

Egyptian Journal of Chemistry

<http://ejchem.journals.ekb.eg/>

Polyaniline-intercalated manganese dioxide Nanomaterial Composites for the Removal of Fe, Al and Sr

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Abstract

Heavy metals (HMs) pollution is one of the most hazardous toxins that can harm people's health; heavy metals (HMs) are naturally occurring components of the environment. Because of their toxicity, enduring nature, and capacity for bioaccumulation, heavy metals (HMs) are well-known environmental pollutants. As a result, excessive amounts of heavy metals like iron, aluminum, strontium, etc. are released into natural resources including soil and marine environments. Volcanic eruptions and the weathering of rocks that contain metals are examples of their natural origins; human sources include mining and other industrial and agricultural activities.

In this study we made Nanomaterial Composites from aniline in organic solvent and potassium permanganate in water and made Polyaniline-intercalated manganese dioxide Nanomaterial Composites and took some quantities from this composite nanomaterial on solutions contains different concentration of individual element such as iron, strontium and aluminium and study the effects of contact time, ionic strength, dose of nanomaterial and concentration of iron, strontium and aluminium elements, then calculated the percentage removal which is raised by increasing these effects.

The kinetic is the second-order kinetic model in terms of higher correlation coefficients (0.98 and 0.95) for Fe and Sr respectively, while in case of Al the data has showed good compliance with pseudo first order with higher correlation coefficients (0.95).

Keywords: heavy metals (HMs), bioaccumulation, human sources, Nanomaterial Composites, kinetic model.

1. Introduction

The removal of iron from water is a major problem. When the concentration of iron in water exceeds a certain threshold, it becomes more hazardous and poses various risks to the environment and public health. The next method for treating iron in wastewater is called biosorption. Microorganisms have a significant role in wastewater bioremediation. The purpose of this study was to examine how *Aspergillus niger* (A. niger) dried biomass removes iron. Iron removal from wastewater using dried A. niger was studied as a sorbent. For ideal circumstances, a number of factors including the starting pH solution, biomass quantity, contact time, and iron content must be considered. The A. Niger may be renewed and utilized again in the removal process, and it has the potential to remove iron effectively. (ZAREH et al., 2022)

Samples of groundwater were tested for the presence of iron pollution. X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier transformed-infrared spectroscopy, and thermogravimetric-differential thermal analysis were used to analyse the samples after they were subjected to zeolite Y. Zeolite Y could remove 98% of iron. (KWAKYE-AWUAH, Bright, et al., 2019).

Iron oxide-coated functional hollow poly (methyl methacrylate) microspheres (FHPMM) were created as a highly effective material for removing iron from water.

Comparing the improved surface area to the traditional iron oxide coated sand used for iron extraction from water, the adsorption isotherm investigation demonstrated an extremely high adsorption capacity. Due to the increasing amount of emerging contaminants, surface and groundwater contamination worldwide poses a severe threat to aquatic life in addition to human health. Iron is thought to be the most prevalent harmful contaminant in water bodies, among other things. One important development in the period of entrapping pollutants in drinking water is the creation of metal organic frameworks (MOFs) with high porosity and surface area. (HALDAR et al., 2020).

The waterworks used a two-stage filtering process, with the first stage being iron removal and the second stage being manganese and ammonium removal. It was recommended that the waterworks be upgraded from operating in series to operating in parallel by simultaneously removing iron, manganese, and ammonium in a single biofilter in order to double it to satisfy the growing demand for water supplies. (ZENG, Huiping, et al., 2020).

Using activated carbons enriched in iron, the simultaneous removal of aluminium from water was investigated. Seven distinct modified carbons were produced by modifying a commercial coconut activated carbon using techniques such as co-precipitation of iron, oxidation with HNO₃, and

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Receive Date: 10 October 2023, Revise Date: 12 November 2023, Accept Date: 03 December 2023

DOI: 10.21608/EJCHEM.2023.239899.8696

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impregnation. (DELGADILLO-VELASCO, Lorena, et al., 2021)

In compounds derived from rare-earth separation, aluminium is frequently present as an impurity due to its association with rare-earth deposits. The removal of trivalent aluminium from aqueous solutions using commercially available BDH activated carbon and locally generated date-pit activated carbon was tested under different circumstances. (LI, Fujian, et al., 2021).

