Original Research Paper

Chemistry

SYNTHESIS AND REMOVAL OF HEAVY METAL FROM WATER BODIES USING BIOSORBENT (HYDROGEL AGAR-AGAR) ADSORBENTS.

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ABSTRACT Heavy metals (Cadmium, Nickel, Lead and chromium) which are natural components of the Earth's crust are usually associated with toxicity. Exposure to heavy metal , even at trace level, is known to be a risk for human being . The presence of zinc, heavy metals, nickel and others metal in the aqueous environment has potentially damaging effect on human physiology and other biological system when the acceptable levels are exceeded. Heavy metals (Heavy metals),Nickel(NI) ,Lead(Pb), Chromium are the common heavy metal and is often released into aquatic environment during mining activities and metallurgical processes. At high concentrations, heavy metal are highly toxic to most organisms and can be accumulated in organisms before entering human body through food chains.   Many technologies have been developed to remediate heavy metals contamination, among which Biosorbents hydrogel Agar-agar is one of the most sustainable and promising. However, high pricing of Biosorbents today   is plaguing its large –scale applications. The increased use of heavy metal in industry has resulted in increased availability of metallic substances in natural water sources. Many technologies like adsorption, precipitation , membrane filtration, and ion –exchange have been used to remove metal pollutants from water. However , adsorption has proven to be economical and efficient for removing heavy metal, organic pollutants and dyes form polluted waters. Several adsorbents such as Biosorbents and Silica can be used in the purification of water. Biosorbents has shown to be an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. Because of its high surface areas is widely used in the treatment of wastewaters. The effectiveness of Hydrogel Agar-agar in cleaning up polluted water is due to its well developed porosity structure as well as the presence of a wide spectrum of surface functional groups. This makes it capable of distributing pollutants on its large internal surface , making them accessible to reactants.

KEYWORDS : Heavy metal, Biosorbents (Hydrogel Agar-agar),Water bodies ,

INTRODUCTION

Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Heavy metals, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries[6,7]. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [18,19]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment[. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge[26,27,28]. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified[37,38]. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials[31,32,33]. Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), Nano filtration (NF) and reverse osmosis (RO)[8,9,10]. Electro treatments such as electro dialysis [22,23,24] has also contributed to environmental protection. Photo catalytic process is an innovative and promising technique for efficient destruction of pollutants in water [3,4,5]. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL) standards established. This article presents an overview of various innovative physico-chemical treatments for removal of heavy metals from industrial wastewater. Their advantages and limitations in application are evaluated. To highlight their removal performance, the main operating conditions such as pH and treatment efficiency are presented as well[20,21].

Heavy metals in industrial waste water

Definition and toxicity Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. A large number of elements fall into this category, but the ones listed in Table 1 are those of relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells[25,29,30]. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA [1,2,6,7]are summarized in Table 1.

Industrial wastewater sources

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as heavy metals, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electro less depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another

significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing[34,35,36]. Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and heavy metals sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and Ferro cyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment[11,12,13].

MATETIALS AND METHODS
The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 1.25g (obtained by the study effect of adsorbent dose) of sorbent with 100 mL of sodium fluoride containing 3 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 250 rpm at room temperature. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose, particle size and influence of coions with fixed dosage[39,40]. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer ll (TISAB ll) solution to maintain pH 5-5.5 and to eliminate the interference effect of complexing ions[14,15,16]. The pH of the samples was also measured by Orion ion selective equipment. All other water quality parameters were analyzed by using standard methods. Kinetic studies of sorbent were carried out in a temperature controlled mechanical shaker. The effect of different initial fluoride concentration viz., 2,4,6,8 and 10 mg/L at four different temperatures viz., 303,313,323and 33k on sorption rate were studied by keeping the mass of sorbent as 1.25 g and volume of solution as 100ml in neutral pH [17,41,42].

Characterization of sorbents:
The X-ray diffraction (XRD) pattern of adsorbent was obtained using a Bruker AXS D8 Advance , Inst ID: OCPL/ARD/26-002 X-ray diffractometer. Fourier transform infrared spectra were recorded using Nicolet 6700 , Thermo Electronic corporation USA made spectrophotometer. The scanning electron microscopy (SEM0) analysis performed using a Philips XL-20 electron microscope. Computations were made using Microcal Origin (Version 6.0) software[43,44]. The accuracy of fit are discussed using regression correlation coefficient (r) and chi-square analysis (SSE). The chi-square statistic test is basically the sum of the square of the difference between the experimental data and data obtained by calculating from the model , with each squared difference divided by the corresponding data obtained by calculating from the models .

Swelling ratio
The swelling ratio was used to characterize the hydrogels and hydrogel Agar-agar composites. Approximately 0.05 g of hydrogel or hydrogel Agar-agar composite was placed in DI water. The weight increase was monitored at room temperature by weighing the material tat was periodically removed from the DI water. Each measurement was repeated for at least three times. The swelling ratio was calculated using the following equation (Eq.(1)).

Swelling ratio(%)=(Wswollen-Wdry)/Wdry x 100 (1)

Where, Wswollen is the measured weight of material after contact with DI water, and Wdry is the measured weight of dry material.

