinking water due to their harmful effects. The efficient removal of these toxic metal ions is a very difficult task due to the high cost of treatment methods. In recent years, research interest has increased in terms of the production of low-cost alternatives.

Microbe-based technologies can provide an alternative to the conventional methods for removal of these metal ions, since they are important in biological systems and in the environment at regulated concentrations. Chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption methods have also been used (Kumar *et al.* 2001; Akkaya & Ulusoy 2008; Chatterjee *et al.* 2010; Cao *et al.* 2011; Yetimoğlu *et al.* 2011; Kumar *et al.* 2012; Wan Ngah *et al.* 2012; Barakat *et al.* 2013; Kipp *et al.* 2013; Wan Ngah *et al.* 2013; Liu *et al.* 2014a; Liu *et al.* 2014b).

However, the common use of ion exchange and reverse osmosis is restricted by the high operating cost. As an alternative to chemical precipitation, membrane filtration or ion exchange and adsorption processes with a wide variety of adsorbents have been used, including hydrogels. The mechanism of biosorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange. Conventional techniques have inherent limitations such as low efficiency, sensitive operating conditions, production of secondary sludge and high cost of disposal (Barakat 2011; Barakat *et al.* 2013). Adsorption of heavy metals by activated carbon is a powerful technology and has been applied mostly in treating domestic and industrial waste water. However, the high cost of activated carbon and loss of the adsorbent during the regeneration process restricts its application. Since the 1990s, the adsorption of heavy metal ions by low-cost renewable organic materials has gained popularity (Wan Ngah & Hanafiah 2008; Zhang *et al.* 2014). The utilization of sea weeds, moulds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (Ng *et al.* 2013; Sun *et al.* 2013). Recently, attention has been diverted towards biomaterial, which comes mostly as by-products of large-scale industrial operations. The major advantages of biosorption over conventional treatment methods for copper, chromium, cadmium, and nickel at the second oxidation state include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, regeneration of biosorbents, and possibility of metal recovery (Demirbas 2008; Doelsch *et al.* 2010). Agricultural materials, particularly those containing cellulose, show potential biosorption capacity for Cd^{2+}, Pb^{2+}, Cu^{2+}, and Mg^{2+}). The basic components of the agricultural waste material biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water, hydrocarbons, and starch containing a variety of functional groups that facilitate metal complexation, which helps in the sequestering of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} (Namasivayam & Sangeetha 2006; Achiba *et al.* 2009; Smith 2009; Ng *et al.* 2013). Most agricultural waste materials are environmentally friendly due to their unique chemical compositions, great abundance, and low cost, and they are an efficient option for heavy metal remediation.

MECHANISM OF BIOSORPTION

The removal of metal ions from aqueous streams using agricultural materials is based upon metal biosorption (Zheng *et al.* 2010). The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing the dissolved species that will be adsorbed. Due to high affinity of the sorbent for the metal ion species, the latter is attracted and bound by a complex process which is affected by several mechanisms involving chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, and entrapment in inter- and intra-fibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion

Figure 1 | Two-stage biosorption diagram.

through cell wall and membrane (Feng *et al.* 2000). Functional groups present in biomass molecules, such as acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups, alcohols and esters, have the affinity for cadmium, copper and lead detection within a limit range of 150–350 mg/L (Wang & Chen 2014). Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending on their chemical composition. The complexation of various functional groups with heavy metal ions (Cd^{2+}, Pb^{2+}, Cu^{2+}, Mg^{2+} and Hg^{2+}) during the biosorption process has been reported by different research workers using spectroscopic techniques (Chen *et al.* 2013; Wang & Chen 2013). The processes of biosorption can be optimized to enhance the regeneration of the biosorbents and recovery of heavy metal ions. Most of the optimizations are performed in the batch process; this allows the design of continuous flow systems for industrial remediation applications (Figure 1).
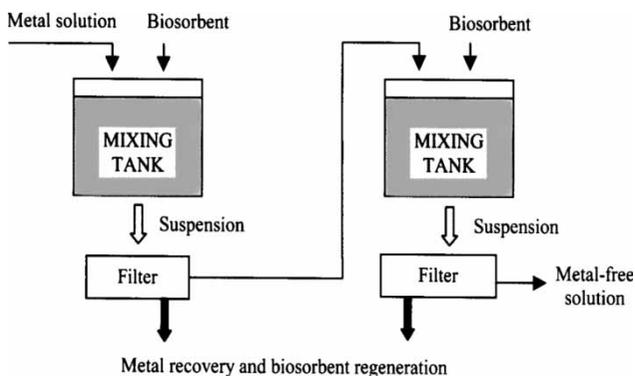
Hydrogels as sorbents