It was discovered that, in contrast to the La/Mg/Si-AC point of zero charge and high temperature, the removal of aluminium by La/Mg/Si-AC was preferred at lower pH values. Due to the strong binding affinity of $\text{Al}(\text{OH})_4^-$ on the protonated surface and the rivalry between F^- and OH^- for the charged adsorption site, the adsorption capacity of $\text{Al}(\text{OH})_4^-$ was about ten times greater than that of F^- . (KIM, Minhee, et al., 2020).

Aluminium ions [Al^{3+}] may be extracted from aqueous solutions selectively using ion-imprinted polymers. As the complexing monomer, N-Methacryloyl-L-glutamic acid (MAGA) was selected. (ANDAÇ, Müge, et al., 2006).

In different experimental settings, trivalent aluminium (Al^{3+}) was removed from wastewater using natural adsorbents derived from wood charcoal, starch, activated charcoal, and clay (type-bleaching earth). This research report examines how biomass content and pH affect adsorption kinetics. (CHOKSI, Pratik M. and JOSHI, Vishal, 2007).

Strontium has been classified as a pollutant for possible regulatory consideration in drinking water on the US EPA pollutant Candidate List 3. There is an urgent need for treatment information because there is very little data on strontium removal from drinking water. This investigation aims to assess the efficacy of lime-soda ash softening treatment and coagulation/filtration techniques in eliminating strontium from surface and ground waters. Results from coagulation/filtration jar tests on natural fluids shown that whereas lime softening removed as much as 78% from naturally occurring ground water containing strontium, conventional treatment with aluminium and iron coagulants was only able to achieve 12% and 5.9% strontium removal. The removal of strontium during the softening of lime-soda ash was shown to be influenced by pH, calcium concentration, and dissolved inorganic carbon concentration, as demonstrated by controlled batch studies conducted on synthetic water. The ultimate concentration of strontium in all softening jar experiments was directly correlated with the beginning concentration, and the removal of strontium was directly linked to the removal of calcium. Depending on the initial circumstances of the water quality, two polymorphs of calcium carbonate (calcite and vaterite), and well-formed crystals or agglomerates of mixed solids. According to X-ray diffraction studies, strontium was most likely removed during the softening of lime and integrated into the calcium carbonate crystal structure. (O'DONNELL, Alissa J., et al., 2016).

Seawater is high in the precious metal strontium (Sr). Despite its wide industrial applications, however, little effort has been dedicated to its recovery from saltwater. With coexisting cations, Sr was adsorbed preferentially on resorcinol formaldehyde (RF) resin. (NUR, T., et al., 2017). In the initial stages, three different solid wastes—almond green hull, eggplant hull, and moss—were processed and employed as adsorbents to remove strontium ions from

aqueous solutions. It has been demonstrated that different adsorbent kinds and chemical treatments have an impact on the Sr(II) ion's ability to bind. (AHMADPOUR, Ali, et al., 2010).

Many variables, including pH, the starting concentration of strontium, particle size, and temperature, were taken into consideration when studying the adsorption of strontium from aqueous solutions onto activated carbon. (CHEGRÓUCHE et al., 2009).

polyaniline has been chosen as a platform to build innovative nanocomposite adsorbents by mixing it with other nanomaterials that exhibit better adsorption capacities, chemical and thermal stability, good regeneration ability, and selectivity toward heavy metals using simple synthesis methods. (HAJJAOU, Hind, et al., 2021)

