Adsorptive Removal of Manganese from Industrial and Mining Wastewater

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Abstract—Improperdisposal of toxic wastes from mining and chemical process industries can yield higher manganese concentrations well above those normally found in environmental water. Consequently, this paper starts with a review of technologies for manganese removal from contaminated wastewater. Various wastewater treatment processes are discussed and compared. Special attention is given to adsorption technology wherein performance of a variety of adsorbents are analysed. Batch adsorption capacity at equilibrium is used as performance indicator. It is revealed that modified or surface re-engineered adsorbents and nanostructured materials offer the best option for manganese removal from environmental water.

Keywords—adsorption; manganese; treatment; wastewater

I. INTRODUCTION

MANGANESE is a brittle, gray-pink metal with an atomic weight of 54.938. It is too brittle to be used unless alloyed. Manganese has only one stable natural isotope, 55Mn. Manganese occurs naturally and is the third most abundant transition metal on the earth crust (9.5×10^2 ppm)[1,2]. It can exist in 11 oxidation states withmanganese compounds Mn(II), Mn(IV) and Mn(VII) being the most environmentally and biologically important [3, 4].Manganese most common minerals are oxides [pyrolusite(MnO_2)] and hydro-oxides [psilomelaneBa$Mn^{2+}Mn^{4+}_8O_{16}(OH)_4$] and braunite $(Mn^{2+}Mn^{3+}_6)(SiO_{12})$, and to a lesser extent as rhodochrosite ($MnCO_3$). Mn(II) compounds are stable in acid solution but are readily oxidized in alkaline medium. South Africa has the world's largest resources of manganese which is estimated to be around 80%. Manganese is used in the manufacture of iron and steel alloys, batteries, glass and fireworks, a significant fertilizer for plants, food additive for stocks and catalyst for organic synthesis [5]. Manganese is also found in the effluents of mine waters, either neutral or acid (AMD) [6]. Mn is one of the most widely used metals in the world and one of the important indexes of water pollutants [7]. Exposure to excess manganese may lead to Mn intoxication that may result in the onset of a neurological phenotype known as manganism which present with motor symptoms resembling Parkinson's disease [8-10].

Several treatment methods to remove Mn from mining and industrial wastewaters have been reported. Mn in wastewater is commonly removed by precipitation [6, 11-14], ion-exchange [15], oxidation and filtration [16, 17], coagulation and flocculation [18], biosorption[19]and adsorption [20]. A lot of efforts have been made on the development of new technologies in which technological, environmental and economic constraints are taken into consideration. The technologies have to avoid generation of secondary waste and involve materials that can be recycled and reused on an industrial scale [21]. Adsorption compared with other methods appears to be an attractive process in view of its efficiency and capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possibly by other methods. It is also environmentally friendly, cost effective and its ease of operation compared to other processes with which it can be applied in the treatment of acid mine and heavy metal containing wastewater [22].

This paper therefore focuses on adsorption technology to ameliorate the quality of environmental water contaminated with manganese. Equilibrium capacity of adsorbents is used as performance indicator. It is shown that re-engineered adsorbents and nanostructured materials provided unprecedented performance.

II. MANGANESE IN WATER AND HEALTH IMPACTS

Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode manganese into waters. Improper disposal of dry-cell batteries or other toxic wastes from industries can yield higher manganese concentrations well above those normally found in environmental water [23] and cause significant harm to public health [24]. Manganese at lower doses is an essential nutrient for humans and animals. Mn at elevated concentrations is a powerful neurotoxin which affects the nervous system and causes learning disabilities and intellectual impairment in children [25, 26]. Studies have shown that children exposed to 240–350 µg manganese/L in water had elevated manganese concentration in their hair and exhibited impaired manual dexterity and speed, short-term memory, and visual

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Proceedings of the
2016 Annual Conference on Sustainable Research and Innovation,
4 – 6 May 2016

identification when compared with children from areas which manganese was controlled [27]. Children exposed to manganese intoxication from water containing above 1,0 µg manganese/L, had attention and memory impairments conditions [28] and others presented neurologic symptoms including a repetitive stuttered speech, poor balance, coordination, and fine motor skills [29]. Manganese intoxication is also linked to Mn induced Parkinsonism [30, 31], low fetal weight [32, 33], infant mortality [34, 35] and increased cancer rates [36].

