Sorption and Desorption of Strontium using Silica extracted from Acid Treated Rice Husk. I: Effect of pH and Interfering Ions.

H. M. H. Gad*, E. E. H. Borai & A. M. K. El-Khalafawy

Hot Laboratories and Waste Management Centre, Egyptian Atomic Energy Authority; P. O. 13759, Cairo, Egypt.

ABSTRACT

Strontium, one of the radio-nuclides most frequently released from low-level radioactive waste to the environment, is a known carcinogen. Migration of Sr$^{+2}$ from waste disposal and nuclear test sites has contaminated adjacent aquifers showing up as hardness in water. Therefore, understanding Sr$^{+2}$ retention and removal through sorption processes is critically important. The effect of contact time, pH, adsorbent weight and interfering ions on the sorption of strontium from solution using silica extracted from acid treated rice husk followed by thermal activation was investigated by using batch experiments. The sorption and desorption of Sr$^{+2}$ were determined at room temperature (20±1°C) and pH 6.6. It was found that 5 hours is sufficient for prepared samples to attain equilibrium. The presence of interfering ions, whether organic or inorganic, is influenced by and affected on the sorption of Sr$^{+2}$ in the aqueous solution. Desorption of Sr$^{+2}$ using different mineral and organic acid illustrated that HNO$_3$ is the best desorbing agent for recovery of Sr$^{+2}$ from loaded silica and the sorption of Sr$^{+2}$ on silica can be described by a reversible sorption process. Finally, the prepared silica can be used as good alternative sorbents for sorption and pre-concentration of Sr$^{+2}$ from aqueous solution.

Key words: Sorption and desorption, Strontium, interfering ions, silica, rice husk.

1-INTRODUCTION

Radio-strontium is the characteristic radionuclide present in fallout of nuclear reactor accidents, nuclear weapon tests and in leakage of cooling water from nuclear power plants. The understanding of the sorption and desorption processes of Sr$^{+2}$ from aqueous solutions on adsorbents is of great importance with regard to the potential contamination of groundwater, because sorption presents a principle control for the mobility of Sr$^{+2}$. It was demonstrated that radio-strontium is a very mobile nuclide in comparison with lanthanide and actinide ions (1). For long-term performance assessment of nuclear waste repositories, the interaction between metal ions, organic substances and backfill materials is the main subject of various investigations (2, 3). Silica has been considered as backfill material for nuclear waste disposal sites due to the low hydraulic conductivity of compacted silica and its large sorption capacity. The retardation capability for radio-nuclides is primarily controlled by their sorption potential. Safety analysis requires the understanding of sorption and removal processes of radio-nuclides on silica.

In this paper we have studied the sorption and desorption of strontium. The factors affecting the sorption process (effect of contact time, pH, adsorbent weight and interfering ions) and the diffusion of Sr$^{+2}$ have been investigated. In this studies, the distribution coefficients ($K_d$) of the sorption of Sr$^{+2}$ on silica from aqueous solution were determined using batch technique. The sorption behavior is often represented by the distribution coefficient, which is characteristic to the sorption ability of radio-nuclides in the solid phase.
2-EXPERIMENTAL

2.1. Chemical Reagents and Apparatus.

All chemicals and reagents used in this work were of analytical grade and used without further purification: (1) The Congo red (CR) dye was first synthesized in 1883 by Paul Bottiger who was working then for the Friedrich Bayer Company in Elberfeld, Germany. Due to a color change from blue to red at pH 3.0-5.2, Congo red can be used as a pH indicator. It is the sodium salt of benzidinediazobis-1-naphthylamine-4-sulfonic acid (formula: C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}; molecular weight: 696.66 g/mol). It is a secondary diazo dye. $\lambda_{max} = 497$nm. (11) (2) The Methylene Blue (MB) dye used was discovered by Caro in 1878. It is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: C_{16}H_{18}N_{3}SCl, Molecular Weight=319.85. $\lambda_{max} = 663$nm. (3) Rhodamine B (RhB) is a chemical compound and a dye. It is often used as a tracer dye within water to determine the rate and direction of flow and transport. Molecular formula: C_{28}H_{31}ClN_{2}O_{3}; molecular weight: 479.02 g/mol.

Atomic absorption spectrometer, Hitachi Z 8100, was used for the determination of the metal ion content in the aqueous phase. Microprocessor pH-Meter (HANNA model HI 9321), was used for all pH measurements.

