POTENTIAL USE OF MODIFIED RICE HUSK FOR REMEDIATION OF WASTEWATER CONTAINING LEAD IONS

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ABSTRACT

A new method has been developed to reduce the concentration of Pb (II) ions present as inorganic impurities in wastewater streams. This method is based on the silica extracted by alkaline treatment of rice husk to prepare modified rice husk (MRH), used as sorbent. Several parameters (contact time, initial lead concentration, sorbent mass, pH and temperature) were examined. Concurrently removals of lead cation from the aqueous medium were found to be not affected by the presence of different concentrations of nitrate or sulfate ion up to 0.1 M. The two-parameters equilibrium models (Langmuir equations) were determined at various temperatures (35, 45 and 55°C). Adsorption isotherm indicates that the monolayer coverage is 124.3, 230.2 and 396.7 mg Pb^{2+} ions per g sorbent at 35, 45 and 55°C, respectively. Therefore, the developed rice husk adsorbent is considered a proper sorbent for removal of Pb^{2+} ions due to its low cost and good efficiency. The ion-exchange reaction on the silica surface is the sorption mechanism of lead ions using modified rice husk (MRH).

INTRODUCTION

Heavy metals are nowadays among the most important pollutants in surface and groundwater. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of affections (Marzal *et al.*, 1996). Levels of heavy metals in the environment have increased due to pollution caused by industries. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. Therefore, a better understanding of heavy metal sources, their accumulation in the soil and the effect of their presence in water and soil on plant systems seem to be particularly important issues of present-day research on risk assessments (Rajesh *et al.*, 2004). The main sources of heavy metals to vegetable crops are their growth media (soil, air and nutrient solutions) from which these are taken up by the roots or foliage. Most of our water resources are gradually becoming polluted due to the addition of foreign materials from the surroundings area. These include organic matter of plant and animal origin, land surface washing, and industrial and sewage effluents (Karnataka State Pollution Control Board, 2002). Rapid urbanization and industrialization with improper environmental planning often lead to discharge of industrial and sewage effluents into lakes. The lakes have a complex and fragile ecosystem, as they do not have self cleaning ability and therefore readily accumulate pollutants. Therefore, the elimination of heavy metals from water is important to protect plant, soil and public health.

Treatment processes for metals contaminated water include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-

precipitation/adsorption (Periasamy and Namasivayam, 1995). Over the last years, adsorption has been shown to be an economically feasible alternative method for removing metal ions from water (Mckay, 1996). Activated carbon has been an effective adsorbent. Many studies have appeared on the development of activated carbon from cheaper and readily available materials. In this concern, agricultural by-products, such as rice husks or coconut shell (Leyva-Ramos *et al.*, 1997) are some of the raw materials used in activated carbon production.

Lead ions (Pb^{2+}) found in fresh water usually indicates contamination from metallurgical wastes or from lead-containing industrial processes. Lead in drinking water is primarily from the corrosion of the lead solder used to put together the copper piping. Lead in the body can cause serious damage to the brain, kidneys, nervous system, and red blood cells. The US Environmental Protection Agency (EPA) considers lead to be a highly toxic metal and a major health threat (Tsalev and Zaprianov, 1985).

In this concern, Rice husk as agricultural waste, was used as a precursor for silica extraction that studied as a potential scavenger of lead from aqueous solutions. Physicochemical parameters such as contact time, initial lead concentration, sorbent mass, pH and temperature were studied to optimize the conditions to be utilized on a commercial scale for the decontamination of effluents using a batch technique.

MATERIALS AND METHODS

Preparation of adsorbent

Rice husk was chosen as a precursor material for preparation of silica extracted by alkaline treatment according to scheme described earlier (Daifullah et al., 2003). In this concern, 25 g of raw material was soaked in 0.5 % (w/w) KOH in amounts sufficient to cover the raw material completely, slightly agitated, boiled for 30 min. and left overnight. The impregnated solid was filtered. The filtrate was washed with distilled water. Then, 10% HCl was added to form precipitate at pH 5, and the formed precipitate was dried at 110°C. The ash content of this sorbent was 88% and the main constituents of this metallic residue (ash content) are silica ≈ 95%.