III. MANGANESE IN ACID MINE DRAINAGE

Mn and other metals such as Fe, Al, Zn and Cu are often present in high concentrations in mine drainage waters than in unpolluted streams and groundwater [37-39]. Concentrations of manganese and other solutes in acid mine drainage are commonly elevated due to aggressive dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water along paths downflow from oxidizing pyrite [40, 41]. The study conducted by Hansen [42] indicated that seepage from the tailings impoundments in the Witwatersrand basin in South Africa are acidic and contain elevated concentrations of trace metal concentrations, specifically Mn, Al, Cr, Co, Cu, Ni, Zn and U, as well as SO_4. The AMD from the gold mines in Gauteng and West Rand have been also found to contain high concentrations of these metals [43]. Manganese generally presents its reduced Mn^{2+} ionic state in anoxic acid mine drainage, and is much more stable at higher pH than the fully oxidized Mn^{4+} ions [44]. Manganese hydrolysis contributes to the total mineral acidity of mine waters as indicated in Eq (1)[38].

$$Mn^{2+} + 0.5O_2 + H_2O \rightarrow MnO_2 + 2H^+ (1)$$
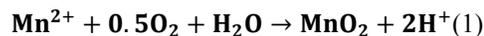
Manganese oxides and oxyhydroxides are the most important scavengers of trace metals in aquatic and soils, sediments and rocks, and have been observed in acid drainage [45, 46]. This is due to their sorption properties which can be explained by the oxidizing capacity of MnO_2 as well as the negative charge of surface [47].

IV. CONVENTIONAL METHODS OF MANGANESE REMOVAL FROM WATER

To remove manganese and other heavy metals several treatment technologies such as chemical precipitation, ultra filtration, adsorption and ion-exchange, reverse osmosis, electrodialysis have been developed [48]. Precipitation is widely used in process industries because it is cheap and relatively easy to operate [49]. Hydroxide precipitation technique is the most widely used chemical precipitation technique due to its relative simplicity, low cost and ease of pH control. Although most metals are precipitated as hydroxides other methods such as sulfide and carbonate precipitation are also used [50]. Lime and limestone are the most commonly employed precipitant agents due to their availability and are inexpensive in most countries and have

been employed to remove manganese [51-53] and other heavy metals in water. The major expense associated with precipitation is the cost of the chemicals and the cost of the precipitated sludge that is produced [50]. Excessive sludge production requires further treatment, and the problems associated with precipitation are slow metal precipitation, poor settling, and the aggregation of metal precipitates have long term environmental effects for sludge disposal [54].

Ion exchange in wastewater treatment is used for demineralization. Ion-exchange processes have been widely used to remove manganese and other heavy metals from wastewater because it is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation [55]. Ion exchange is the exchange of ions between the substrate and surrounding medium. Ion exchange resins are suitable to use at wide range of different pH values and at high temperatures and are insoluble in most organic and aqueous solutions [56]. They contain a covalent bonding between the charged functional groups and the cross linked polymer matrix [57]. The disadvantage of using this technology is that ion exchange media is easily fouled by organics and other solids in the wastewater.

The electrochemical method is one of the technologies that are used as alternative option for the remediation of water and wastewaters mainly due to its advantages such as environmental compatibility, versatility, high energy efficiency, amenability of automation and safety. Electrochemical methods include electrocoagulation, electro-oxidation and electro-reduction [58]. This process uses an electric field as the driving force for the separation of ions using ion exchange membranes or plates to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Metallic ions that are positively charged cling to cathodes that is negatively charged and the metal deposit can be stripped and recovered. Corrosion of the electrodes is the maindisadvantage of using this method because electrodes would frequently have to be replaced [53]. Electrochemical water or wastewater technologies have not been widely used because they involve relatively large capital investment and expensive electricity supply [59].

Coagulation and flocculation are important pretreatment processes. The coagulants that are used often in water treatment are aluminum and ferric salts. The purposes of coagulation are to destabilize particles present in the raw water and to convert dissolved natural organic matter into particles [60]. The main objects of coagulation are the hydrophobic colloid and suspended particle which consist of insoluble particles [61]. Flocculation utilizes polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps that can be removed by filtration, straining or floatation [50]. Heavy metals that are soluble in water after coagulation cannot be effectively removed and coagulation units must be followed by other treatment techniques [61].