2.2. Preparation of silica from rice husk using mineral acids.

The rice husk was mixed with 1N HCl in the ratio of 100 g husk per 1.2 L acid and heated at 105°C for 2 h with stirring until the color of the husk gradually changed from yellow to dark brown. The husk was cleaned to remove excess of acid using distilled water. It was then dried in an oven at 110°C. Subsequently, the treated husk was burnt in an electric muffle furnace at 700°C for 1.5 h. The produced silica materials take the abbreviation: S1. The same procedure was performed with HNO3 pretreatment and S2 was obtained. Figure 1 shows the flow chart for the process of prepared silica.

Figure (1): The flow chart for preparation of silica from rice husk using HCl and HNO3.

2.3. Determination of total silica (SiO2):

Total SiO_{2} solution was obtained by fusing the sample of prepared silica with alkaline caustic soda, and then the concentration of SiO_{2} was determined using UV spectrophotometer in the samples through its complexing color with ammonium molybdate reagent. (18, 19) Tartaric acid solution was added and allows the solution to stand for 45 min. The absorbance was measured using a Shimadzu UV-Vis. (160 A) Spectrophotometer at $\lambda$ 640 nm. The % of SiO_{2} in the prepared samples is shown in table (1).

2.4. Adsorption Experiments.

Kinetic analysis of the adsorption process for Sr^{2+} ions on silica and all distribution coefficients, $K_d$ (metal ion concentration in solid/metal ion concentration in solution), were calculated in batch adsorption experiments. A weighed amount of each of prepared silica, 0.03 g, was mixed with 40.0 ml of aqueous solution containing 200 mg/l of Sr^{2+} ions. The resultant mixture was shaken mechanically at 250 rpm, optimum pH and time to achieve equilibrium. The reaction vessels were kept at 20°C ±1 in a
thermostatically controlled water bath. The mixture was then centrifuged until the supernatant was free of suspended materials. Aliquots (5.0-cm³) of the liquid were sampled and measured with atomic absorption spectrometer (Hitachi Z 8100).

The distribution coefficients (K_d) of the Sr^{2+} ions, the percentage removal (% R), and the amount of metal ion adsorbed at any time, q (mg/g), were calculated from the following equations:

\[ K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \text{ (mL/g)} \]  
\[ \% R = \frac{C_o - C_e}{C_o} \times 100 \]  
\[ q_t = (C_o - C_e) \frac{V}{m} \]

Where C_o and C_e are the initial and equilibrium concentration of solution for the corresponding metal ion (mg/L), V is volume of the aqueous phase (L), and m is the weight of the adsorbent silica (g).

2.5. Desorption procedure.

Strontium loaded silica was obtained from adsorption experiment. Five replicate samples of Sr^{2+} loaded silica were collected from each treatment. At the end of the adsorption process, the silica was separated from the liquid by centrifugation. After the wet weights of the silica were obtained, the Sr^{2+} was desorbed using distilled water, NaOH, HNO_3, HCL, and oxalic acid. Desorption was processed for 24 hours. The same agitating and centrifuging procedures used in the sorption experiments were applied. The concentration of Sr^{2+} in the extract was measured using atomic absorption spectroscopy.

3-RESULTS & DISCUSSION

3.1. Some characterization of the prepared silica.

The following table summarizes some of physico-chemical characterization of prepared silica. As shown from this table, it is clear that the sample S1 has a higher surface area, total pore volume and average pore size. These characters can be enables and increase the adsorptive capacity of S1 than S2.

Table (1): Some characterization of silica prepared from acid treated rice husk.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>S_1 (HCl treated)</th>
<th>S_2 (HNO_3 treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>100.5</td>
<td>87.95</td>
</tr>
<tr>
<td>Total pore volume (cc/g)</td>
<td>5.189e⁻²</td>
<td>4.462e⁻²</td>
</tr>
<tr>
<td>Average Pore Size (nm)</td>
<td>14.16</td>
<td>12.07</td>
</tr>
<tr>
<td>% of SiO₂</td>
<td>40.11</td>
<td>43.48</td>
</tr>
</tbody>
</table>

3.1.1. Morphology of prepared samples:

As seen from figure (2): the prepared silica maintain the skeleton of the original rice husk after treatment with both of HCL and HNO_3 and thermal activation at 700°C indicating the high mechanical stability of the resulted adsorbents.
3.2. Time-dependence of sorption.