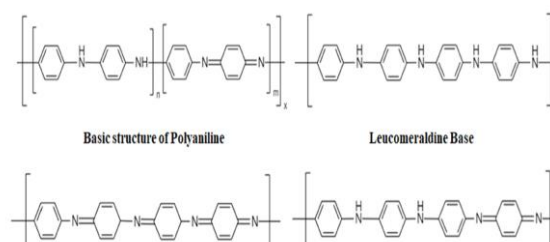


Figure 1 Polyaniline structure

2. Material and Method:

2.1 preparation of Polyaniline-intercalated manganese dioxide Nanomaterial Composites:

Material gets prepared. In a standard synthesis, 450 mL of CCl_4 organic phase was used to dissolve aniline monomer (9 mL) and 450 mL of distilled water (pH 7) to dissolve potassium permanganate (0.45 g). To create an aqueous/organic stratification system with a distinct interface, the solution was combined. For a whole day, the reaction system was maintained at 5 °C. Similar to our earlier findings, the chemical oxidative polymerization of aniline and reduction of potassium permanganate transpired concurrently at the aqueous/organic interface. Layer-by-layer self-assembly of layered manganese dioxide and polymer was created by continuous diffusion of aniline from the organic phase to the aqueous phase. The final products were obtained following centrifugation and freeze drying. (Huang et al., 2018).

2.2 Experiment:

2.2.1 Effect of adsorbent dose:

individual concentrations were been prepared from Fe, Al and Sr (3 ppm), added for 100 ml from each individual element different doses from composite nanomaterial (0.1g, 0.2g, 0.3g, 0.4g and 0.5g) shook for one hour at temperature 25°C, measured the remaining concentration of Fe, Al and Sr in water and calculated percentage of removal for each element, show the results in (Figure 3.1).

2.2.2 Effect of Metal concentration & Effect of adsorption capacity:

individual concentrations were been prepared from Fe, Al and Sr (1, 2, 3, 4 and 5) ppm, added for 100 ml from each different individual concentration element different constant dose from composite nanomaterial (0.2g) shook for one hour at temperature 25°C, measured the remaining for each concentration from Fe, Al and Sr in water and

calculated percentage of removal for each individual concentration element and adsorption capacity for nanomaterial, show the results in (Figure 3.2 a and b).

2.2.3 Effect of agitation time:

individual concentrations were been prepared from Fe, Al and Sr (2 ppm) , added for 100 ml from each individual element constant dose from composite nanomaterial (0.2g) shook at different times (15,30,60,90 and 120) minutes at temperature 25°C, measured the remaining concentration of Fe, Al and Sr in water and calculated percentage of removal for each element at each time, show the results in(Figure 3.3).

2.2.4 Adsorption kinetic:

In first order reaction We plot relation between reaction we take Ln of equilibrium concentration and time while in second order reaction We plot relation between equilibrium concentration and time and make compare between them in R2 the largest is better, show in Fig 3.4 a and b).

2.2.5 Effect of ionic strength:

individual concentration were been prepared from Fe, Al and Sr (2 ppm) , added different concentration from material has strong ionic strength such as CaCl₂ (2,5,10,20and 50ppm) for 100 ml from each individual element with constant dose from composite nanomaterial (0.2g) shook for one hour at temperature 25°C, measured the remaining concentration of Fe, Al and Sr in water and calculated percentage of removal for each element at each concentration of ionic strength, show the results in(Figure 3.5).

2.2.6 Effect of temperature:

individual concentrations were been prepared from Fe, Al and Sr (2 ppm), added for 100 ml from each individual element constant dose from composite nanomaterial (0.2g) shook for one hour at different temperatures (25°,30°,40°and45°C), measured the remaining concentration of Fe, Al and Sr in water and calculated percentage of removal for each element at each temperature, show the results in(Figure 3.6 a and b).

