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# $MnO_2$ NPs-AgX zeolite composite as adsorbent for removal of strontium-90 ($^{90}Sr$) from water samples: Kinetics and thermodynamic reactions study

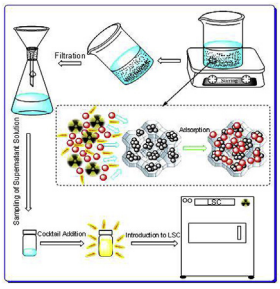
Meysam Sadeghi [a], Sina Yekta [b], Hamed Ghaedi [c, *], Esmaeil Babanezhad [b]

[a] Department of Chemistry, Lorestan University, Khorramabad, Iran
[b] Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran
[c] Faculty of Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran

## HIGHLIGHTS

- The effective removal of radioactive Strontium-90 ($^{90}Sr$) from water samples has been investigated.
- A novel adsorbent $MnO_2$ NPs-AgX Zeolite Composite was synthesized via impregnation method.
- The perfect removal gained in 8 h with the yield of 100% for $^{90}Sr$.
- The reaction kinetic was more consistent to the pseudo second order model.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this research, the $MnO_2$NPs-AgX zeolite as a novel composite adsorbent was synthesized and identified via Scanning electron microscopy (SEM), Atomic adsorption spectrometry (AAS), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) techniques. Furthermore, the removal of radioactive strontium-90 ($^{90}Sr$) from drinking tap water of Ramsar city was investigated via the synthesized $MnO_2$NPs-AgX zeolite composite. A single radiometric technique, Ultra Low-Level Liquid Scintillation Counting (LSC), was also exerted to monitor the reaction progress. The obtained results revealed that the $^{90}Sr$ was perfectly removed after 8 h by the $MnO_2$NPs-AgX zeolite composite. Also, the reaction kinetic information was studied applying pseudo first and second order kinetic Elovich and Intra particle diffusion kinetic models. The adsorption kinetics of $^{90}Sr$ was matched appropriately to the pseudo second order kinetic model. Further, the evaluation of the thermodynamic parameters such as $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$, specified that the adsorption procedure of $^{90}Sr$ was spontaneous and illustrates physical adsorption properties and exothermic nature of the adsorption. It is emphasized that the $MnO_2$NPs-AgX zeolite as a novel composite represents a high capacity and potential for the removal of radioactive $^{90}Sr$ from drinking water samples.



## 1. Introduction

For decades, it had been a great challenge to protect the environment against hazardous radioactive materials likely to get

* Corresponding author.
*E-mail address:* hamedghaedi@gmail.com (H. Ghaedi).

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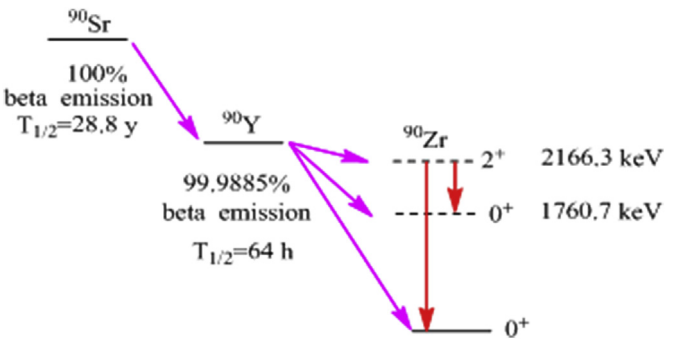
released from nuclear activities or incidents. After the explosion took place in Chernobyl in Russia and Fukushima in Japan power plants accident, the enormous amounts of radioactive hazardous elements found their way to the natural environment [1]. One of the most anthropogenic radionuclides is strontium-90 ($^{90}$Sr) due to its existence in worldwide fall out. Strontium isotopes can be classified into two various and separated groups containing stable isotopes ($^{84}$Sr, $^{86}$Sr, $^{87}$Sr, and $^{88}$Sr) and radioactive isotopes including (e.g., $^{82}$Sr, $^{83}$Sr, $^{85}$Sr, $^{89}$Sr, $^{90}$Sr). Radioactive strontium can replace calcium in biosphere and it can also get transferred to human body through food chain in which it has long retention time. $^{90}$Sr is taken up via gastrointestinal system and aggregate in the body turning to a part of the bone marrow tissue and hurting blood-producing cells [2]. Also it can be cause of leukemia or skeletal cancer. This is because of its chemical propinquity and alkaline earth metallic characteristics.