Membrane filtration technologies that are used for removal of heavy metals include microfiltration, ultrafiltration

Proceedings of the
2016 Annual Conference on Sustainable Research and Innovation,
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nanofiltration and reverse osmosis depending on the size of the particle that can be retained. Ultrafiltration membrane is used to remove heavy metals, organic and inorganic contaminants in aqueous solution.   Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. Then micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) techniques are normally proposed to effectively remove heavy metals [62]. Nanofiltration is the intermediate process between ultrafiltration and reverse osmosis and the advantages of this process include ease of operation, reliability and comparatively low energy consumption [63].   It also helps to minimize scale formation on the equipment involved in both reverse osmosis and thermal desalination processes [64]. Membrane filtration technology can remove heavy metal ions with high efficiency but high costs, process complexities, membrane fouling, and low permeate flux have limited its use for heavy metal removal [49].

V. ADSORPTION

Adsorption is a common method of heavy metal removal from water. Several physicochemical properties such as specific surface area, pore structure, and surface chemistry of adsorbents regulate the adsorption efficiency, selectivity, equilibrium time of adsorption, regeneration capacity, and their stability in aqueous solutions [65-68]. The adsorptive capacity of the adsorbent is also influenced by the adsorbate properties of group functionality, branching or geometry, polarity, hydrophobicity, dipole moment, molecular weight and size, and aqueous solubility. The solution conditions such as pH, temperature, adsorbate concentration, ionic strength, and competitive solutes also have an effect on the adsorption capacity [68].

Physico-chemical treatment methods have important role to play in today's wastewater treatment contaminated with Mn and other heavy metal ions   and will continue to have increased use because of established practice and continued improvisation. Adsorption, ion exchange, and coagulation, continue to dominate the wastewater treatment mainly through improved materials, devices, and practices [69]. They offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike in biological system, physico-chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Chemical plants can be modified if required and the treatment system generally requires a lower space and installation cost. [70;53].

Adsorption technique is one of the wastewater treatment technology that is recognized as an effective, economically favorable, and easy to operate method for heavy metal wastewater treatment and has a wide range of applications [71, 72]. It offers flexibility in design and operation and mostly it will produce treated effluent that is odorless, free of colour and is suitable for reuse. Adsorption process is usually

reversible and the regeneration of the adsorbent will result in economical desorption processes [73, 74]

A. Activated carbon as an adsorbent for manganese

Activated carbon has been found to be a good adsorbent due to its high capacity of adsorption because of small particle sizes and active free valences. Goher *et al.* [56]investigated the removal manganese and other metal ions from industrial wastes using granular activated carbon which recorded an adsorption capacity of 2 mg/g for manganese ion removal. Modification and impregnation of the activated carbon has also been used to increase the surface adsorption and removal capacity and to add selectivity to activated carbon. Granulated activated carbon modified with tannic acid [75], Fe^{3+} impregnated activated carbon [76] were used for the removal of manganese and other heavy metals ions.

However activated carbon as an adsorbent for water treatment is restricted due to its high production cost and the regeneration process that involves costly chemicals [71].   To decrease the high cost of activated carbon several studies on using waste materials have been conducted to find a low-cost adsorbent [77]. Budinova *et al*[78] explored the use of biomass waste-derived activated carbon to remove arsenic and manganese. The maximum sorption capacity for Mn (II) ions was 23.4 mg/g. The removal of manganese ionic species was observed to increase sharply between pH 2 and 4, and the maximum uptake was attained and remained constant at pH values above 4. This was attributed to partial hydrolysis of Mn (II) ions with increasing pH, resulting in the formation of complexes with OH^- such as $Mn(OH)^+$, $Mn(OH)_2$, $Mn_2(OH)_3^+$, Mn_2OH^{3+}, $Mn(OH)_4^{2-}$ species in solution.