Hydrogels are three-dimensional networks of crosslinked polymers which are able to swell rapidly and retain large volumes of water in their swollen structure (Figure 2). They are usually made of hydrophilic polymer molecules which are crosslinked by either chemical bonding or other cohesion forces such as ionic interaction, hydrogen bonding
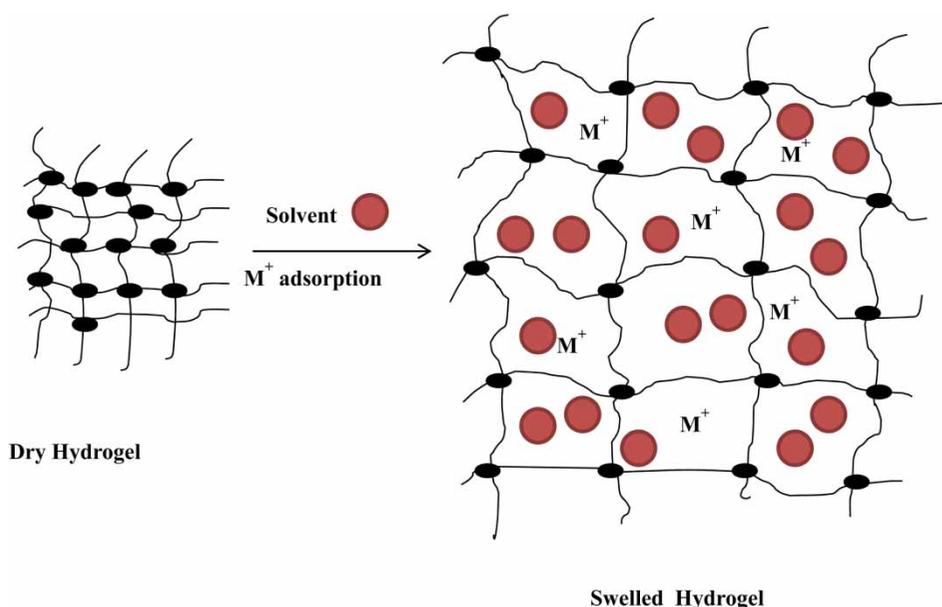

Figure 2 | Hydrogel adsorption mechanism.

or hydrophobic interaction (Holback *et al.* 2011; Buenger *et al.* 2012; Abeer *et al.* 2014; Liu *et al.* 2014a; Pourbeyram & Mohammadi 2014).

They are also used in the preparation of molecular recognition interfaces for biosensors (Holback *et al.* 2011; Buenger *et al.* 2012; Oun *et al.* 2014). Various hydrogels have been employed in biosynthesis processes and adsorbents such as cellulose graft acrylic acid (C-g-AA), chitosan hydrogel with 2,5-dimercapto-1,3,4-thiodiazole (CTS-DMTD), PVA-hydrogel biomass of *Penicillium cyclopium* and starch graft acrylic acid/montmorillonite (S-g-AA/MMT) (Jamnongkan *et al.* 2014).

PVA-hydrogel synthesis was achieved by precipitation of an aqueous solution of PVA out of absolute ethanol (Al-qudah *et al.* 2014). Glutaraldehyde was used as cross-linking agent to PVA polymer and HCl as catalyst. The hydrogel was further immobilized with *P. cyclopium* by dispersing a pre-weighed amount of wet biomass in the PVA aqueous solution prior to the precipitation. Hydrogels' adsorptive capacities and absorption kinetics are influenced by many factors, like metal concentration (Kaksonen *et al.* 2003), pH of the solution (Cao *et al.* 2011), composition of the absorbent (Chen *et al.* 2000; Chen *et al.* 2013; Bekin *et al.* 2014), and contact time (Chatterjee *et al.* 2010). pH is an important parameter that affects hydrogel performance by influencing its swelling and metal ion chelation on chelating adsorbents. For selective adsorption, besides the use of a specific ligand-modified sorbent, selectivity could be achieved by adjusting the pH to different values, and maximum adsorption is achieved at pH range 4–6 (Hua *et al.* 2012; Dragan 2014). pH control is the most important parameter for the selective adsorption of metal ions. pH 5.0 was found to be the optimal condition for Cd(II) and Pb(II) in controlled laboratory work. The sorption of Cd(II) and Pb(II) ions by hydrogel was found to be minimal at pH 2. The minimum adsorption observed at low pH was due to the higher mobility of H^+ ions present, favoring the preferential adsorption of hydrogen ions compared with metal ions (Cd^{2+}, Pb^{2+}, Cu^{2+}, and Mg^{2+}). At lower pH values, the surface of the adsorbent is surrounded by hydronium ions (H^+), thereby preventing the metal ions from approaching the binding sites of the sorbent. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged, such that the attraction between biomass and metal cations is reduced. In contrast, as the pH increases, more negatively charged surface becomes available, thus facilitating greater metal removal. It is commonly agreed that the sorption of metal cations increases with increasing pH as the metal ionic species become less stable in the solution.