3. Results & discussions:

3.1 Effect of adsorbent dose

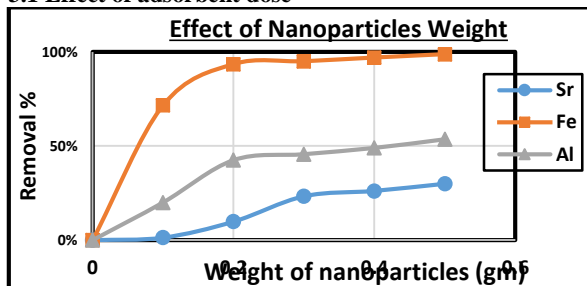


Figure 3.1: Effect of (MnO₂/PAN) weight on the removal % of Sr, Fe and Al

Fig.3.1 shows the adsorption profile of Sr, Fe and Al versus different adsorbent amount in the range of 0.1–0.5 g/100 ml with initial concentration 3.0 mg/L and contact time 1.0h. It is observed that the percentage of Sr, Fe and Al removal has been increased with increasing the adsorbent dose from 0.1g/100ml to 0.2g/100ml, and then slightly increased with increasing the adsorbent dose from 0.2g/100ml to 0.5g/100ml. Such a trend is mostly attributed to an increase in the adsorbent surface area and the availability of more active adsorption sites, the result also shows that, the

maximum removal for Fe, Al and Sr is (94%, 43% and 10%) respectively was recorded at 0.2g/100ml of adsorbent dose and any further increase in adsorbent dose will not significantly change the adsorption yield, This might be related to the decrease in the total adsorption surface area available to Fe, Al and Sr molecules resulting from overlapping or aggregation of adsorption sites.

3.2 Effect of Metal concentration:

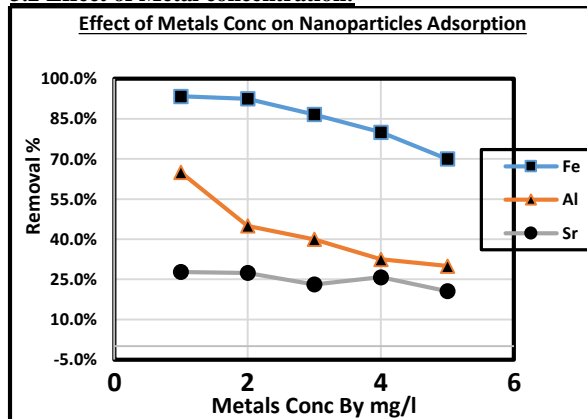


Figure 3.2: (a) Effect of initial concentration against the removal%.

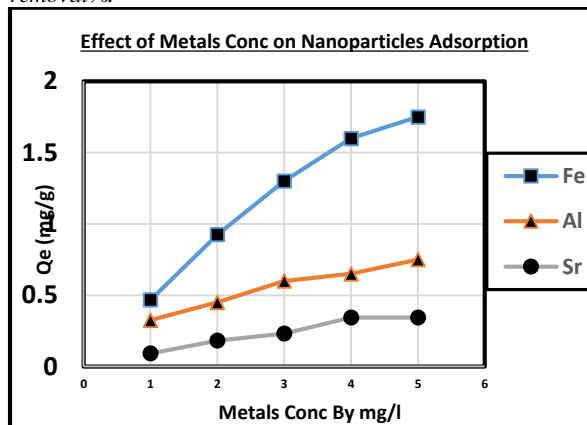


Figure 3.2: (b) Effect of adsorption capacity against initial concentration at adsorbent dose 0.2g/100ml for Fe & Al and Sr (Q_e: concentration which adsorbed by composite nanomaterial)

Effect of different Metals concentrations adsorption onto nanoparticle adsorbent (MnO₂/PAN) is presented in Fig. 3.2(a and b). It could be noticed that the removal percentage of Sr, Fe and Al were (27.8%, 93.4% and 65% respectively) at initial concentration 2 mg/l, and has been decreased by increasing the initial concentration of Sr, Fe and Al. This can clarify that the Polyaniline-intercalated manganese dioxide Nanomaterial Composites (MnO₂/PAN) has a limited number of active sites, which become saturated at a certain concentration. However, the adsorption capacity at equilibrium could increase by increasing initial Sr, Fe and Al concentrations. This is due to the increase in the concentration gradient which acts as an increasing in the driving force to overcome all mass transfer resistances of the metals concentration between aqueous and solid phase.