Adsorption of manganese (II) ions from aqueous solution using activated carbon derived *Ziziphusa spina-christi seed was* investigated byOmri & Benzina [79]. It was suggested that the adsorption mechanism involved chemical bonding and cation exchange on the surface of the prepared activated carbon which contains functional groups of oxygen and aromatic compounds. The possible mechanisms of ion exchange considered   was that a manganese ion (Mn^{2+}) attaches itself to two adjacent hydroxyl groups and two-oxyl groups which donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. The Langmuir adsorption capacity was found to be 172.41 mg/g.

Akl *et al.*[80]demonstrated the potential use of activated carbons derived from olive stones for the removal of Fe (ΙΙΙ) and Mn (ΙΙ) from aqueous solutions. Some of studies done and the results obtained on activated carbon are summarized in TABLE I.

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TABLE I
MN ADSORPTION STUDIES USING ACTIVATED CARBON

Sorbent	Experimental conditions	Initial concentration (mg/L)	Adsorbent dosage (g/L)	pH	Removal efficiency (%)	Adsorption capacity (mg/g)	Reference
Surfactant modified carbon	Batch experiments Temp: 70±℃ Time : 420 min						[81]
unmodified mesoporous carbon		50	1	7	56.8	40	
*cetyltrimethyl ammonium bromide		50	1	7	82.2	43	
*sodium dodecyl sulfate		50	1	7	70.5	47	
Activated carbon-granular	Batch experiments Temp: Room Temp Time: 6hrs	n/a	0.1-.6 0.2-0.9	n/a	n/a	2.5	[82]

n/a : not available

B. Low cost adsorbents

Industrial byproducts, agricultural wastes and natural materials locally available in certain regions have been utilized as low-cost adsorbents. Adsorption of Mn(II) from water was investigated using a thermally decomposed leaf [5]. The adsorbent dosage used was 10 g/L for a concentration of 100 mg/L. According to their results the removal percentage of manganese increased from 0-99% for pH values between 1.8 - 3.84, with the adsorption capacity determined at 61–66mg/g. The adsorption on the thermally decomposed leaf involved the chemisorption relevant to phosphate, ferrous oxide and carbonate while physisorption was attributed to carbon black containing abundant microspheres. Maize husk, which is an abundant agricultural waste was used to prepare a biosorbent for Mn(II) and Pb(II) ions [83]. In another study green tomato husk modified and unmodified with formaldehyde was evaluated for simultaneous removal of iron and manganese [84].

Rice husk is the by-product of the rice milling industry produced in large quantities as a waste. It consists of crude protein, ash (including silica), lignin, hemicellulose, and cellulose. It is insoluble in water, has good chemical stability, high mechanical strength and possesses a granular structure, making it a good adsorbent material suitable for treating heavy metals from wastewater [85]. It has been suggested that the removal of Mn(II) ions by rice husk from aqueous solutions is a chemisorption process, where there is a chemical reaction between surface OH-groups of SiO_2 and Mn (II), releasing H^+ ions in the solution [1]. The removal of heavy metals including Mn (Langmuir maximum adsorption capacity 8.3 mg/g) by rice husk has been extensively studied [86]. The results of rice husks and other agricultural by-products are shown in TABLE II.

C. Biosorbents

Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to be an alternative replacement of conventional physicochemical treatment methods for the removal of metals [88, 89]. Biosorption is the binding of metals to organic matter; it is a passive metabolic independent process [90]. Biomaterials of microbial and plant origin interact effectively with heavy metals [89] and the sorption on these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions [91].Biosorbent materials that are easily available include three groups: algae, fungi, and bacteria [92, 93]. *Saccharomyces cerevisiae*has received increasing attention due to its unique nature and its metal sorption capacity [94-97]. Eleven *S. cerevisiae* yeast strains in live and dead forms were screened and studied [97] for biosorption and bioaccumulation of manganese from synthetic aqueous solution. It was found that *S. cerevisiae*F-25 in live form was the most effective biosorbent for Mn(II) and biosorbed 22.5 mg Mn^{2+}/gm yeast biomass. The results revealed that environmental conditions that favored maximum Mn(II) concentrations biosorption by *S. cerevisiae* F-25 in live form were 4.8 mg $Mn2^+$/l after 30 min at pH 7, agitation at 150 rpm and yeast biomass concentration of 0.1 gm/l at 30 ℃. Hasan *et al*. [98] studied the biosorption isotherms of *Bacillus sp*. and sewage activated sludge in laboratory-scale experiments using the isotherm models developed by Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, and Redlich-Peterson (R-P). It was revealed that *Bacillus sp*. is a more effective biosorbent than sewerage activated sludge. Biosorption of manganese by *Bacillus sp*. was found to be significantly better fitted to the Langmuir-1 isotherm than the