Factors affecting sorption investigation

Stock solution (200 ppm) of lead was prepared by dissolving the required amount of the pure reagent (lead nitrate) in double distilled water, and then transferring to a volumetric

Effect of Contact Time (Minimum Contact Time Determination)

In order to determine the contact time required for the sorption equilibrium, the sorption kinetic experiments were conducted first. 20 mg of the adsorbent in 100 ml reagent bottles containing 25 ml of lead solution (200 ppm) were mixed and placed in the shaker at 25± 1 ^{0}C for different intervals time. The adsorbent was finally removed by filtration, lead concentration was determined. The contact time required for complete metal adsorption was determined and utilized in the remaining tests.

Effect of Adsorbate Concentration

The effect of metal ion concentration was studied by agitation 25 ml of different concentrations (5-150 ppm) of lead solution with 20 mg of adsorbent for equilibrium time at pH 5.5 for lead.

Effect of adsorbent mass

The effect of adsorbent mass was studied by agitation 25 ml of different masses (5-100 mg) of MRH with 100 ppm of lead solution for equilibrium time.

Effect of pH (Optimum pH Determination)

Influence of the pH on the metal adsorption was studied by using 25 ml of 100 ppm solution of lead, adjusted to an initial pH of 2-8 and agitated with 20 mg of MRH. The equilibrium concentration was measured after equilibrium contact time. The lowest solution pH for maximum metal adsorption was then selected.

Temperature Effect and Adsorption Isotherm

The temperature affects each of the adsorption rates and the degree of adsorption. In this concern, 25 ml solution containing lead solution with different concentrations (5-100 mg/l) were agitated with 20 mg MRH for equilibrium at various temperatures 35, 45 and 55 ^{0}C.

In all experimental runs, each mixture was filtered and the difference between the initial concentration (C_0) and the equilibrium concentration (C_e) was calculated to determine the adsorptive capacity (q_e) as follows (Daifullah and Girgis 2003).

$$q_e = V (C_0 - C_e)/M$$
………………………………….…………..……….. (1)

Where V: is the total volume of solute solution (L), M: is the weight of adsorbent used (gm), C_0: is the initial concentration of the solute (mg/L), and C_e: is the residual equilibrium concentration of the solute (mg/L).
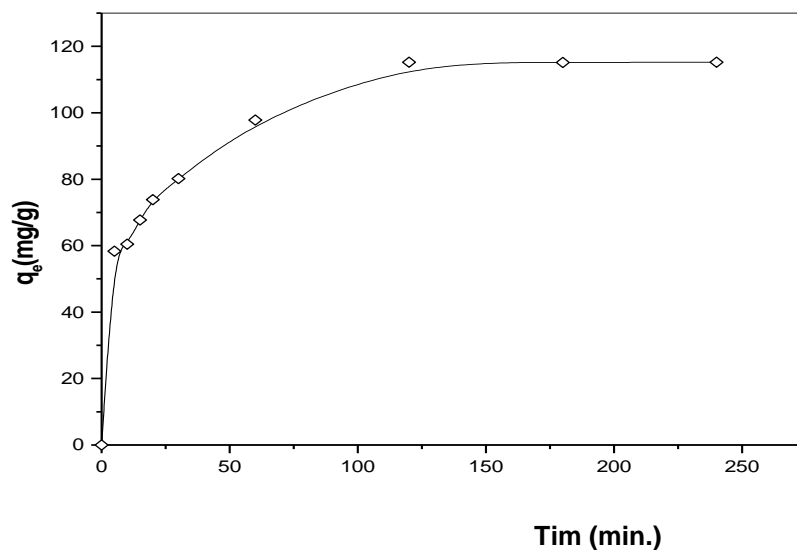
Effect of Some Interfering Anions and Complexing Agents

In this concern, 20 mg of the adsorbent and 25 ml of   lead solution (200 ppm) were mixed in 100 ml reagent bottles and placed in the shaker at 25± 1 ^{0}C for 2 hours. The adsorbent was finally removed by filtration and lead concentration was determined. This experiment was repeated with various concentrations of the anions and complexing agents to find out the effect of their interferences. These concentrations were as follows:

(2 x10^{-4}, 5 x 10^{-4}, 1 x 10^{-3}, 1 x 10^{-2}, 1 x10^{-1}, 5 x 10^{-1} and 1M) of the anions: NO_3 and SO_4.