Using the batch technique the dependence of the q and kₐ value on the contact time was investigated using 0.03 gm silica and 40 ml at an initial Sr⁺² concentration of 200 mg/l at pH 6.6 and temperature of 20 ±1°C. The results are shown in Figure (3) which clearly revealed that rate of adsorption is high at the beginning. This is due to availability of a large number of active sites on the S₁ and S₂ adsorbent. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Maximum removals of Sr⁺² (approximately 80%) were attained within the first 1 hour of stirring time for two samples (S₁ and S₂) and the steady state value of qₑ and kₐ are obtained. There must not be seemed to be much benefit after 5 hours. Therefore the equilibrium time was set to be 5 hours. As seen from the figure (3), it clear that the silica extracted by HCl treatment (S₁) has (a higher surface area, total pore volume and average pore size and consequently) higher capacity for removal of Sr⁺² than the other HNO₃ extracted silica (S₂).

![Figure (3): Effect of shaking time on the uptake (qₑ, mg/g) and kₐ of Sr⁺² using prepared silica.](image)

3.3. Effect of pH on the sorption isotherm.

The pH dependence of Sr⁺² sorption on S₁ and S₂ at an initial Sr⁺² concentration of 300 mg/l is shown by qₑ (mg/g) and a log Kₐ versus pH plot in Figure (4). qₑ and the Kₐ values of Sr⁺² sorption are pH independent in the range of 2 to 8 (this is may be due to the competition between excess of H⁺ ions and Sr⁺² ions in solution), then they increases slightly at pH > 8 after which the dominant sorption process for Sr⁺² is ion exchange although the small increase in Kₐ values for pH>8 is ascribed to surface complexation. Molera and Eriksen also investigated the sorption and diffusion of Sr⁺² in bentonite in 0.1M NaClO₄. Their results are quite close and similar to those of our work.
The concentration of surface species (=SiOH uncharged surface group, =SiOH\(^+\) positively charged surface group, =SiO\(^-\) negatively charged surface group) can be obtained as a function of pH. Various mechanisms have been developed to describe the metal ion sorption on an adsorbent. Approximately, they are, (a): including the ion exchange reaction (7):

\[
m(=\text{Si-OH}) + M^{z+} = (=\text{Si-O})_m M^{z-m} + mH^+ \]

(b): the sorption and hydrolysis at the surface of the adsorbent:

\[
(=\text{Si-OH}) + mH_2O + M^{z+} = (=\text{Si-})_m M(\text{OH})^{z-m} + mH^+ \]

(c): and the hydrolysis followed by a sorption reaction:

\[
M^{z+} + mH_2O = M(\text{OH})^{z-m} + mH^+ \]

\[
(=\text{Si-OH}) + M(\text{OH})^{z-m} = (=\text{Si-})_m M(\text{OH})^{z-m+1} \]

As seen from above, pH is important factor for the adsorption of Sr\(^{+2}\) ions on the new adsorbents. According to pH results, we can assume that Sr\(^{+2}\) ions in solution can able to bind chemically with hydroxyl groups in the adsorbents (mechanism (a)). This means that an ion-exchange reaction takes place in the adsorption of Sr\(^{+2}\) ions on the silica bearing silanolic functional groups.

Comparing to the sorption of Sr\(^{+2}\) on bentonite (13-16) and hydrous alumina, (17) the sorption mechanism of Sr\(^{+2}\) on silica is very similar to that on clay and minerals. The sorption of Sr\(^{+2}\) is mainly dominated by the free cations at the solid surface, which could provide the exchange sites to adsorb strontium. TRIVEDI and AXE (17) studied the sorption of Sr\(^{+2}\) on hydrous alumina and manganese oxides and found that the sorption is a physical reaction and it is also a rapid and reversible adsorption reaction to the external surface. WANG and LIU (14) studied the sorption of Sr\(^{+2}\) on bentonite by using capillary method and found that Sr\(^{+2}\) sorption is very weakly dependent on pH, independent on Sr\(^{+2}\) concentration, which indicates a linear sorption.