Measurement of Heavy metals in aqueous media
Stock Heavy metals solution of 1000 mg/L were prepared by dissolving the exact quantity of Heavy metals (N03)2.4 H20 in DI water. The concentrations of Heavy metals in this study were determined using a microwave Plasma-Atomic Emission Spectrometer (4200 MP-AES, Agilent, Santa Clara, CA).

Sorption experiments
Following the procedure described in a previous study 16, batch sorption experiments were conducted at room temperature to investigate the sorption of heavy metals by the hydrogel Agar-agar, and hydrogel Agar-agar composite. A series of solutions (20mL) with heavy metals concentrations of 50,100, 200, 400, and 800mg/L were added into 25-mL polyethylene centrifuge tube , together with 0.05 g of the sorbent. The mixture was agitated on a wrist-action shaker (Model 75 , Burrel Scientific, Pittsburg, PA) for 72 h to reach equilibrium. The amount of heavy metals adsorbed by the sorbent was calculated as below (Eq.(2)).

Where, q (mg/g) is the amount of adsorbed heavy metals per unit mass of sorbent, C0 (mg/L) and Ce (mg/L) are respectively the initial and equilibrium concentration of heavy metals , V (L) id the volume of Heavy metals solution added for the sorption, and M (g) is the mass of sorbent added for the sorption . To estimate the maximum adsorption capacity of the sorbent , the data obtained from sorption experiments were best – fitted and simulated using the Langmuir sorption isotherm model 17.

STATISTICAL ANALYSIS
The means and errors of the experimental data were statistically analyzed with the use of SPSS for Windows 14.0 (IBM, Armonk, NY). Based on the analysis of variance (ANOVA) performed with Graphpad® Prism, a Significance level of 5% ($p<0.05$) was used to evaluate the differences between different tested values 18.

RESULTS AND DISCUSSION
Swelling capacity of hydrogels and composites
The swelling ratio is one of the most important parameters for evaluating the effectiveness of hydrogel materials After 48 h of swelling in DI water, both the polyacrylamide hydrogel and hydrogel Agar-agar composites reached their macimum swelling capacities (Figure1). It was observed that the hydrogel-Agar-agar composites were able to swell to much larger amounts of water comparing to the untreated polyacrylamide hydrogel. The swelling capacity was found to increase more with a higher weight ratio of Agar-agar in the composites, which was probably due to the presence of hydrophilic functional groups introduced by Agar-agar 9. The swelling ratios of the tested hydrogel materials were in the order (from large to small): hydrogel composite with 5% bichar > hydrogel composite with 3% Agar-agar> hydrogel composite with 1% Agar-agar > untreated hydrogel. The result showed consistency with the level of hydrophilicity of the hydrogel materials. The experimental results were also best – fitted with hyperbolic nonlinear regressions ($p< 0.001$) to estimate the macimum swelling capacities. The fitting results indicated that the maximum swelling ratios were 818% for untreated hydrogel, 1220% for hydrogel composite with 1% Agar-agar, 1349% for hydrogel composite with 3% Agar-agar, and 1506% for hydrogel composite with 5% Agar-agar. The above results showed that the water swelling capacities of the hydrogel Agar-agar composites was significantly better than that of the untreated polyacrylamide hydrogel , implying that the composites might be more appropriate for environmental applications in aqueous media.

Sorption of Heavy metals by Agar-agar

Agar-agar demonstrated effective removal of Heavy metals from the aqueous media (Figure 2). The equilibrium adsorption capacity (qe), I.e., the adsorbed mass of Heavy metals per unit weight of Agar-agar at equilibrium, consistently increased with the increasing initial Heavy metals concentration (Figure 2 (a)). The increasing trend became less pronounced at higher concentrations because the sorbent (i.e., Agar-agar) was approaching its maximum adsorption capacity (qmac). In Figure2 (b), qe was plotted against the concentrations of Heavy metals at equilibrium (Ce). By simulating the experimental data using Langmuir isotherm model, the isotherm curve (dash line) of Heavy metals sorption by Agar-agar was generated (R2= 0.954). The maximum adsorption capacity (qmax) of the tested Agar-agar for Heavy metals2+ was estimated to be 88.3 mg/g (p-value=0.004), Which was similar to the results reported in previous studies 8, 11, 15. The result above showed that the Agar-agar used for producing the hydrogel –Agar-agar composites in this study had a good ability for attracting and retaining Heavy metals2+ ion. The maximum adsorption capacity of Agar-agar (88.03 mg /g) was also used as a reference for that of the Hydrogel and its composites.