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other isotherms, while the Dubinin-Radushkevich isotherm was the best fit for sewage activated sludge. The Langmuir maximum biosorption capacities of manganese onto *Bacillus sp.* and sewage activated sludge were 43.5 mg Mn^{2+}/g biomass and 12.7 mg Mn^{2+}/g biomass, respectively. The D-R isotherm showed that the biosorption processes by both *Bacillus sp.* and sewage activated sludge occurred via the chemical ion-exchange mechanism between the functional groups and Mn^{2+} ion.

Mn(II) ions biosorption was studied [99] using *Pleurotus*spent mushroom compost performed in a fixed-bed column. Mn(II) ions biosorption in fixed-bed column achieved better performance at a flow rate of 1 mL/min, bed height of 30 cm and initial Mn(II) concentration of 10 mg/L. The breakthrough time and exhaustion time were obtained at 16.5 hours and 26.7 hours, respectively.

The ability of *in vitro* roots cultures of *Typhalatifolia* and *Scirpusamericanus* to remove Mn and other metal ions was studied by Santos-Díaz & Barrón-Cruz[100]. *T. latifolia* roots were able to uptake 1680 µgMn/g, while the *S. americanus*roots removed 4037 µgMn/g. The potential of macrophyte*Spirodelapolyrhiza* (L.)Schleiden from the phoomdibiomass of*Loktak* lake, India as an adsorbent to remove Mn (II) and other metal ions from metal solution system was investigated by Meitei & Prasad [101]. Metal adsorption was fast and equilibrium was attained within 120 min. Langmuir isotherm best described the equilibrium with maximum adsorption capacities of 35.7 mg/g for Mn (II) ions. Adsorption of the specific metal ions from binary and ternary metal solution system showed antagonistic nature due to screening effect and competition between the metal ions for active sites on the biomass.

TABLE II
MN UPTAKE USING LOW COST AGRICULTURAL WASTE THROUGH SORPTION

Sorbent	Mode of operation	Initial concentration (mg/L)	Adsorbent dosage (g/L)	pH	Removal efficiency (%)	Adsorption capacity (mg/g)	Reference
Thermally decomposed leaf	Batch experiments	100	10	3.84	99	61-66	[5]
Maize husk	Batch experiments	100	0.8	2	93.4	9	[83]
Rice husk	Batch experiments	100	2.5	7	26.62	12-18	[1]
Rice husk	Batch and column experiments	200	3	6	n/a	7.7	[86]
Banana peel	Batch experiments	10	4	4	90	3.6	[87]
Green tomato husk	Batch experiments	10	0.1	6	84.8	15.2	[84]

n/a : not available

D.Chitosan

Chitosan occurs naturally and as a polysaccharide which is found in insects, arthropods and crustaceans, fungal biomass and algae by deacetylation of chitin, and has an ability to effectively remove heavy metal due to its amino groups and hydroxyl groups [102,103]. It is inexpensive, abundant, biodegradable, and widely available from sea food-processing wastes [104-107].

Abdeen *et al.* [108] in their study explored the ability of polyvinyl alcohol/chitosan binary dry blend as an adsorbent for removal of Mn(II) ion from aqueous solution. The chitosan material was made from shell from shrimps collected from sea food shops. It was found that the biosorption capacity of the polyvinyl alcohol/chitosan adsorbent increased from 0.6 to 9.2 mg/g with an increase of metal ion concentrations from 5 to 100 mg/L. They also concluded from their study that the optimum pH for biosorption of Mn (II) ion on polyvinyl alcohol/chitosan was 5.0. In a study done byAl-Wakeel *et al.*[109] the adsorption capacity of glycine onto modified chitosan resin was found to be 71.4mg/g at pH 6. Reiad *at el.*[110] investigated the adsorption of manganese using microporous chitosan/polyethylene glycol blend membrane

which showed adsorption capacity of up to 18 mg/g for manganese ions at pH 5.9.

