Effect of Suez Canal Marine Sediment on Sorption of Cesium.

Hassan, H.B.

ABSTRACT

Suez Canal is surrounded by navigation, industrial, agricultural activities and suffers from high rate of population growth that discharging waste into Suez Canal. The Suez Canal coastal waters are influenced by a complex variety of physical, geochemical and biological processes, which influence the behavior, transport and fate of containments released into the marine environment. Sorption of releasing containment such as cesium in Suez Canal water is investigated because of its toxic effect on the marine environment. The object of present study is to determine the effects some of physical and chemical characteristics of collected sediment samples from the three important locations on Suez Canal (Suez Bay, Bitter Lakes and El- Temsah Lake beaches) on sorption behavior of cesium by using batch experiment. Batch experiment was used to study the sorption of the cesium ion. The sorption process is dependent on mineral constituents of Suez Canal sediment and their characteristics. Analytical methods which included particle size and X-ray diffraction (XRD) analyses found that particle size of Suez Canal sediment samples is characterized by sand to fine sand and quartz is the main mineralogical species. Distribution coefficient (K_d) which represent geochemical processes and particle size of these sediment samples effect on the degree of cesium sorption to the sediment. Also (K_d) increase with increase cation exchangeable capacity (CEC). The Suez Canal sediment samples have low (K_d) values which effected by their physical and chemical properties.

1.   Siting and Environmental Department, Nuclear and Radiological Regulatory Authority (NRRA), Cairo, Egypt.

Sample (2) has highest distribution coefficient (K_d) between measured samples due to containing ratio 30% of fine sand and high ratio of organic matter.

INTRODUCTION

Suez Canal is the shortest international passage for marine shipping with lots of traffic carrying petrochemicals, crude oil and fertilizers or radioactive materials. It passes through an area of considerable industrial, agricultural and tourist activities which may be released heavy metals into marine environment. The most of heavy metals have toxic effects on living organisms when exceeding a certain concentration. ^{133}Cesium is the only stable isotope of cesium. In seawater, Cs exists predominantly as a free cation (Cs^+, 99%) with about 1% of the total dissolved species a $CsSO^{-4}$ **(Byrne, 2002).** Cs can be transfer from water to sediment by direct adsorption that efficiency of adsorption depend on characteristic of marine sediment such as type of clay mineral, clay content, sediment texture as particle size, cation exchange capacity (CEC), and organic matter. The solubility, potential mobility and bioavailability are responsible for the harmful effects of cesium on animals and the environment.

Natural sediments usually act as a sink for various contaminants, but they may also become a source under the drastically changing environmental conditions in the fresh and saline water mixing zones **(Buesseler et al., 2011).**

The transport of the Cs radionuclide through aquatic systems is partially dependent on its physical and chemical properties and on the sediment characteristics **(Taira and Hatoyama, 2011).**

It is assumed that the fate of radionuclides in the environment follows the behavior of stable elements. According to many authors **[Tsukada et al., 2002; Yoshida et al., 2004]** the properties of stable Cs in different ecosystems may be regarded as a useful tool in predicting the behavior of ^{137,134}Cs. Therefore to facilitate experimental studies on radiocesium sorption and mobility in the environment, the utilization of stable Cs was applied.

MATERIAL AND METHOD

Description of study sites

The Suez Canal is located in northeast Egypt. The geographical position of the Suez Canal makes it the shortest route between east and west that led to increase the passage of many tender convoys and ships through it. The study area includes, Suez Bay, Bitter Lakes and El– Timsah Lake and bounded by latitudes 29° 50`– 30$^O$ 36` N and longitudes 32° 15`– 32$^O$ 37` E. Shore sediment samples were collected from the three important sites Suez Bay, Bitter Lakes and El– Timsah Lake in Table (1).