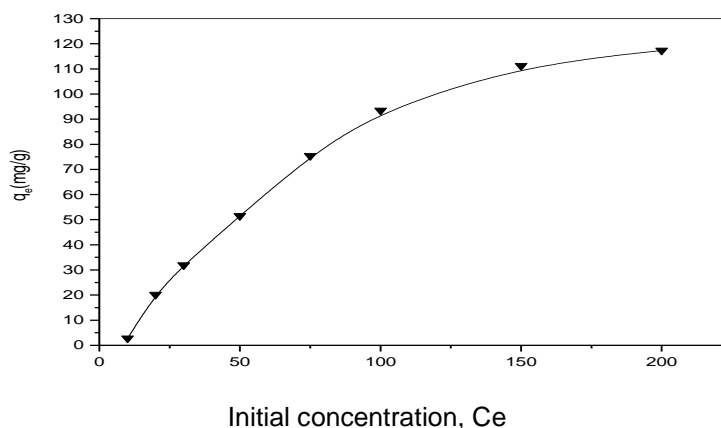# RESULTS AND DISCUSSION

Effect of agitation time.

The kinetic investigation on the adsorption of lead solution by Modified Rice Husk (MRH) is given in Fig. (1). As agitation time increased, lead removal also increases initially, but then gradually approaches a constant value, denoting attainment of an equilibrium (Kadirvelu *et al.,* 2001). Obviously, the equilibrium was attained after shaking for about 2 hr., beyond which   there is no further increase in the adsorption**.**

Tim (min.)
Fig. (1): Effect of time on adsorption of lead by MRH

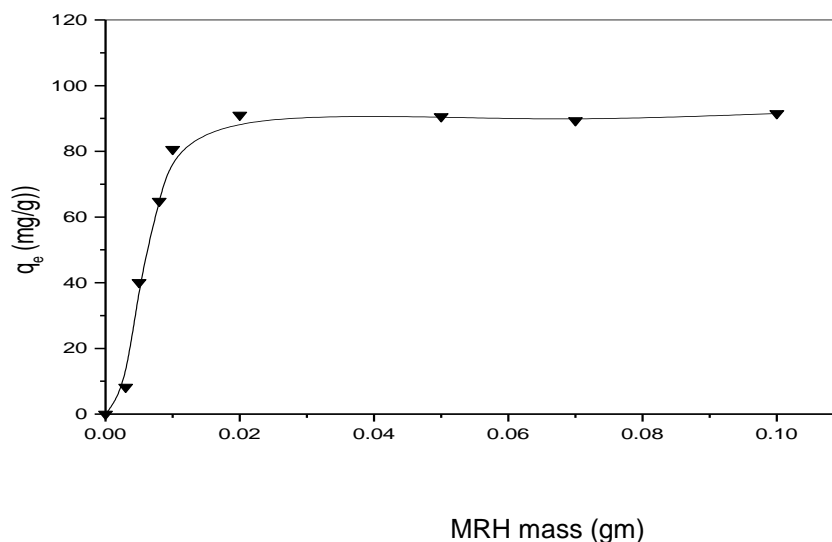**Effect of initial lead concentration.**

The effect of lead concentration was studied using varying initial concentrations from 5 to 200 ppm. The results are shown in Fig. (2). It is clear that as the initial concentration increased the equilibrium uptake q_e increased till saturation. This indicates that the adsorption process appears to proceed rapidly when the number of available sites is much larger than the number of metal species that can be adsorbed and more favorable sites became involved first. As the metal concentration increases, the high-affinity sites begin to reach saturation, and energetically less favorable ones (low affinity surface sites) become involved in the adsorption process causing reduction of removal efficiency (Montanher *et al.,* 2005). It is evident from Fig. (2) that the amount adsorbed on the solid phase at a lower initial concentration of adsorbate was smaller than the corresponding amount when higher initial concentration were used.

Initial concentration, Ce

Fig.(2): **Influence** **of** **initial** **concentration** **of** **lead** **on** **equilibrium uptake q_e**

Effect of sorbent mass.