3.4. Effect of weight of prepared silica.

Study of the effect of silica amount for Sr\(^{+2}\) removal is important to get the trade-off between the adsorbent capacity and percentage removal of Sr\(^{+2}\) resulting in optimum silica amount. The influence of silica amount, varying from 0.5 – 2.5 g/L on the Sr\(^{+2}\) adsorption are shown in Figures (5a and 5b) for the two prepared silica (S\(_1\) and S\(_2\)) at a constant initial Sr\(^{+2}\) concentration of 200 mg/L. It is clearly seen that the removal efficiency increases as the silica mass increases and this may be due to; as the silica mass increases, the number of binding sites for the Sr\(^{+2}\) ions also increases (9). Removal efficiency increases for Sr\(^{+2}\) from 69.4 to 97.5 % and from 49 to 95 % as the mass of S\(_1\) and S\(_2\) increases, respectively. This difference in adsorption shows that the S\(_1\) silica has much affinity towards Sr\(^{+2}\) than S\(_2\). After some point, sorption capacity was steady or decreased (from 277.6 to 78 mg/g and from 196 to 76 mg/g for S\(_1\) and S\(_2\), respectively) with silica mass concentration due to a screen effect between silica particles (and may be agglomeration and/or accumulation of silica particle); this produced a block of the active sites by an increase of adsorbent mass in the system (10) and the drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process.
0.005 0.010 0.015 0.020 0.025

Weight of S₁ adsorbent

Figure (5a): Effect of adsorbent mass on the uptake \(q_e\) (mg/g) and % removal of Sr\(^{+2}\) using S₁ silica. Condition: (V = 10 ml, pH=6.5, Température =20 \(^{\circ}\)C, \(C_0=200\text{mg/L}\) and time = 24hr).

0.005 0.010 0.015 0.020 0.025

Weight of S₂ adsorbent

Figure (5b): Effect of adsorbent mass on the uptake \(q_e\) (mg/g) and % removal of Sr\(^{+2}\) using S₂ silica. Condition: (V = 10 ml, pH=6.5, Température =20 \(^{\circ}\)C, \(C_0=200\text{mg/L}\) and time = 24hr).

For the 1 g m/L of S₁ and S₂ dosage, the optimum values of Sr\(^{+2}\) % removal and adsorption capacity are found to be 80% and 160.2 mg/g for S₁ and 76.5 % and 144 mg/g for S₂, respectively.

3.5. Effect of interfering ions (organic and inorganic).

3.5.1. Effect of inorganic interfering ions.

In the present study, the effect of interfering of other ions such as Co\(^{2+}\), Fe\(^{2+}\) and Pb\(^{2+}\) present in fallout of nuclear reactor accidents, nuclear weapon tests and in leakage of cooling water from nuclear power plants on the Sr\(^{+2}\) removal was studied.
Table (2): Effect of interfering inorganic ions on the uptake, \( q_e \) (mg/g) of Sr\(^{+2} \) using S\(_1\) and S\(_2\) silica.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Uptake of Sr(^{+2} ) only</th>
<th>Uptake of all cations</th>
<th>Inorganic Cations</th>
<th>Uptake of metal ions (single metal)</th>
<th>Uptake of metal ions In presence of Sr(^{+2} )</th>
<th>Sr(^{+2} ) (In presence of metal ions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/g</td>
<td>%R</td>
<td>mg/g</td>
<td>%R</td>
<td>mg/g</td>
<td>%R</td>
</tr>
<tr>
<td>S(_1)</td>
<td>123.2</td>
<td>61.6</td>
<td>Co</td>
<td>102.4</td>
<td>51.2</td>
<td>69.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>147.8</td>
<td>73.9</td>
<td>109.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
<td>43.2</td>
<td>21.6</td>
<td>23.8</td>
</tr>
<tr>
<td>S(_2)</td>
<td>113.4</td>
<td>56.7</td>
<td>Co</td>
<td>92.2</td>
<td>46.1</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>185.8</td>
<td>92.9</td>
<td>111.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
<td>41</td>
<td>20.5</td>
<td>17.2</td>
</tr>
</tbody>
</table>

[Condition: V= 10 ml, m= 0.01 gm, pH=6.5, Température =20\(^\circ\)C, \( C_o =200 \) mg/l for Sr\(^{+2} \) and other inorganic catios, time = 24hr].