Effect of adsorbate solution pH

The pH of the metal ions strongly affects the adsorption properties of hydrogels, as discussed (Akkaya & Ulusoy 2008; Cao *et al.* 2011). At pH > 6, precipitation of hydroxides may occur simultaneously, depending on the metal and its oxidation state, and may not lead to accurate interpretation of adsorption. However at low pH ≤ 3 condition, the main effective adsorption sites of the hydrogel, namely, the alcoholic and carboxyl groups, are both easily protonated, leading to the reduction of the adsorptive activity. At higher pH conditions, the protonated functional groups may be deprotonated, resulting in higher adsorption activity (Al-qudah *et al.* 2014).

Effect of contact time and adsorption kinetics

The time for treatment is an important factor in metal uptake, and thus, the effect of immersion time on the metal uptake of different metal ions was investigated. It could be observed that the increase in immersion duration is accompanied by an increase in metal ion adsorption, and this reaches its maximum value after 180 min of soaking, and then levels out (Jamnongkan *et al.* 2014). The results of much research revealed that at the initial immersion time the metal ion adsorption is fast, and it becomes slower near the equilibrium. Such behavior occurs due to the fact that during the initial stage, a large number of vacant active sites were available for adsorption; after that, repulsion occurred between the adsorbate molecules on the adsorbent surface, which slowed down the adsorption process (Al-qudah *et al.* 2014). Therefore, it is imperative to consider the time positively in future research and monitor the adsorption during timed intervals in order to maximize the adsorption and detection of a specific metal.

Effect of initial concentration and adsorption isotherms

Metal ion concentration has an effect on the adsorption capacity. It could be observed that as the initial concentration increased, the adsorption capacities also increased, but the rate of increase became slow after the concentration reached 150 mg/L for Zn^{2+}, Co^{2+} and Mn^{2+} (Lazaridis *et al.* 2004; Al-qudah *et al.* 2014). This indicates that there were few empty adsorption sites on the adsorbents and suggests that the adsorption almost reached equilibrium. The initial concentration provided the driving force needed to overcome the resistance due to the mass transfer of metal ions between adsorbed and adsorbate. Therefore, if the initial concentration is high, the driving force will also be high;

consequently, the adsorption capacity will be high. The adsorption capacities of hydrogels are based on adsorption isotherm and the kinetics of adsorption and typically modeled as first and second order kinetic models.

For this study, the Langmuir equation is a fairly good fit to the adsorption isotherms of Pb^{2+} and Cd^{2+} ions on the hydrogels. The maximum adsorption capacity found for Pb^{2+} and Cd^{2+} ions by using the Langmuir equation was in milligrams per gram (El-Sayed & Mostafa 2014). Therefore, more research should be conducted on the same hydrogel to improve selectivity and sensitivity and enhance the detection of these metal ions at micrograms per litre if not nanograms per litre. Conversely, the kinetics of the adsorption data was calculated using kinetic models to understand the dynamic of the adsorption process in terms of the order and rate constant of Pb(II) into hydrogel beads. These models were pseudo-first order and pseudo-second order models (Féris *et al.* 2004; Chen *et al.* 2009; Cheng *et al.* 2011; Dragan 2014; El-Sayed & Mostafa 2014). The adsorption model predicts the rate at which adsorption takes place for a given system, and it is probably the most important factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics. The sorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium (Féris *et al.* 2004). Langmuir and Freundlich isotherm models are frequently used for describing short-term and mono-component adsorption of metal ions. The reaction orders based on the capacity of the adsorbents have also been studied, such as Lagergren's first-order equation, the Redlich Peterson model and the Brunauer, Emmett and Teller (BET) model. However, Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and mono-component adsorption of metal ions by different biosorbents. The adsorption kinetic data were described by the Lagergren pseudo-first order model, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The adsorption isotherm data were evaluated by means of the Langmuir and Freundlich adsorption models. The two models are expressed by the following equations:

$$\frac{Ce}{qe} = \frac{1}{bq_m} + \frac{Ce}{q_m} \qquad (1)$$

$$qe = K_F Ce^{1/n} \qquad (2)$$

In the above equations, q_m (mg/g) is representative of monolayer maximum uptake of metal ions, and b (L/mg) is the Langmuir adsorption constant and is related to the free energy of adsorption. K_F (mg/g) and n are the Freundlich adsorption constants indicative of the adsorption extent and adsorption intensity, respectively. Based on these equations, the slope and intercepts of Ce/qe versus Ce are used to determine q_m and b, and in the same way K_F and n can be obtained from the plot of (ln qe) versus (ln Ce) (Demirbas 2008; Doelsch *et al.* 2010).

Selected kinetics parameters for metal adsorption (cadmium, lead and copper) by common adsorbent materials have been extracted for comparison (Table 1). The performances of the hydrogel adsorbents have been extracted to highlight the sorption parameters (Figure 3). Alginate beads and chitosan nanofibrils showed high adsorption capacity for Cd, Pd and Cu at pH 5, respectively (Table 1). Maximum adsorption was observed due to the fact that at that pH the biomass becomes preferentially protonated and releases the reduced metal cations, which adsorb onto the alginate beads, resulting in improved metal removal. PAA hydrogels and Poly(EGDMA–VIM) hydrogel showed very poor adsorptive capacity (Table 2). The mobility of H^+ ions present favored the preferential adsorption of hydrogen ions compared with metal ions, and the surface of the adsorbent is surrounded by hydronium ions (H^+), thereby preventing the metal ions from approaching the binding sites of the sorbent and resulting in poor adsorption (Figure 3). Alginate beads showed the highest sorption capacity for cadmium and lead (182 and 165 mg/g, respectively). Chitosan indicated the second highest sorption for cadmium (140 mg/g), lowest for lead (61 mg/g) and highest for copper (169 mg/g), whereas PAA hydrogel adsorbed only lead with a maximum sorption of 113 mg/g, and Poly(EGDMA–VIM) hydrogel displayed significant adsorption of cadmium (71 mg/g) and lead (118 mg/g). Based on the information provided (Figure 3), chitosan performed as the best adsorbent based on its sensitivity and selectivity toward a wide range of metal ions (Cd, Pd and Cu) compared with other adsorbents, in particular PAA hydrogel, which was only capable of detecting lead.

The adsorption capacity of hydrogels is based on isotherms and the kinetics of adsorption, which predict the rate at which adsorption takes place for a given system. The data derived from comparing the different hydrogels showed that their reactions were mostly pseudo-first order kinetics. Chitosan nanofibril, Poly(EGDMA–VIM) hydrogel and alginate beads exhibited high pseudo-first order rate constant for cadmium and lead, respectively, whereas PAA