Table (1) *Selected sites of studied sediment samples.*

Sites	No	Sample name	Coordinate	
			Longitude	Latitude
Suez Bay	1	Beach club	32.548	29.950
	2	Kabanon	32.48	29.947
Bitter Lakes	3	Kasfaret	32.428	30.243
	4	Fayed	32.323	30.317
El- Temsah Lake	5	Norus village	32.271	30.573
	6	El- Malaha Club	32.380	30.571

Sampling and analytical procedures

Shore sediment samples were taken from three sites Suez Bay, Bitter Lakes and El- Temsah Lake beaches of Suez Canal at January 2016. The samples were air dried for physical and chemical analysis to determine texture, mineral composition, pH, Electrical conductivity (EC), Percentage of $CaCO_3$ Estimation, Cation exchange capacity (CEC) and sorption coefficient K_d. Field and laboratory data were analyzed to evaluate the characteristics of the Suez marine sediment.

Particle size analysis

Particle size analysis of the studied sediment samples were carried out. The samples were air dried and placed in polyethylene-lined paper bags. All samples were hand ground to pass a gravel and carbonate, or gypsum particles that were > 2mm. The percentage of > 2 mm gravel was determined by weighing the portion of the sample not passing a 2 mm sieve. Results are reported on a weight percentage basis. Much of the carbonates often exist as sand-sized particles (0.05-2 mm) **(Bowman and Hutka, 2002).** The sizes of the mesh in this study sediment samples were from 2 (very coarse sand) to 0.0625 mm (very fine sand).

Preparation of sediment samples for X-ray diffraction (XRD)

Mineralogical, characteristic of the studied sediment samples were determined. X-ray diffraction (XRD) is a non-destructive technique for characterization of minerals, including quartz, feldspars, calcite, dolomite, clay minerals, and iron oxides, particularly for the fine soil and dust fractions.

Representative powdered Suez sediment samples were smeared over a glass slides. Each dry slide was placed in the X-Ray diffractometer (Shimadzu XRD 6000). The operating conditions are characterized by a sin angle (2θ) from 2 to 60°, 60kv, 80mA,

and 0.05- 25°/min goniometer speed. Each sample is analyzed three times to improve the signal-to-noise ratio, and the combined scans are then imported into the Microsoft Excel RockJock macro program **(Eberl, 2003).**

Chemical analysis

Chemical analysis of studied Suez sediment samples characteristics as (pH), Electrical conductivity (EC), $CaCO_3$% estimation, Organic matter (O. M%), Cation Exchange Capacity (CEC), exchangeable bases (Ca, Mg, K and Na) and distribution coefficient (K_d) were occurred to determine the relationship between CEC and (K_d) with each physicochemical parameter.

pH and EC

The studied sediment pH and EC are determined in water with a glass electrode at sediment to water ratio of 1:1. pH and EC are measured using pH and EC electrodes (WTW) with accuracy $\pm 0.1°C$ **(Evangelou, 1998).**

Estimation of CaCO3%

Carbonate and bicarbonate ions in the studied sediment samples were determined by titration method which is based on neutralization of the sediment sample by a titrated acid. Back-titration by a base is determined equivalent calcium carbonate. The percent calcium carbonate was calculated. **(Jamal et al., 2016) .**

Cation exchange capacity (CEC):

Cation-exchange capacity (CEC) is a measurement of the soil's ability to hold positively charged ions and nutrients. (CEC) is expressed in milliequivalents (meq) per 100 grams of soil, the CEC of a soil increases with increasing clay or organic matter content. The high exchangeable Na^+ in studied sediment samples from the influence of seawater. CEC was determined by measuring the exchangeable

cations displace from sediment by adding the ammonium chloride (NH_4Cl) to determine the sodium (Na^+) **(Apello and Postma, 2005; Aris *et al.*, 2010).** The sediment sample was analyzed using the flame emission spectrometer (Jenway, PFP7 Model. UK).

Organic Matter

The most common procedure involves reduction of potassium dichromate ($K_2Cr_2O_7$) by organic carbon compounds and subsequent determination of the unreduced dichromate by oxidation- reduction titration with ferrous ammonium sulfate. While the actual measurement is of oxidizable organic carbon, the data are nominally converted to percentage organic matter using a constant factor, assuming that contains 58% organic carbon. However, as this proportion is not in fact constant, we prefer to report results as oxidizable organic matter, or multiplied by 1.334 as organic carbon (**Walkley, 1947**).