Fig. (3) represents the relationship between the uptake of lead ions (mg/g) and various MRH masses (mg). Results showed that the uptake of lead ions are increased with increasing the adsorbent mass and attained plateau at 20 mg of MRH for Pb^{2+} ions studied (Kadirvelu, and Namasivayam 2000 and Kadirvelu *et al.,* 2000). However, the adsorption values are not affected by increasing the amount of adsorbent mass more than 20 mg, this may be due to saturation of active sites.
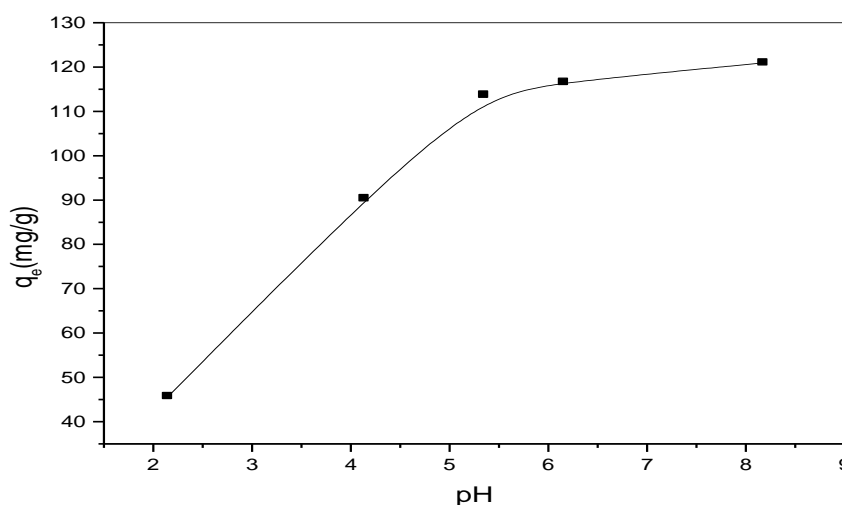

MRH mass (gm)
Fig. (3): Effect of MRH mass on lead adsorption.

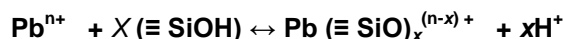**589**

Effect of solution pH on lead adsorption

The experimental with a variable solution of pH was conducted to determine the lowest pH range for maximum metal adsorption by MRH. The adsorption edge for Pb (II) is found in the pH range between 2 to 5 as shown in Fig. (4).

It was clear that the adsorption of lead increased considerably due to the changes in the surface charge at different pH values (Belmouden *et al.,* 2000). At pH values lower than 2 the electrostatic repulsion between the positively charged surface and the Pb^{2+} metal ions prevents their adsorption. As the pH is raised the surface charge of the adsorbent changes and thus, at pH = 4-6, there was a dramatic increase in metal adsorption. As solution pH is increased, the onset of metal hydrolysis and precipitation (at a metal concentration of 100 mg/l) began at a pH of 6 for lead. As solution pH is increased the onset of adsorption therefore occurs before the beginning of hydrolysis (and precipitation) for Pb^{2+}.

Fig (4): Effect of pH on the adsorption of lead Mechanism of metal ion adsorption.

The ion – exchange reaction on the silica surface is accomplished through the substitution of protons of the surface silanol groups by the lead ions from solution, as follows:

$$Pb^{n+} + X (\equiv SiOH) \leftrightarrow Pb (\equiv SiO)_x^{(n-x)+} + xH^+$$

Where -SiOH = silanol group on the SiO2 surface and xH^+= number of protons released. The acidic nature of MRH (pH = 3.6) suggests that the lower pH at which it deprotonates and takes on a negative surface charge (i.e., lower the pH_{zpc}). A negatively charged surface favors cation removal. The pH of the prepared adsorbent is 3.6 (i.e, acidic nature). This means that a negative surface charge over a wide pH-range. Therefore, it is likely that

Pb^{2+} adsorption occurs by ion exchange mechanism releasing protons from the sorbent into the surrounding aqueous media.

Effect of temperature.

The effect of temperature on the uptake of lead from 35 ^{0}C to 55 ^{0}C was investigated. The experimental results given in Fig. (5) Indicates that the magnitude of adsorption is proportional to the solution temperature in adsorption of lead.

It was found that, according to the adsorption isotherm, the amount of lead adsorbed increased with increasing solution temperature. The increase of lead capacity with respect to temperature may be due to enhance mobility of lead ions from the bulk solution towards the adsorbent surface and extend of penetration within the adsorbent structure.

Data obtained from adsorption isotherms was fitted to linearized form of Langmuir (Walter and Weber1972), Eq. (2)

$$\frac{C_e}{q_e} = \frac{1}{bq^0} + \frac{C_e}{q^0}$$ …………………………………… (2)

where:

q_e is the equilibrium uptake (mg/g).

C_e is the equilibrium concentration (mg/l), and q^0 and b are the Langmuir constants related to the maximum adsorption corresponding to complete monolayer coverage and energy of adsorption respectively.

The Langmuir parameters for the adsorption isotherms obtained at different temperatures were calculated from the C_e/q_e versus C_e plots (Figs. 6). Results in Table (1), showed that the value of q^0 for lead increases with increasing temperature.