3.3 Effect of agitation time

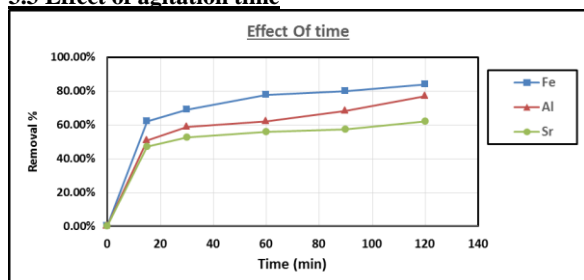


Figure 3.3: Effect of agitation time on removal % of Sr, Fe and Al.

The effect of contact time in figure 3.3 is essential in the sorption experiment as the data will allow confirmation on the length of agitation time. This will achieve equilibrium of the adsorption processes between the solid phase (adsorbent) and the aqueous phase (adsorbates). The adsorption of metals has increased with the rise up of the agitation time. The adsorption process has attained the equilibrium after 60 min. for Sr, Fe and Al. The fast adsorption rate at the initial stage (after 15 min.), could be explained by increased percentage removal of each element.

3.4 Adsorption kinetic:

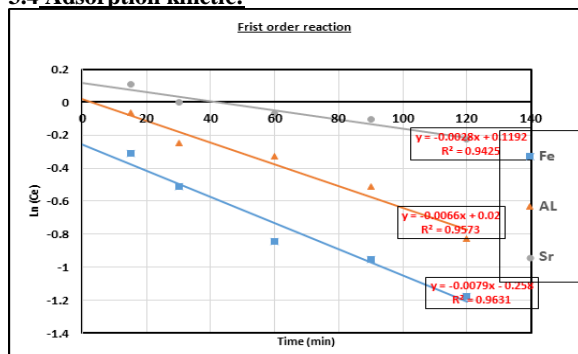


Figure 3.4 a: Kinetic plots of pseudo first of Sr, Fe and Al over (MnO₂/PAN).

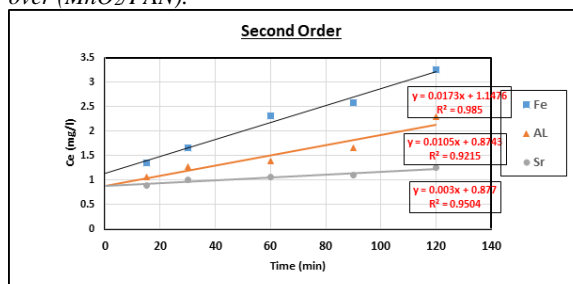


Figure 3.4 b: Kinetic plots of second order for the adsorption of Sr, Fe and Al over (MnO₂/PAN).

(C_e: equilibrium concentration)

Adsorption kinetics of Sr, Fe and AL describes the solute uptake rate and evidently this rate controls the residence time of the adsorb at uptake at the solid–solution interface. Adsorption rate constants for the Sr, Fe and Al were calculated by using pseudo-first-order (Fig 3.4a) and pseudo-second-order (Fig 3.4 b) kinetic models which were used to describe the mechanism of the adsorption. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R²). A relatively high R² values indicate that the model has successfully described the kinetics of Sr, Fe

and Al adsorption. (Fig 3.4a and b) present the pseudo first-order and second order graphics for the adsorption kinetics of studied metal. The data has showed good compliance with the second-order kinetic model in terms of higher correlation coefficients (0.98 and 0.95) for Fe and Sr respectively, while in case of Al the data has showed good compliance with pseudo first order with higher correlation coefficients (0.95).

3.5 Effect of ionic strength

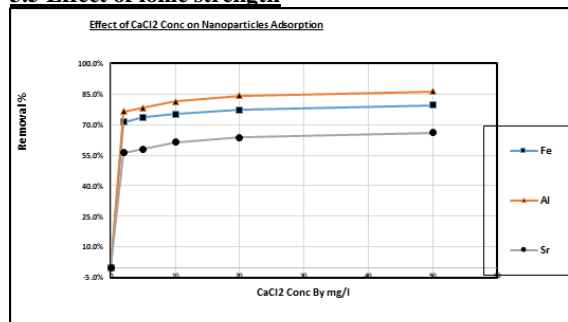


Figure 3.5: Effect of ions strength on removal% of Sr, Fe and Al over (MnO₂/PAN).