Sorption experiment

Sorbents Batch technique was applied in this work to study adsorption behavior of the studied sediment samples towards cesium ions. Batch experiments were conducted to determine the distribution coefficient (K_d) of the isotopes between the

waters and the chemisorbents overtime K_d depends on (V/m), in many systems (**Atsushi *et al.*, 2012; Abdullaha and Hussin, 2016**) The relationship between sorption coefficient and (sediment/water) ratio ca   :

$$K_d = \frac{C_0 - C_t}{C_t} \; X \; \frac{V}{m} \frac{C_0 - C_t}{C_t} \; X \; \frac{V}{m}$$

K_d sorption coefficient (ml/g), C_0 initial concentration (mg/l), C_t equilibrium concentration (mg/l), V volume of solution (ml) and m mass of solid (g).

Sorption experiments were performed by mixing 0.2g of studied sediment samples with tubes. The ratio of mass of studied sediment sample to volume of solution (V/M) was 1:100. After shaking for 8h, the solution was immediately separated from suspensions by centrifuging for 15 min, at 3000rpm mixtures were shacked at 700osc/min.

The investigated cesium ion measurements at absorbance 852 nm were carried out as shown in Table (2) by using Leeman (ICP) optical emission Spectroscopy (USA) which has measuring concentration error from 1- 5%. The Blank bottle is used to neglect the uptake percent of the ions on the wall of the bottles.

Table (2) *Concentration of cesium absorbed by the studied sediment samples.*

Sites	Samples Number	Concentration cesium (mg/l)
Suez Bay	(C_0) Blank	12.0
	(C_t) Sample (1)	11.36
	(C_t) Sample (2)	11.20
Bitter lakes	(C_0) Blank	12.0
	(C_t) Sample (3)	11.28
	(C_t) Sample (4)	11.27
El- Temsah Lake	(C_0) Blank	10.0
	(C_t) Sample (5)	9.5
	(C_t) Sample (6)	9.4

RESULT AND DISCUSSION

The grain size distribution of the sediment affects the sorption of cesium, as the sorption increases with decreasing grain size (**Paul *et al.,* 2016).** In sand soils the dominant grain size group is sand, 0.2-2.0 mm in diameter. Sand soils are further divided into coarse sand soils (0.6- 2.0 mm) and fine sand soils (0.2- 0.6 mm) (S☐derlund *et al.,* **2011).** The grain size analysis showed that studied shore sediment samples are characterized by sand to fine sand as shown in table (3) and figure (1). And sample (2) has largest percentage of fine sand.

Table (3) *Some physical and chemical properties of studied sediment samples.*

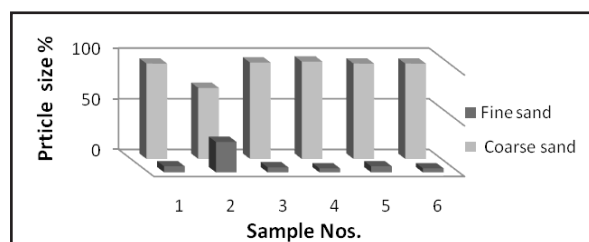| S. No	Fine sand%	Coarse sand%	Texture class	pH	EC ms/cm	O.M%	CEC meq/100g	K_d (ml/g)	CaCo3% Carbonate
1	6	94	Sand	≤8.5	1.33	0.65	0.65	5.4	15
2	30	70	Sand	≤8.5	9.30	5.00	1.6	7.0	5
3	5	95	Sand	≤8.5	2.05	0.90	0.73	6.3	15
4	4	96	Sand	≤8.5	2.85	0.85	0.8	6.4	15
5	5	94	Sand	≤8.5	1.16	1.50	0.7	5.0	5
6	4	96	Sand	≤8.5	2.06	0.71	0.75	6.3	5

Fig. (1): Percentage of particle size in Suez sediment samples.