Table (1): Langmuir   parameters   for   lead adsorption at different temperature.

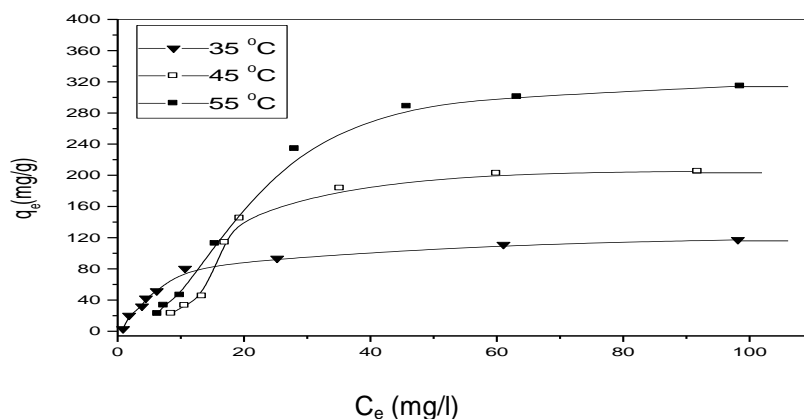| Metal	Temperature	q^0 mg/g	b l/g	R^2
Lead	35 ^{0}C	124.3	0.110	0.999
	45 ^{0}C	230.2	0.090	0.998
	55 ^{0}C	396.7	0.047	0.991

C_e (mg/l)

Fig. (5): The effect of temperature on lead adsorption
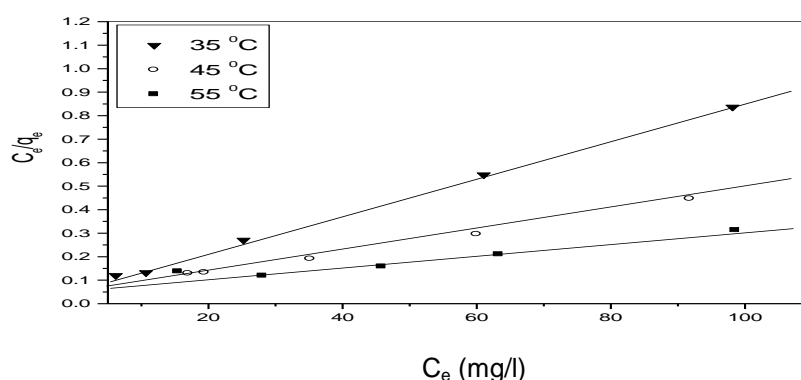

C_e (mg/l)

Fig. (6): The effect of temperature on lead adsorption (Langmuir plot).

Effect of Some Interfering Anions and Complexing Agents

Generally, the adsorption capacity for heavy metals by any sorbent is reduced with the presence of more than one metal ion in solution (Netzer and Hughes1984). Thus, Table (2) showed the effect of different concentrations $(0, 2 \times 10^{-4}, 5 \times 10^{-4}, 1 \times 10^{-3}, 1 \times 10^{-2}, 1 \times 10^{-1}, 5 \times 10^{-1}$ and 1M) of the anions NO_3 and SO_4 on the adsorption of metal ions from aqueous medium by using the selected sorbent. It is worth mentioning that if the concentration of the interfering ions causes unsteady state conditions and exceeds its Ksp (solubility product constant), the precipitation will occur immediately.

Table (2): Percent Removal of Pb $^{2+}$ ions using MRH at various molarity of interfering types.

Interfering type	Concentration of interfering type (M)							
	0	2×10^{-4}	5×10^{-4}	1×10^{-3}	0.01	0.1	0.5	1
Nitrate	91.7	91.7	91.5	91.3	90.9	91.3	91.8	92.0
Sulfate	91.6	91.7	91.6	91.5	91.3	91.7	ppt	ppt

Where ppt means precipitate

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As shown in Table (2), the interfering type may have a slight or insignificant effect even at concentration level 0.001 M. This can be referred to the nature of the slightly soluble salt formed and its affinity to the solid surface. The %R of Pb^{2+} is not affected at all by nitrate at levels from 0 up to 1 M. This may be attributed to the common ion effect. The %R of Pb^{2+} ion is not affected by the presence of different concentrations of sulfate ion up to 0.1 M, and the precipitation occurred only at a higher concentration of sulfate, due to the formation of lead sulfate.