Robinson-Lora & Brennan [111] evaluated the role of chitin derived from processed crab shells and its associated proteins in the removal of manganese from mine impacted waters under abiotic and anoxic conditions using sorption processes. According to them the maximum sorption capacity was found to depend greatly on the pH of the solution, with very minimal or no adsorption observed at pH less than 5. At pH 5.4 values the adsorption capacity was 0.165 mg/g and 0.981 mg/g at pH 8.7.

Crab shells were found to possess better uptake capacities of 69.9 mg/g for Mn(II). The removal of Mn(II) by crab shell was found to be pH dependent, with optimum sorption occurring at pH 6. The mechanism of metal removal by crab shell was identified as micro-precipitation of metal carbonates followed by adsorption onto chitin at the surface of crab shell [19].

Masukume *at el.*[112] found that the adsorption of Mnonsea shells as adsorbents from acid mine water is very low compared to Fe adsorption. The removal efficiencies of

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manganese ranged from 12.1% (sorbent mass, 0.1 g/50mL) to 54.4% (sorbent mass, 1 g/50 mL).

E. Natural minerals

Natural materials clays and zeolites have been explored for treating wastewater contaminated with metals due to their metal-binding capacity [90], low cost and abundance. Dimirkou & Doula [113] studied the removal of Zn^{2+} and Mn^{2+} in drinking water using clinoptilolite (natural zeolite). According to them clinoptilolite modified Fe adsorbs significantly higher manganese amounts (27.1 mg/g) than unmodified clinoptilolite (7.69 mg/g,). Doula [114] noted that

high manganese adsorption capacity of clinoptilolite modified with Fe was due to Fe-clusters located on the surface and to high surface negative charge. The removal of metals by zeolite is known to be a complex process which involves ion exchange and adsorption [115]. Yavuz *et al.*[116], explored the removal of manganese and some heavy metals from aqueous solution by adsorption on natural kaolinite. The Langmuir adsorption capacity for Mn was found to be 0.446 mg/g. Several studies have been conducted on metal uptake including manganese using clays and minerals and the results are shown in TABLE III.

TABLE III
MAXIMUM SORPTION CAPACITIES OF Mn IONS ON CLAY MINERALS

Clay Sorbent	Initial concentration (mg/L)	Adsorbent dosage (g/L)	pH	Adsorption capacity	Reference
Clinoptilolite	0.2 -1000	1	7.53	7.69	[113, 114]
Fe- Clinoptilolite		1	8.14	27.1 mg/g	
Clinoptilolite	0.5	40	7.1± 0.2	N/a (70 % Mn removal)	[117]
Vermiculite				N/a (80 % Mn removal)	
Serbian natural zeolite	400	10	5.5	10 mg/g	[118]
Brazilian vermiculite	550	2.5	6.4	31.53 mg/g	[119]
Kaolite	N/a	10	N/a	0.446 mg/g	[116]
Synthetic zeolite made from fly ash	10	100	2-12	N/a	[120]
Natural zeolite	25-250	N/a	6	7.69 mg/g	[121]
Al-Natural zeolite			6	25.12 mg/g	
NH4-Natural zeolite			6	24.33 mg/g	
Turkey natural zeolite	20	37	2.5	0.37 mg/g	[122]
			3.5 4.5	0.52 mg/g	
				0.52 mg/g	
Natural zeolite – Slovakia	14.4	40	7	0.076 mg/g	[123]
Brazilian natural scolecite	50	16.7	6	2.1 mg/g	[124]
Chilean zeolites	100	2.5	6-6.8		[125]
*natural zeolite				0.256 meq/g	
*activated zeolite- NaOH					
Na2CO3				0.761 meq/g	
NH4Cl				0.718 meq/g	
NaCl				0.675 meq/g	
				0.774 meq/g	
Mexican natural zeolite	10	10	6	138.8 meq/kg	[126]
Na modified natural zeolite				232.55 meq/kg	
Nigerian kaolin clay	100-500	1	6	111.11 mg/g	[127]
Magnesium enriched kaolinite-bentonite ceramics	0.53-530	108	3	n/a (80% Mn removal)	[128]
Fly ash	1.5	20	3-8.5	n/a (74.2 % Mn removal)	[129]
Coal	0.05-100	4	6.85-7.35	n/a (63 % Mn removal	[130]
Lignite	100	6	6	3.4 & 18.7 mg/g	[131]
Surfactant modified alumina	10-70	20	6	1.31 mg/g	[132]