By comparing results of studied sediment samples from XRD analysis to reference minerals to find the best match X-ray diffraction as shown in figure (2), It is found that X-ray diffractogram (peak) at 2θ =26.60 correspond to the quartz minerals at a spacing 3.338 A⁰. This type of corresponding 2 θ values and d-spacing observed at all studied sediment samples which indicate that these sediment samples consist dominantly of quartz. Also in comparison with previous research, as **(El Mongy, 1995)** which showed that Suez sediments are mainly sand and quartz are the main mineral species of the Suez area sediments. The relation between d- spacing (2θ) and (count) intensity (I) in the results of XRD analysis of studied sediment samples are shown in Fig (3).
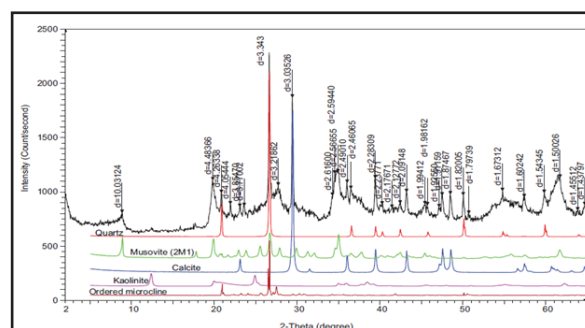

Fig. (2): Comparing a recorded XRD pattern to those reported in program ROCKJOCK (Eberl, 2003).
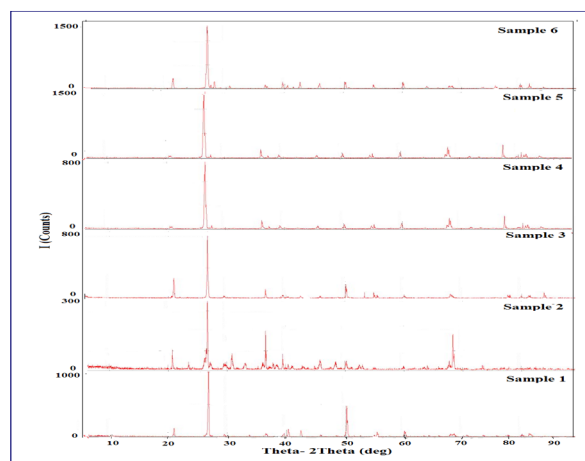

Fig. (3): X- ray diffraction (XRD) result of studied sediment samples.

Table (3) shows the results of chemical analyses of studied sediment samples as (pH), (EC) Electrical conductivity, CaCO3% estimation, Organic matter (O. M%), Cation exchange capacity (CEC), exchangeable bases (Ca, Mg, K and Na) and Distribution coefficient (K_d). pH is the most important sediment property that affect many sediment processes including sorption. pH of the studied sediment samples solution maintained at alkaline condition which leads to low mobility of ions. pH values of sediment samples in the three locations (Suez Bay, Bitter Lakes and El- Temsah Lake) lie in the range of slightly alkaline media pH>8.1 where alkalinity is influenced by carbonates (CO_3^{-2}) and bicarbonate (HCO_3^-) ions, as a result of weathering of carbonate rocks calcite $CaCO_3$, dolomite $Ca\,Mg\,(CO_3)_2$.

Surface water salinity in the Red Sea is generally high within the range 36-46 % (**Khadija and Salah, 2016**). Electric conductivity (EC) of the studied sediment samples solution is ranged between 1.33 to 9.30 mS/cm, which affected by salinity of Red Sea. (EC) plays a major part in controlling all the exchangeable cations especially exchangeable (CEC) Na^+ and K^+. (CEC) refers to the quantity of negative charges in soil existing on the surfaces of clay and organic matter and the capacity of sediment to adsorb and exchange cations (**Tan, 1993; Radojevic and Bashkin, 2007**). Also particle size is an important factor in determining CEC of soils with large amounts of clay and organic matter have higher CEC. While sandy and sandy loam soils, the CEC concentration will drop drastically to 1–5meq/100g (**Bohn et al., 2011**). The cation exchange capacity (CEC) of studied sediment samples are ranged between 0.6 to 1.6meq/100. The (CEC) is lowest value in sample (1) and reached to 0.6 meq/100g While, sample (2) has highest (CEC) and reached to 1.6 meq/100g because sample (2) includes (30%) fine sand.

The distribution coefficients (K_d) were measured to estimate capacity of sediment samples to sorption.