In Fig 3.5, the effect of calcium chloride on the adsorption of Sr, Fe and Al over (MnO₂/PAN) has been shown. By increasing the calcium chloride concentration from 2.00 to 50.0 mg/L, the adsorption percentage of Sr, Fe and Al has increased from 56.1 to 66.0%, from 76.3 to 86.4% and from 71.2 to 79.5% respectively. This is due to the partial neutralization of the positive charge on the (MnO₂/PAN) surface and the consequent compression of the electrical double layer of the Cl⁻ anion. The chloride ion can also enhance the adsorption of Sr, Fe and Al over (MnO₂/PAN) surface by pairing their charges and hence reducing the repulsion between the MG molecules adsorbed on the surface.

3.6 Effect of temperature

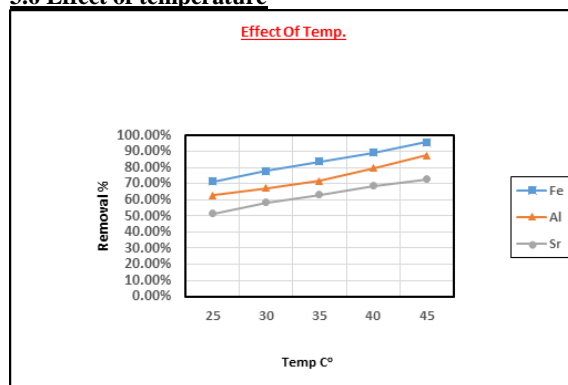


Figure 3.6 a: Effect of temperature on removal% of Sr, Fe and Al over (MnO₂/PAN).

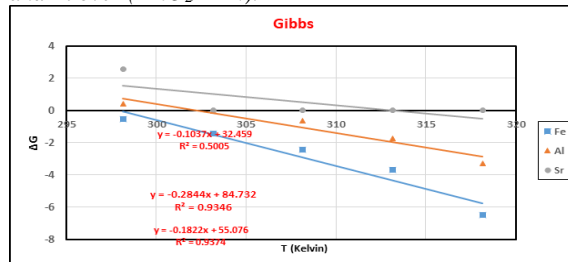


Figure 3.6 b: Plots ΔG° versus T for adsorption of Sr, Fe and Al over (MnO₂/PAN).

($T(\text{kelvin})$: temperature with Celsius plus 273.15)
(ΔG° : the change in Gibbs free energy of a chemical reaction)

In Fig 3.6 a, the effect of temperature on the adsorption of Sr, Fe and Al over (MnO₂/PANI) has been shown. By increasing the temperature from 25°C to 45°C, the adsorption percentage of Sr, Fe and Al has increased, this is because increase in the kinetic movement of metals in the solution, also high temperature could destroy the boundary layer between adsorbent material and solution in order to increase the adsorption capacity of metal over (MnO₂/PAN), Fig 3.6 b has showed that the negative values of ΔG° so give positive value of ΔH° (Enthalpy change) indicate that the Sr, Fe and Al adsorption process is a spontaneous and endothermic process.

4. Conclusion:

This method is considered one of the appropriate methods for removing drinking water contaminants such as aluminium, iron and strontium, which are dangerous to public health. This method is characterized by its simplicity and effectiveness.

This method can remove high concentrations of iron, aluminium and strontium and can be applied to treated drinking water as well as raw water and ground water.

In this process the removal of elements is increasing with increasing nanoparticles amount, reaction temperature, reaction contact time and ionic strength.

The kinetic is the second-order kinetic model in terms of higher correlation coefficients (0.98 and 0.95) for Fe and Sr respectively, while in case of Al the data has showed good compliance with pseudo first order with higher correlation coefficients (0.95).

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