The effect of each ion on the uptake of Sr\(^{+2} \) and the effect of Sr\(^{+2} \) on the uptake of the other ions is plotted in figure (6). It can be seen from this figure that:

1- For S\(_1\) prepared silica:
   a) The \% removal of Sr\(^{+2} \) is marginally decreased (from 61.6 \% to 56.4 \% i.e. decreased by 8.4\%) by the presence of Co. Fe approximately has no effect on the \% removal (or uptake, \( q_e \) mg/g) of Sr\(^{+2} \) ion. This may be due to the more ionic charge of the Sr\(^{+2} \) which dominates in the adsorption as compared to the other divalent ions such as Fe.

![Figure 6: Effect of metal ions on the uptake, \( q_e \) (mg/g) of Sr\(^{+2} \) using S\(_1\) adsorbent.](image)

b) The presence of Pb greatly increase the \% removal of Sr\(^{+2} \) (61.6 \% to 100 \%) and this may be due to the competition between the two metal ions toward the active site on the surface of the prepared silica depending on the increase of ionic strength in the solution.

c) Due to the presence of Sr\(^{+2} \) ions in solution containing metal ions of Co, Fe and Pb, the \% removal of all metal ions is greatly decreased using the S\(_1\) prepared silica as adsorbent. The \% removal of Co decreased from 51.2 \% to 34.6 \% and Fe from 73.9 \% to 54.9 \% and finally Pb from 21.6 \% to 11.9 \%.
As a conclusion; the presence of metal ions of Co, Fe and Pb affect positively on the removal of Sr$^{+2}$ and the Sr$^{+2}$ affect negatively on the adsorption of these metal ions using S$_1$ as adsorbent.

2- For S$_2$ prepared silica:

a) The % removal of Sr$^{+2}$ is significantly decreased (56.7% to 43.3%) by the presence of Co. In contrast to the Co, the Fe and Pb have a great effect on the increase of the % removal of Sr$^{+2}$ ion from a solution containing a mixture of these ions. The presence of Fe significantly increase the % removal of Sr$^{+2}$ (56.7% to 70.6%) and the presence of Pb has a higher effect on the % removal of Sr$^{+2}$ (56.7% to 76.0%). This may be, also, due to the competition between the metal ions toward the active site on the surface of the HNO$_3$ prepared silica because of the increase of ionic strength in solution.

b) Because of the presence of Sr$^{+2}$ ions in solution containing metal ions of Co, Fe and Pb, the % removal of all metal ions is greatly decreased by using of the S$_2$ prepared silica as adsorbent. The % removal of Co decreased from 46.1% to 24.5% and Fe from 92.9% to 55.8% and finally Pb from 20.5% to 8.6%.

c) Generally, the total capacity (uptake, q$_e$(mg/g) or % removal) of prepared silica increased in case of binary solution than in single metal ions.

d) The total capacity of S$_1$ is higher than that of S$_2$ in case of adsorption of Sr$^{+2}$ in single metal ion and in binary solution (presence of metal ions in solution of Sr$^{+2}$ and vice versa). But, in case of metal ion (Co, Fe and Pb) in single solution the capacity of S$_2$ is higher than that of S$_1$.

3.5.2. Effect of interfering organic compounds.

As seen from above, the presence of metal ions affected on the adsorption of Sr$^{+2}$ from solution. Also, the presence of interfering organic compounds has a great effect on removal of Sr$^{+2}$ ion from aqueous solution as illustrated below. The sorption of Sr$^{+2}$ using S$_1$ and S$_2$ in presence and in absence of Congo Red (CR), Methylene Blue (MB) and Rhodamine B (RhB) are shown in Figure (7). Three dyes each with concentration of 100 mg/l is used for experimental purpose:
Table (3): Effect of organic interfering ions on the uptake (and %R) of Sr\(^{+2}\) using prepared silica.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Organic Compound (single component)</th>
<th>Organic Compound (In presence of Sr(^{+2}))</th>
<th>Sr(^{+2}) In presence of organic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic compound</td>
<td>Organic compound</td>
<td>Sr(^{+2})</td>
</tr>
<tr>
<td></td>
<td>Sample No.</td>
<td>Sr(^{+2}) only</td>
<td>Uptake, q.e(mg.g(^{-1}))</td>
</tr>
<tr>
<td>S1</td>
<td>Congo red (CR)</td>
<td>123.2 (82%)</td>
<td>50.91</td>
</tr>
<tr>
<td></td>
<td>Methylene blue (MB)</td>
<td>60.7</td>
<td>60.7</td>
</tr>
<tr>
<td></td>
<td>Rhodamine B (Rh.B)</td>
<td>47.8</td>
<td>47.8</td>
</tr>
<tr>
<td>S2</td>
<td>Congo red (CR)</td>
<td>113.4 (76%)</td>
<td>51.25</td>
</tr>
<tr>
<td></td>
<td>Methylene blue (MB)</td>
<td>62.4</td>
<td>62.4</td>
</tr>
<tr>
<td></td>
<td>Rhodamine B (Rh.B)</td>
<td>48.46</td>
<td>48.4</td>
</tr>
</tbody>
</table>