Comparison with other adsorbents:

In order to justify the validity of MRH as an effective adsorbent for lead removal, its adsorption potential must be compared with other adsorbents reported. The values of q^0 for adsorption of Pb^{2+} on different adsorbents are compared to MRH adsorbent at ambient temperature and summarized in Table (3). In general, the lead uptake capacity of MRH is far exceeded the uptake capacities of all adsorbents listed in table (3), but less than that of peat only. However, a fair and objective evaluation concerning the potential of any material as an adsorbent at commercial level should consider its local availability, as this factor closely related with cost minimization. Egypt has abundantly available agricultural waste, such as rice husk, which has little economic value and in fact, often creates a serious problem of disposal for local environment. To achieve an economically feasible and effective treatment of metal-contaminated water, the utilization of such resources from an agriculture waste as an alternative adsorbent for lead removal is highly desirable.

Table (3): Comparison between lead sorption capacity with published data

Adsorbent	q^0 (mg/g)	Ref.
MRH	124.3	This work
Peat	110	Majid *et al.* (1996)
Zoogloea ramigera	110	Sag and Kutsal (1995)
Resting cells	79.9	Chang *et al.* (1997)
Inactivated cells	78.7	Chang *et al.* (1997)
Tea leaves	71.8	Tan and Abd. Rahman (1988)
Montmorillonite clay	63	Farrah *et al.* (1980)
Penicillium chrysogenum	61.9	Holan and Volesky (1995)
Sphagnum Peat moss	55	Allen *et al.* (1992)
Rhizopus arrhizus	55	Holan and Volesky (1995)
High carbon content sludge	40	Lo´ pez-delgado *et al.* (1996)
Tree Fern	39.4	Yuh-Shan Ho *et al* (2004)
Groundnut husks	30.7	Okieimen *et al.* (1991)
Sphagnum moss peat	19.1	Ho *et al.* (1996)
Coke	15	Lo´ pez-delgado *et al.* (1996)
Spruce sawdust	14.1	Holan and Volesky (1995)
Illite clay	12.6	Farrah *et al.* (1980)
Soil	12	Majid *et al.* (1996)
Linden sawdust	9.37	Holan and Volesky (1995)
Kaolinitic clay	6.46	Majone *et al.* (1993)
Kaolinitic clay	3.93	Orumwense (1996)
Kaolinitic clay	1.68	Farrah *et al.* (1980)
Wollastonite	0.411	Yadava *et al.* (1991)
China clay	0.368	Yadava *et al.* (1991)

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Yuh-Shan Ho⸴ , Wen-Ta Chiu, Chun-Sen Hsu and Chien-Tsung Huang , (2004**).** Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy, 73: 55-61.

إمكانيـة استخدام قش الأرز المحـور لمعالجـة ميـاه الصرف المحتويـة على ايونـات الرصاص

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هنـاك طريقـة جديدة للحد من تركيز الرصـاص - ثنـائى التكـافؤ- الموجودة كشـوائب غيـر عضـوية فـي ميـاه الصـرف العادمـة. وتتلخص هذه الطريقـة فى إستخلاص السيليكا بالمعالجة القلوية لقش الأرز لإعداد قش أرز المحورالذى أستخدم كمادة مازة. ولقد تم دراسه العوامل المؤثرة فى عمليه الأمتزاز مثل: (زمن التلامس, التركيز الأولى للرصـاص, كتلـة المادة الممتصـة, درجـة الحموضـة ودرجـة الحرارة) علاوة على أثر تركيزات مختلفة من بعض الانيونات مثل النترات و الكبريتات على إزالة كاتيون الرصاص في الوسط المـائي . أشار الامتزاز الحراري إلى تغطية الطبقة الأحادية للمادة الماصة بايونات الرصاص الثنائي وكانت كالاتى 124.3 230.2 ;396.7 ملجم ايون Pb^{2+} لكل جرام من المادة المـازة عند درجات حرارة مختلفة (35 و 45 و55 درجـة مئويـة) علـى التوالي باستخدام معادلـة لانجمير. لذلك فان مادة (قش الأرز المحور) مادة مناسبة لإزالة الرصاص - ثنـائى التكافؤ - في الوسط المائي وذلك لقلة التكلفة وكفاءتها في الإزالة. وبدراسه ميكانيكيه التفاعل وجد أن التبادل الايونى على سطح السليكا بقش الأرز المحور هو المسئول عن عمليه الأمتزاز لايون الرصاص.

قام بتحكيم البحث

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