Table 1 │ Coefficient of pseudo-first and second order kinetics models

Adsorbent	Metal ions	Adsorption capacity (mg/g)	$K_f(l/g)$	q_e	R^2	Ks	K_F	R^2	References
			Pseudo-first order kinetics			**Pseudo- second order kinetics**			
Alginate beads	Cd^{2+}	182	0.063	–	0.898	8.07	2.97	0.992	Mandal & Ray (2013)
	Pb^{2+}	165	0.069	–	0.910	6.55	3.65	0.994	
AMPS/PVAc Copolymer hydrogel	Ni^{2+}	230	1.064	–	0.995	0.013	4.94	0.986	Al-qudah *et al.* (2014)
	Mn^{2+}	160	0.719	–	0.996	0.011	4.99	0.989	
Chitosan nanofibril	Cd^{2+}	140	0.400	–	0.990	0.008	6.14	0.994	Liu *et al.* (2014a)
	Cu^{3+}	169	0.021	86	0.970	0.0008	0.41	0.999	
	Pb^{2+}	61	0.017	114	0.986	0.0001	0.44	0.995	
PVA/AAc hydrogel	Zn^{2+}	388	0.017	415	0.942	1.76	2.40	0.991	Al-qudah *et al.* (2014)
	Co^{2+}	245	0.015	278	0.960	5.17	2.03	0.998	
	Mn^{2+}	152	0.03	145	0.948	8.11	1.42	0.997	
PAA hydrogel	Pb^{2+}	113	0.23	119	1.000	51.85	6.32	0.857	Akkaya & Ulusoy (2008)
PVA	Cu^{2+}	14	0.049	–	0.99	4.298	0.43	0.95	Jamnongkan *et al.* (2014)
Poly(EGDMA–VIM) hydrogel	Cd^{2+}	71	0.106		0.99	24	5.25	0.93	Vogel *et al.* (2014)
	Pb^{2+}	118	0.098		0.99	38	5.19	0.96	
	Hg^{2+}	172	0.070		0.99	43	4.17	0.90	
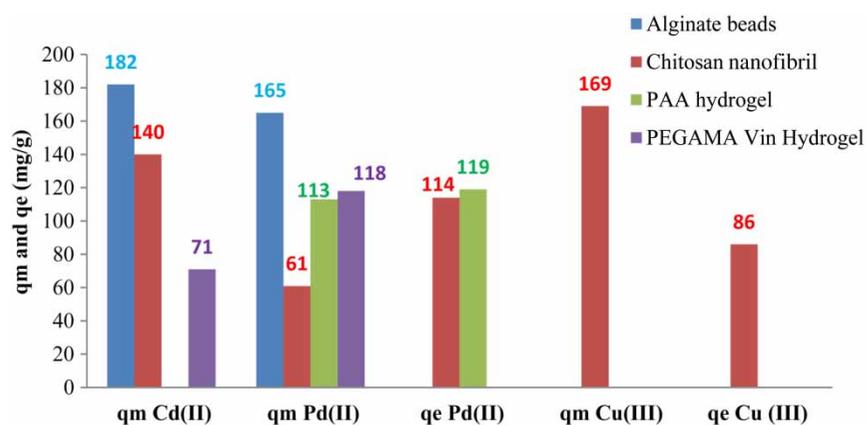
Figure 3 │ Comparison of kinetics parameters (q_m and q_e) of different metal ions and adsorbents.

hydrogel only showed a high value for lead (Figure 4). In contrast, chitosan and alginate beads showed the highest rate of adsorption for all four metals evaluated.

ELECTROCHEMICAL DETECTION OF METALS

Today, electrochemical sensors are tightly integrated and hyphenated with sampling, fluidic handling, separation and other detection principles. Unfortunately, this review does not have sufficient room to cover these topics, and the reader should keep in mind that the topic of electrochemical sensors

is relatively mature and has found its way into commercial products and advanced integrated sensing systems. A steady effort has been made on the development of efficient and easy-use electrochemical sensors. Hydrogel sensors for heavy metals, with rapid and highly sensitive detection capabilities, are in great demand in many areas of science. Developing hydrogel sensors for detecting lower concentrations of heavy metal ions becomes very significant due to the fact that they hold special advantages in drug delivery based on their loading capacity and controlled drug release. Electrochemical devices with accuracy and sensitivity have already been developed for certain applications. Although still at the basic research stage,

Table 2 │ Summary table of metals ions concentrations dependence based on pH, adsorbent time and concentration

| Adsorbent | Pseudo-first and second order kinetics | | | | | |
	Metal ions	Metal concentration	pH	Kinetic model	Adsorption capacity (mg/g)	References
PVA/AAc	Cu^{2+}	300 mg/L	4.5	K_S	13	Jamnongkan *et al.* (2014)
Poly(EGDMA–VIM) hydrogel	Cd^{2+}	300 mg/L	3–5	K_S	69	Panic *et al.* (2013)
	Pb^{2+}	300 mg/L	3–5	K_S	112	Panic *et al.* (2013)
	Hg^{2+}	300 mg/L	3–5	K_S	162	Panic *et al.* (2013)
Alginate beads	Cd^{2+}	200–300 mg/L	6.5	K_S	182	Mandal & Ray (2013)
	Pd^{2+}	100 mg/L	6.0	K_S	165	
AMPS/PVAc Copolymer hydrogel	Ni^{2+}	200 mg/L	6.5	K_S	230	Al-qudah *et al.* (2014)
	Mn^{2+}	350 mg/L	5.5	K_S	160	
PAA hydrogel	Pb^{2+}	150 mg/L	6.5	K_S	113	Akkaya & Ulusoy (2008)
Chitosan nanofibril	Cd^{2+}	300 mg/L	6.0	K_S	140	Liu *et al.* (2014a)
	Cu^{3+}	250 mg/L	5.5	K_S	169	
	Pb^{2+}	200 mg/L	6.7	K_S	61	
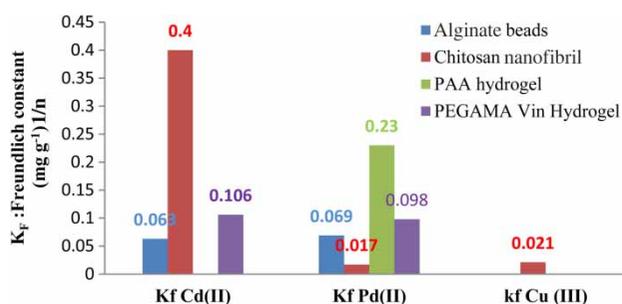
Figure 4 │ Comparison of kinetics parameters (K_f) of different metal ions and adsorbents.