$^{90}$Sr is a substantial component of superabundant nuclear wastes and also a high yield fission product of $^{235}$U [3]. It undergoes $\beta^{-1}$ decay, emitting electrons with energy of 0.546 MeV and has a half life of 28.8 years. Yttrium-90 isotope ($^{90}$Y) is its decay product which is $\beta^{-}$ emitter with half-life of 64 h and decay energy of 2.28 MeV distributed to an electron, an antineutrino and zirconium-90 ($^{90}$Zr) which is stable [4]. Scheme 1, represents the $^{90}$Sr decay equation. Besides, various radiometric methods such as gas flow GM (Geiger–Müller) counting and liquid scintillation counting are usually employed for direct measurement of 90Sr and its daughter 90Y subsequently [5]. Ultra low level liquid scintillation counting (LSC) can be successfully utilized to count alpha and beta activity derived from alpha, beta emitters to monitor the natural radioactivity, contamination corresponded to the nuclear fallouts, contaminants branched from nuclear power stations or fuel reprocessing plants [5]. Reduced equipment requirements and relative readiness of radiochemical procedures make the LSC as an attractive technique which can be employed also by laboratories even with lack of specific radiochemistry facilities or experience. The determination of radio-strontium by this technique is based on the high counting efficiency for high-energy β-particles in aqueous solutions. 90Sr might enter the water from naturally occurring deposits or human activities. Therefore, the removal of 90Sr from drinking water is recognized as a serious issue that should not be condoned.

There are several available studies on application of inorganic materials and their ion exchange properties. Zeolites and metal oxide nanoparticles are of the most significant inorganic materials for the removal of $^{90}$Sr from nuclear waste [6–10]. These compounds are extremely beneficial for their vast application as catalysts and adsorbents. Zeolites constitute an important class of aluminosilicate crystalline micro porous materials comprising natural and synthetic species. They introduce particular physicochemical properties owing to their singular structure and also have




**Scheme 1.** The strontium-90 ($^{90}$Sr) decay equation.

been extensively employed as molecular sieves, ion-exchangers, absorbents, catalysts, vapor-sensing applications and several other applications [11–14]. The combination of zeolites and metal oxide nanoparticles attains solid catalysts in which the high surface area of nanoparticles and the absorbent capacity provided by zeolites cooperate to increase the efficiency of the catalytic process [15]. The customary methods for modification of zeolites are impregnation [16] and ion-exchange [17]. In present research, the combination of AgX zeolite as host and $MnO_2$ nanoparticles as guest materials were considered to synthesize a new and applying adsorbent catalyst with both features of high surface area of nanoparticles and the absorbent capacity of the zeolite which lead to an enhancement of efficiency for the removal process of $^{90}$Sr from drinking water. Nevertheless, to the best of our knowledge, except our previous research [18] which has exploited the same concept with dissimilar agents and conditions, there has not been any reported study on the mentioned matter in previous works.

## 2. Experimental

### 2.1. Materials and reagents

Sodium aluminate ($NaAlO_2$), sodium silicate ($Na_2SiO_3$), aluminum sulfate ($Al_2$ $(SO_4)_3$), tetramethyl ammonium chloride ($(CH_3)_4NCl$), silver nitrate ($AgNO_3$), manganese nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$), potassium permanganate ($KMnO_4$) were all purchased from Merck (Merck, Darmstadt, Germany). The high-capacity cocktail OptiPhase HiSafe-3 (Wallac Oy, Turku, Finland) and double-distilled water were used throughout the work.

### 2.2. Instrumentation

The morphology and size monitoring of the prepared adsorbent catalyst were performed via SEM micrographs using a scanning electron microscope (SEM, LEO-1530VP). Moreover, weight percentages of the elements (silver and manganese) were measured via atomic adsorption spectrometry (AAS, PerkinElmer, USA) coupled to a HGA 400 programmer hybrid system and equipped with a hollow cathode lamp at respective wavelength using an acetylene-air flame. The powder X-ray diffraction (XRD) patterns were recorded at room temperature using a Philips X'pert Pro diffractometer equipped with CuKα radiation and a wavelength of 1.54056 E (30 mA and 40 kV). Data were collected over the range 4–90° in $2\theta$ with a scanning speed of 2° $min^{-1}$. Further, the IR spectra were scanned on a PerkinElmer model 2000 FT-IR spectrometer (USA) in the wavelength range of 400–4000 $cm^{-1}$ using KBr pellets. An ultra-low level Quantulus 1220 liquid scintillation counter had been employed for all measurements. Besides, a shaker Heidolph Vibramax 100 (Heidolph Co., Schwabach, Germany) was utilized for mixing of cocktail and sample. Samples and cocktail were mixed in 20 mL polyethylene vials, Polyvial (Zinsser Analytik Co., Frankfurt, Germany).

### 2.3. Synthesis of NaX zeolite by hydrothermal method

First, 20 g of sodium aluminate ($NaAlO_2$) was dissolved in 30 mL deionized water and gradually heated up to 80 °C under vigorous stirring and maintained at this temperature. 55 g of sodium silicate ($NaSiO_3$) was then slowly added to the sodium aluminate solution and together stirred for 2 h. Afterwards, the heating stirrer was put away and the mixture left at 25 °C for 48 h (solution A). 78 g of sodium silicate was dissolved in 120 mL deionized water, 16 g of aluminum sulfate ($Al_2$ $(SO_4)_3$) added and the mixture stirred incessantly for 2 h (solution B). 10 g of sodium aluminate was diluted with 10 mL deionized water, then added drop-wise and