Sorption of Heavy metals by Hydrogel materials

Similar to the increasing trend of Agar-agar, the sorption of Heavy metals by polyacrylamide hydrogel and its composites also increased as the initial concentration of Heavy metals increased (Figure 3(a)). It was obvious that the removal of Heavy metals was significantly enhanced with the small amount of incorporated Agar-agar in the hydrogel –Agar-agar composites. The degree of improvement was greater when a higher weight ratio of Agar-agar was incorporated. According to the sorption isotherms of Heavy metals and simulations of the experimental results using Langmuir isotherm model 9Figure 39b), R2 = 0.996), the maximum adsorption capacity of the untreated polyacrylamide hydrogel was 24.73 mg/g (p-value = 0.027), of the composite with 1% Agar-agar was 30.63 mg/g 9p-value=0.001), of the composites with 3% Agar-agar was 59.21 mg/g 9p-value=0.001), and of the composites with 5% Agar-agar was 63.58 mg/g (p-value=0.001), as shown in Table 1. These results showed that the sorption of Heavy metals by the hydrogel composites were greatly improved due to the presence of Agar-agar within the crosslinked structures. Besides the increased swelling capacities of these composites, the improvement can also be attributed to the ionic and magnetic attraction introduced by the diverse functional groups on the surface of Agar-agar. These surface functional group, which have been identified in our previous studies include carboxylic acid, amine, hydroxyl and sulfonic acid group , etc.

Interestingly, the increased maximum adsorption capacities (qmax) of the hydrogel composites were significantly larger than solely the sums of the qmax of the untreated polyacrylamide hydrogel and the qmax of the incorporated Agar-agar for the synthesis . The results demonstrated that the combination of polyacrylamide hydrogel and Agar-agar was synergistic in terms of the composites' capacities of removing Heavy metals from aqueous media. The reason for this synergistic effect was probably that each single Agar-agar particle scattered in the composite created an ionic attraction field for attracting and retaining metallic ions such as Heavy metal ions . This ionic attraction field significantly extended the potential of each Agar-agar particle to capture ions . Within the cross linked structures of the Hydrogel Agar-agar composites, high concentrations of metallic ions could be entrapped against a larger scattered Agar-agar particle made it possible to overcome the ionic osmotic stress, the main factor regulation the sorption and release of ions in Hydrogel materials.

Table1: Summary of sorption kinetics of Heavy metals adsorption by Agar-agar and Hydrogel materials

Absorbent	Qmax(mg/g)	R2	p- value
Agar-agar	88.03	0.954	0.004
Hydrogel	24.72	0.973	0.027
Composite with 1%Agar-agar	30.63	0.994	0.001
Composite with 3% Agar-agar	59.21	0.996	0.001
Composites with 5% Agar-agar	63.58	0.995	0.001

Influence of Agar-agar dosage for Hydrogel-Agar-agar composite

The usage of synthesized Hydrogel-Agar-agar composite with Agar-agar weight ratios of 1, 3 and 5% increased the Heavy metals sorption by 23.9%, 139.5% and 157.2%, respectively. Notably, the fitting curve generated from linear regression derived an unsatisfactory correlation (R2 = 0.848), suggesting that the synergistic effect of Hydrogel-Agar-agar composite does not linearly increase with the dosage of Hydrogel Agar-agar used for the syntheses . Instead, the experimental data fitted well with sigmoidal nonlinear regression (dotted line). When a small dosage of Agar-agar (e.g., , 1%) was used for the composite synthesis, the increase of Heavy metals sorption (,20%) was obvious although less sound comparing to the increase (30- 150%) when a relatively higher dosage of Agar-agar (e.g., 1- 3 %) was used. However, when more Agar-agar (.3%) was used for the synthesis of hydrogel Agar-agar composite, the improvement of Heavy metals sorption became much less significant. These results complied with the hypothesis that and ionic attraction field was formed around each Agar-agar particle. With the increasing number of scattered Agar-agar particle, the average distance between each particle became smaller, thus creating more mutual coverages of different ionic attraction fields by different Agar-agar particles. When the crosslinked space of the composite became more crowded and saturated, the overall effectiveness of the ionic attraction fields diminished as a result. These results also indicated that there would be no need to level up the dosage of Agar-agar to more than 3% when synthesizing polyacrylamide Hydrogel Agar-agar composites for Heavy metals removal. A higher dosage of bochar(>3%) is not only economically inefficient , it also does not bring significant further improvement.

CONCLUSIONS

Analytical application of various modified Hydrogel Agar-agar surface , in particular , Adsorption of trace elements taking separation and pre concentration into account from complex synthetic mixture as well as natural water is presented.In order to improve the effectiveness of polyacrylamide Hydrogel in removing Heavy metals form aqueous media, small amount of Agar-agar at three different weight ratios (i.e., 1, 3 and 5%), together with acrylamide as monomer, were used for synthesizing hydrogel Agar-agar composites. The resulting composite had significantly improved ability to entrap water and Heavy metals 2+ ions, and therefore was more capable of removing these ions from aqueous media. The swelling ratio of the hydrogel Agar-agar composite with 5% Agar-agar was almost doubled comparing to the untreated hydrogel . With significant increases as high as 157.2%, the composites also demonstrated a great potential for Heavy metals removal from aqueous media. However, a dosage higher than 3% did not result in significant further improvement for Heavy metals removal. Therefore, the weight ratio of 3% can be considered optimal for the composite synthesis. Considering the high costs of large-scale Agar-agar application, using hydrogel-Agar-agar composites is a more cost-effective approach for Heavy metals removal from the contaminated environment.

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