[Condition: (V= 10 ml, m= 0.01 gm, pH=6.5, Température =20 °C, \(C_o=150\) mg/l for Sr\(^{+2}\) and 100 for other organic compounds, time = 24hr).]

Mechanism of adsorption of organic dyes in absence and in presence of Sr\(^{+2}\) (and vice versa) using silica prepared from acid treated rice husk can be illustrated as following: Ion-chelating organic molecules are usually bound to silica surface via silanization procedure that involves covalent grafting. However, a number of desirable ion-chelating groups do not contain a reactive functional group suitable for chemical bonding to the silanized surface. In such a case, physical adsorption of the chelating agent on the solid support is useful, which can be achieved through hydrophilic attraction such as Van der Waals interaction between the silanized surface and the carbon chain of the chelating agent. Such hydrophilic attraction or Van der Waals interaction has been suggested by a number of authors. Silica is a polymer of silicic acid, consisting of inter-linked SiO\(_4\) in tetrahedral fashion, which has the stoichiometry SiO\(_2\). In presence of acid or base hydrolysis process of sodium silicate or alkoxysilane produces Si-(OH)\(_4\) entities.

At the surface, the structure terminates in either siloxane group (=Si–O–Si=) with the oxygen atom on the surface, or one of the several forms of silanol groups (=Si–OH). The silanol groups could be isolated (free silanol groups), where the surface silicon atom has three bonds into the bulk structure and the fourth to OH group and the vicinal or bridged silanols, where two isolated silanol groups attached to two different silicon atoms are bridged by H-bond. A third type of silanols called geminal silanols consists of two hydroxyl groups attached to one silicon atom. The geminal silanols are close enough to have H-bond whereas free silanols are too far separated. The pioneering work has shown the presence of two types of silanol at the silica/water interface with pKa values 4.9 and 8.5 with surface population of 19 and 81%, respectively.
The silica surface is a major factor contributing to the separation technique in chromatography. Mainly, surface hydroxyl groups are responsible for adsorption properties. From table (3) it is clear that:

**a) For S\textsubscript{1} prepared silica:**

1. For organic compounds in single component (or in absence of Sr\textsuperscript{2+} ions), the uptake, \(q_e\) (mg/g), (or % removal) take the following order: MB > CR > RhB. The higher uptake (and % removal) MB may be due to: (a) lower molecular weight (and consequently molecular size) leading to higher mobility of MB molecules to the active site on the surface of prepared silica. (b) High electrostatic attraction between positively charged dissociated cationic molecules of MB (MB\textsuperscript{+}) and negatively charged de-protonated silanol groups (=Si-O\textsuperscript{-}) on the surface of the silica adsorbent.

2. The presence of Sr\textsuperscript{2+} in the solution of investigated dyes affects on the uptake of these dyes. The uptake of MB decreases and that of RhB increases whereas the uptake of CR is greatly increases from 50.9 to 97.2 mg/g.