n/a : not available

F. Other adsorbents

Other adsorbents such as poly(sodium acrylate)–graphene oxide double network hydrogel adsorbent have been prepared and studied for the removal of Cd^{2+} and Mn^{2+} . The maximum Langmuir adsorption capacity for Mn^{2+} was found to be 165.5 mg/g at pH 6 and a temperature of 303 K. The adsorbent indicated good reusability performance [133].

Idris [134] studied functionalized mesoporous silica employed as adsorbent for Mn(II) from aqueous solutions. The surface area of functionalized mesoporoussilica anddiethylenetriamine functionalized-mesoporous silicawas found to be 760 and 318 m^2 /g (N_2 adsorption). Mn(II) adsorption was found to be pH dependent and best results were obtained at pH 6.5–7.0. The adsorption onto the diethylenetriamine functionalized-mesoporous silica followed the pseudo-second-order kinetic model. The equilibrium data fitted well to the Langmuir isotherm model and the maximum adsorption capacity of

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Mn(II) was found to be 88.9 mg/g. The authors suggested that the results indicated that the adsorption occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed ions.

The adsorption of manganese ions from aqueous solution by polyaniline/sawdust nanocomposite was experimentally investigated [135]. The experiments evaluated the effect of various experimental parameters i.e., pH, adsorbent dosage and contact time on the removal efficiency. The results showed that optimum conditions for manganese removal were found to be at pH10, adsorbent dosage of 10 g/L and equilibrium contact time of 30 min.

Moawed *et al.* [136] modified polyurethane foam with polyhydroxyl and used it as a new sorbent for separation of manganese and iron ions in natural samples. The maximum sorption of Mn(II) was found in the pH range of 6–8. The kinetics of sorption of the Mn(II) was found to be fast with an average value of half-life of sorption of 11.7 min. The sorption capacity of polyhydroxyl polyurethane foam was 8.7 µmol/g and the recovery of tested ions achieved was 99–100%.

Khan *et al.*[137] performed comparative sorption study of dissolved manganese and cobalt ions onto alginate beads and thermally activated nano-carbon beads. Optimum metal uptake was observed at pH 8 with about 80–92% metal ions adsorbed within 4 h, followed by a slower adsorption stage. It was revealed that increases in initial Mn(II) concentration from 52.28 to 891.5 mg/L increased sorption on alginate beads and activated nano-carbon beads from 18.07 to 63.7 mg/g and 23 to 78 mg/g, respectively.

Islam *et al.*[65]prepared phosphine-functionalized electrospunpoly(vinyl alcohol)/silica composite nanofiber porous adsorbent using a facile electrospinning technique. The composite nanofibers with 0.5 g/L fiber loading was found to be able to remove almost completely 96–98% the Mn^{2+} and Ni^{2+} ions from aqueous solutions with an initial concentration of 120 mg/L, at pH 6 within 15 min of contact time. A reasonably simple acid treatment with a 1 M HCl solution was found to be extremely effective in regenerating the nanofiber adsorbent, and 92.5% of the metal ions were removed from the adsorbent even in the fifth regeneration/reuse cycle. The adsorption equilibrium studies revealed the excellent adsorption capacities of the nanofiber for both Mn^{2+} and Ni^{2+} ions to be 234.7 and 229.9 mg/g, respectively.

VI. CONCLUSION

All heavy metals treatment methods have their advantages and limitations. Adsorption can be considered as the most effective and economic method for the treatment of wastewaters containing heavy metals because it is low cost, and locally and naturally available material can be utilized efficiently for the removal of Mn and other heavy metals ions from environmental water.Whereas commercial activatedcarbon is as an effective adsorbent for the removal of Mn, its high cost restricts its use.The review showed that agricultural waste, waste based chitosan and clay minerals are low-cost alternative adsorbents in which surface modification of these material surfaces provides increased capacity for adsorption and selectivity of Mn ions. Furthermore the review showed that the use of nanomaterialscould offer alternative solution to manganese problem in environmental water.

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