many new applications are yet to be discovered. The detection of low concentration of toxic heavy metal ions in environment water is essential because of its lethal effects on the environment and living organisms. To date, only a few researchers have reported on hydrogel sensors for detection of heavy metals, including: hydrogel sensor for metal oxide (Chen *et al.* 2009), PVA hydrogel sensor for heavy metal cations, P(MBTVBC-co-VIM)-coated QCM (Cao *et al.* 2011), and P(NIPAM-co-BCAm) hydrogels (Chen *et al.* 2013). However most of them could not detect heavy metals at lower levels (micrograms and nanograms) except PVA hydrogel, which detected nickel at a range of 0.1–0.214 μM.

DISCUSSION AND RECOMMENDATION

The World Health Organization and Environmental Protection Agency (EPA) have established a maximum concentration for toxic heavy metals and precious metals in drinking water. A maximum of 5–20 μg/L is permissible for toxic heavy metals (Ar, Cr, Cu and Pb) as well as 0.1 μg/L for Hg and 500 μg/L for precious metals (Zn, Mn) in their secondary oxidation states (Mohod & Dhote 2013). The use of hydrogels in heavy metal remediation showed better performance than precipitation methods, activated carbon, and agricultural waste, and offers promising application prospects. To date, research has focused mainly on specific metals, including copper, lead, silver, cadmium, nickel, chromium, gold and mercury. Other transition metals with high toxicity or transition metals which are known disease markers have not been as widely addressed. Vanadium and selenium have been identified as carcinogenic agents that disrupt cellular metabolic processes at high dosage (200 μg/L) in drinking water. Evidence from literature indicates that exposure to selenium could induce neuro-mental effects on the development of fetuses, infants and children as well as development of diabetes type II (Crans *et al.* 2011; Gad & Pham 2014). These metals block the reactivity of essential functional groups of biomolecules and disrupt the integrity of bio-membranes. There is also a need to investigate the simultaneous removal of many co-existing pollutants in waste water. It is preferable to develop a multipurpose adsorbent which can remove different kinds of pollutants at micro and nano scale. To achieve these aims, new materials and methods are required that utilize our understanding of parameters which affect adsorption of heavy metal ions, including pH, analyte concentration, contact time and adsorbent functional group. Hydrogels are a promising group of materials due to their compatibility with the aqueous phase, and future work should involve functionalization of hydrogel materials for

selective and sensitive metal remediation as well as sensitive analytical methods for ultra-low concentration evaluation. Electrochemical methods for metal quantification and speciation have emerged as a promising tool for evaluation of a wide range of metal ion species. The success of electrochemical detection of nickel, lead, copper, mercury and cadmium has been established using chemical sensors (hydrogel sensors) with results possible in the micrograms per milliliter range. Hence, the combination of electrochemical methods with the removal efficiency of stimuli-responsive hydrogel materials could produce highly efficient water treatment solutions, in particular for metal remediation.

CONCLUSION

A wide range of treatment technologies have been developed for heavy metal removal from wastewater. Agricultural waste and hydrogels are relatively new processes that have shown a significant contribution to the removal of these contaminants from aqueous effluents. However, it is evident from the literature that agricultural waste, activated carbon and hydrogel adsorbents do not adequately remove heavy metals at micro and nano scale. Even though hydrogels have shown improved adsorption efficiency, they still suffer from a number of limitations, such as low tensile strength, which limit their use in load-bearing applications and result in the premature dissolution or flow away from the hydrogel for a targeted purpose, and hence low sorption capacity. Therefore, it is essential to identify new hydrogel composites with the appropriate physical and chemical properties capable of comprehensive metal species adsorption from aqueous media. The advantage offered by electrochemical control of hydrogel sorption shows great promise with respect to adsorption of a wide range of transition metal species at very low concentration.

ACKNOWLEDGEMENTS

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