3. For Sr\textsuperscript{2+} ions; the presence of CR in binary solution with Sr\textsuperscript{2+} decreases its % removal from 82.1% to 48.9 %, whereas the presence of RhB decreased the % removal by 35.3%. On contrast to the CR and RhB, the MB increases the % removal from 82.1 to 84.7 (increased by 3.2%). i.e. the MB has a positive contribution to the sorption of Sr\textsuperscript{2+} on S\textsubscript{1}. DU et al.\textsuperscript{(12)} investigated the sorption of Sr\textsuperscript{2+} on calcareous soils using batch experiments and a selective extraction method, and found that organic matters in calcareous soil contributes to the sorption of Sr\textsuperscript{2+} significantly. This suggests that organic matter has a relative affinity for Sr\textsuperscript{2+}. In our study, the % removal of Sr\textsuperscript{2+} is 84.7 % in presence of MB, which is higher than that of Sr\textsuperscript{2+} sorption in absence of MB. The high % removal values on S\textsubscript{1} suggest a high relative affinity of Sr\textsuperscript{2+} to MB sorbed on S\textsubscript{1}. Whether CR-Sr\textsuperscript{2+} or RhB-Sr\textsuperscript{2+} complexes are formed in solution or Sr\textsuperscript{2+}-CRS\textsubscript{1} (Sr\textsuperscript{2+}-RhBS\textsubscript{1})/CR-Sr\textsuperscript{2+}-S\textsubscript{1} (RhB-Sr\textsuperscript{2+}-S\textsubscript{1}) sorption takes place on the surface of S\textsubscript{1}, it is difficult for the large molecules of organic substance-metal ion complexes to be transported in the pore volume of S\textsubscript{1}, thus CR or RhB inhibits the transport of Sr\textsuperscript{2+} ions in this phase.

**b) For S\textsubscript{2} prepared silica:**

1. As seen from table (3), the behavior of organic compound toward the S\textsubscript{1} is the same as for S\textsubscript{1} adsorbent. And the adsorption of organic dyes affected in the same way as in the case of S\textsubscript{1} prepared silica by the presence of Sr\textsuperscript{2+} ions in the same solution.

2. The exception in the case of S\textsubscript{2} silica is, all studied organic dyes greatly decreases the % removal (or uptake, \(q_e\) (mg/g)) of Sr\textsuperscript{2+}.
Generally, the % removal of CR dye is enhanced by presence of Sr\(^{+2}\) ions in solution in the case of both of S\(_1\) and S\(_2\) adsorbents, while MB and RhB are slightly affected. On the other hand, the % removal of Sr\(^{+2}\) is enhanced by the presence of MB in solution in case of S\(_1\) only.

3.6: Desorption of Sr\(^{+2}\) from loaded S\(_1\) and S\(_2\) prepared silica.

**Eluant selection:** Sr\(^{+2}\) desorption was measured by immersing the Sr\(^{+2}\) loaded S\(_1\) and S\(_2\) samples into distilled water and 0.1N NaOH, HNO\(_3\), HCl and oxalic acid (to investigate the effect of base and mineral or organic acid on the desorption process), shaking 250 rpm and at 20 ±1°C. The duration of desorption was similar to adsorption time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorption (Uptake, mg.g(^{-1}))</th>
<th>Desorption (mg.l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption (mg.g(^{-1}))</td>
<td>Desorption (mg.l(^{-1}))</td>
</tr>
<tr>
<td>S(_1)</td>
<td>125.2</td>
<td>40.72</td>
</tr>
<tr>
<td></td>
<td>83.5</td>
<td>32.54</td>
</tr>
<tr>
<td></td>
<td>127.15</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>84.76</td>
<td>11.33</td>
</tr>
<tr>
<td></td>
<td>126.5</td>
<td>50.51</td>
</tr>
<tr>
<td></td>
<td>84.3</td>
<td>39.97</td>
</tr>
<tr>
<td></td>
<td>84.86</td>
<td>33.94</td>
</tr>
<tr>
<td></td>
<td>127.3</td>
<td>43.21</td>
</tr>
<tr>
<td></td>
<td>84.4</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(_2)</td>
<td>112.4</td>
<td>39.35</td>
</tr>
<tr>
<td></td>
<td>74.93</td>
<td>55.00</td>
</tr>
<tr>
<td></td>
<td>113.1</td>
<td>22.14</td>
</tr>
<tr>
<td></td>
<td>75.4</td>
<td>19.58</td>
</tr>
<tr>
<td></td>
<td>111.9</td>
<td>82.86</td>
</tr>
<tr>
<td></td>
<td>74.6</td>
<td>46.03</td>
</tr>
<tr>
<td></td>
<td>75.26</td>
<td>40.77</td>
</tr>
<tr>
<td></td>
<td>112.9</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>75.46</td>
<td></td>
</tr>
</tbody>
</table>

(D. water NaOH HNO\(_3\) HCl Oxalic)

[Condition: M=0.02, Time = 24 h, C\(_0\) = 150 mg/l, Temp.= 20 °C, V=10 mL]