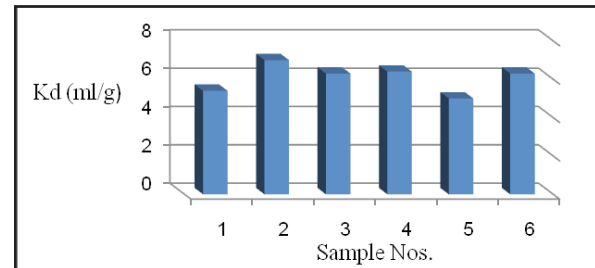The K_d value of studied sediment samples are ranged between 5.0 to 7.0 ml/g as shown in figure (4).

Fig. (4): K_d values of Suez Canal sediment samples.

It is found that K_d of studied sediment samples increase with increasing cation exchangeable capacity (CEC). The highest K_d value of sample (2) indicate that the exhibit the highest sorption of cesium ion because this sample consists 30% percentage of fine sand particle size and contains significant amount of organic matter. The highest amount of organic matter in this sample is due to fertilizer factory and sewage effluents in this sample site.

CONCLUSION

- The particle size plays an important role on sorption of cesium ion and the distribution coefficient K_d exhibited relation with clay content and CEC.

- The specific surface area is increase as a particle size become small that important for sorption capacity and ion exchange capacity.

- Both stable and radioactive cesium the same element and behave in a similar manner chemically and in the body.

- The clay and organic matter in sediment are the primary factors for the determination of cation exchange capacity (CEC).

The studied sediment samples have low K_d value because their textures mostly are coarse sand and consist dominantly of quartz.

- -Sample (2) has highest K_d and CEC because it

consists of 30% percentage of fine sand particle size and contain highest amount of organic matter.

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تأثير الرواسب البحرية لقناة السويس على امتصاص السيزيوم

حنان بدوى حسن

تتمتع قناة السويس بمكانة جغرافية واستراتيجية هامة جعلها اقصر الطرق بين الشرق والغرب. وتمر قناة السويس بمنطقة تتميز بانشطة انسانية ونمو سكانى كبير مما قد تؤدى الى وصول العناصر الثقيلة مثل عنصر السيزيوم الى القناة.

وتهدف الدراسة الحالية لمعرفة بعض الخواص الفيزيائية والكيميائية للرواسب البحرية الشاطئية التى أخذت من المناطق الواقعة على قناة السويس وهى مدخل قناة السويس والبحيرات المرة وبحيرة التمساح والتى تتميز بانشطة ملاحية كبيرة ومدى تاثيرها على امتصاص عنصر السيزيوم.

وقد اخذت عينات الرواسب البحرية من شواطئ مدخل قناة السويس والبحيرات المرة وبحيرة التمساح الواقعة على قناة السويس وتم تحضيرها وتحليل خواصها الفيزيائية والكيميائية لمعرفة مدى تاثيرها على امتصاصها لمادة السيزيوم. واوجدت النتائج ان حبيبات الرواسب البحرية رملية وحجمها يتراوح بين ٦٥- ٢٠٠٠ ميكروميتر وان اصلها المعدنى من مادة الكوارتز وقلوية الاس الهيدروجينى وكذلك بانها ذات ملوحة عالية وبها نسبة من كربونات الكالسيوم ومواد عضوية قليلة. وسجلت النتائج ان التبادل الايونى (CEC) بين الكتيونات ومادة السيزيوم يزيد بزيادة معامل التوزيع K_d بين الرواسب والمياه لمادة السيزيوم. كما سجلت النتائج ان قيمة معامل التوزيع K_d للعينات المقاسة منخفض لتاثره بخواص العينات الفيزيائية والكيميائية وان عينة (٢) لها اعلى قيمة لمعامل التوزيع بين العينات المقاسة نظرا لان نسبة حبيبات الرمل الصغيرة ذات حجم ٦٥ ميكروميتر بالعينة حيث يصل الى ٣٠٪ من وزن العينة كما تحتوى العينة على نسبة عالية من المواد العضوية.

1. قسم المواقع والبيئة- هيئة الرقابة النووية والاشعاعية- القاهرة.