Desorption values for Sr\(^{+2}\) from loaded S\(_1\) and S\(_2\) samples are summarized in Table 4. From this table, we can conclude that:

1. Sr\(^{+2}\) desorption values for S\(_1\) samples are 32.54%, 11.33%, 39.97%, 33.94 and 0.00 % in distilled water, NaOH, HNO\(_3\), HCl and oxalic acid respectively. However, desorption of Sr\(^{+2}\) from loaded S\(_2\) in the same desorbing agents are 55.00%, 19.58%, 82.86%, 40.77% and 0.00%. This is indicative of physical attraction between Sr\(^{+2}\) species and S\(_1\). Besides, attraction between Sr\(^{+2}\) species and S\(_2\) sample may be greater than that of S\(_2\) sample leading to low desorption values.

2. HNO\(_3\) is the best desorbing agent for Sr\(^{+2}\) ions from loaded S\(_1\) and S\(_2\) prepared silica. So, it can be used for regeneration of the two adsorbent and recovery of the Sr\(^{+2}\) ions.

3. Oxalic acid has no effect on desorption of Sr\(^{+2}\) ions from the two new prepared adsorbents.

4. The distilled water has a moderate effect on the desorption process of Sr\(^{+2}\) ions indicating reversibility of adsorption of Sr\(^{+2}\) using S\(_1\) and S\(_2\) demonstrating that the adsorption of Sr\(^{+2}\) ions is physical rather than chemical one as shown in figure 9.
Figure (9): Effect of eluant type on the recovery of Sr\textsuperscript{+2} ions from loaded S\textsubscript{1} and S\textsubscript{2}.

[Conditions: V= 10 mL, M= 0.02 g m, eluant V = 10 mL, eluant conc. = 0.1N, temp= 20\textdegree}C and time = 24 hr.]

4-CONCLUSIONS

A wide range of low-cost adsorbents have been studied worldwide for Sr\textsuperscript{+2} removal and it is evident from this work, that inexpensive and locally available materials could be used. Based upon the experimental results carried out in this work, the following conclusions can be drawn:

- Prepared silica from acid treated rice husk can easily be applied as a cheap adsorbent for Sr\textsuperscript{+2} removal.
- It clear that the silica extracted by HCl treatment has a higher surface area, total pore volume and average pore size and consequently higher capacity for removal of Sr\textsuperscript{+2} than the other HNO\textsubscript{3} extracted silica.
- Adsorption of Sr\textsuperscript{+2} ions using extracted silica is very rapid in the first 1hr and the equilibrium time is 5 hr.
- Uptake and the $K_d$ values of Sr\textsuperscript{+2} sorption are pH independent in the range of 2 to 8, then they increases slightly at pH>8. The dominant sorption process for Sr\textsuperscript{+2} is ion exchange although the small increase in $K_d$ values for pH>8 is ascribed to surface complexation.
- Adsorbent concentration was a main variable in the sorption process with extracted silica and in this case it was found that for the 1 gm/L of S\textsubscript{1} and S\textsubscript{2} dosage, the optimum values of Sr\textsuperscript{+2} removal and adsorption capacity are found to be 80% and 160.2 mg/g for S\textsubscript{1} and 76.5 % and 144 mg/g for S\textsubscript{2}, respectively.
- The adsorption capacity of the prepared silica for the adsorption of Sr\textsuperscript{+2} was found to be affected by the presence of interfering ions (organic or inorganic).
- Also, adsorptions of metal ions or organic molecules were found to be affected by the presence of Sr\textsuperscript{+2} in solution.
- HNO\textsubscript{3} is the best desorbing agent for Sr\textsuperscript{+2} ions from loaded S\textsubscript{1} and S\textsubscript{2} prepared silica. So, it can be used for regeneration of the two adsorbent and recovery of the Sr\textsuperscript{+2} ions.
5-REFERENCES


(11) "Competitive Adsorption of dyes (congo red, methylene blue, malachite green) on Activated Carbon” A Project submitted to the National Institute of Technology, Rourkela In partial fulfillment of the requirements of Bachelor of Technology (Chemical Engineering) By Bibek Dash Roll No. 10600008 Under the guidance of Prof. S. Mishra DEPARTMENT OF CHEMICAL ENGINEERING NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA ORISSA -769 008, INDIA 2010.


