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Modified Eggshells as Cost Effective Adsorbent for the Treatment of Arsenic(III) Contaminated Industrial Effluents

S. MUBARAK[1,*], M. ZIA-UR-REHMAN[1] and M. NAWAZ CHAUDHRY[2]

[1]Applied Chemistry Research Centre, PCSIR laboratories Complex, Lahore-54600, Pakistan
[2]College of Earth and Environmental Sciences, University of the Punjab, Lahore, Pakistan

*Corresponding author: Tel: +92 3074013632, E-mail: shafaq.mubarak@gmail.com

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The present work is based on the uptake of arsenic(III) ions from aqueous solution by new laboratory prepared manganese oxide coated egg shell powder. Manganese oxide coating on poultry egg shells increased the removal efficiency of arsenic(III) from 86 % of unmodified shells to 91.5 % of modified shell. The adsorption potential of a new sorbent manganese-oxide-coated egg shells (MOCES) was investigated for the removal of arsenic from industrial effluent using batch sorption experiments. The effects of different parameters such as adsorbent dose, pH, initial arsenic concentration, contact time and temperature were studied to monitor the adsorption behavior of the sorbent under these conditions. Equilibrium data was examined through Langmuir and Freundlich's isothermal models. Regression values were found to be 0.992 and 0.805, respectively which showed a fit of the equilibrium data in both of the models.

Keywords: Metal adsorption, Arsenic contamination, Solid waste management, Egg shells, Industrial effluent treatment.

INTRODUCTION

Due to exponential increase of our knowledge of science and technology and its application globally, the ecological and environmental deterioration of our biosphere has increased. Presence of toxic heavy metals in air, water and soil is becoming a global problem, posing a serious threat to the environment. Most of the metals are harmless upto their specific threshold values but when present in excess can cause serious health problem[1]. Among these toxic metals, arsenic contamination in ground water, is one of the most challenging, environmental problems today. Millions of people are exposed to arsenic toxicity from natural as well as anthropogenic sources as estimated in a report by Johnston *et al.*[2] that 60 to 100 million people in India and Bangladesh are currently at risk as a result of drinking water, contaminated by arsenic. Permissible value of arsenic, according to US EPA is 10 ppb[3]. Long-term arsenic exposure in drinking water has been associated with liver, kidney, lung and bladder cancers. It can also cause skin cancer as indicated by Huang and Dasgupta[4] and Wu *et al.*[5]

Numerous technologies have been adopted for arsenic removal from waste water such as worked on coagulation and electro-coagulation techniques by Parga *et al.*[6] and ion exchange & precipitation methodologies by Shao *et al.*[7]. Membrane processes and adsorption technique have been adopted for the removal of toxic metals from water with varying degrees of success by Peters *et al.*[8] The effluent treatment for arsenic removal both by conventional and non-conventional methods has been explored by Ngo *et al.*[9] Adsorption technique is one of the most common available technologies being used for the removal of metal cations. Various adsorbents developed for arsenic removal include activated carbon[10], coal, coconut shell and peat carbon[11]. Different soil minerals and California soil have been studied as potential adsorbents for arsenic by Zhang and Selim[12] as well as by Manning and Goldberg[13]. The biomaterials like, algae, fungi and bacteria have also been investigated by Gadd and Rehm[14], Brierley[15] and Sag[16] as arsenic adsorbent. Agricultural products and their by-products such as rice husk have shown efficient arsenic removal[17,18].

In numerous cases, it has been observed that structural modification of traditional adsorbents improves their performance, *e.g.* use of iron oxide[19] and manganese dioxide enhances the adsorption activities of a number of adsorbents. Verma[20] worked on arsenic adsorption from ground water by manganese coated sand.

Successful application of adsorption technology demands innovation of cheap, non-toxic and easily available adsorbents. In recent years, application of poultry waste to improve the adsorption capacities of heavy-metal ions, has been explored. Alejandro *et al.*[21], investigated the calcium solution, extracted from egg shell waste as a low-cost activation agent, to improve the adsorption properties of, three commercial carbons. Studies of Oke *et al.*[22] and Arunlertaree *et al.*[23], showed efficient metal adsorption on powdered eggshells. Ahmad *et al.*[24], investigated the modification of eggshells with iron oxide to explore the adsorption behavior for Cu^{2+} ion from their aqueous solutions.

The present work was carried out to investigate the uptake of arsenic(III) on the manganese coated hen egg shell powder from aqueous media and to study the optimal conditions of sorption parameters like contact time, pH and adsorbent dose to remove arsenic from industrial effluents.

EXPERIMENTAL

Collection of waste poultry egg shells: To study the effect of arsenic adsorption, waste poultry egg shells were collected from burger shops and restaurants of Lahore, Pakistan. These eggs shells were washed with water to remove dust and egg membrane. These washed egg shells were dried at 105 °C for 3 h and ground to fine powder for further treatment.

Chemical modification of egg shell powder: Chemical modification of powdered egg shells has been done by manganese chloride. The powdered egg shells (100 g) were placed in a heat resistant crucible. To this, the mixture of 100 mL of 2.5 M aqueous manganese chloride and 1 mL of 10 M aqueous NaOH were added. The contents were then heated for 5 h at 150 °C[25] followed by baking of the resultant solids at 500 °C for further 4 h. Baked material was then washed with distilled water to remove any uncoated impurity and dried at 110 °C for 2 h. A dark brown coloured coating was observed on the surface of egg shell powder forming Manganese Oxide Coated Egg Shell (MOCES) adsorbent.

Preparation of arsenic stock solution: Arsenic(III) stock solution of 1000 ppm was prepared by taking sodium arsenite (2.401 g) in 1000 mL of distilled water in a measuring flask. The stock solution was further diluted to get required concentration (ppm) of arsenic solutions.

Comparison of unmodified and modified egg shell powder for adsorption: To compare the unmodified and MOCES for arsenic adsorption, 0.5 g of both the materials were taken in separate 100 mL beakers. To this 50 mL arsenic solution (2 ppm) was added. The mixture was stirred magnetically for 40 min and filtered. The filtrate was checked for its arsenic concentration *via* atomic absorption spectrometer. Percentage adsorptions of arsenic on both adsorbents were then calculated.

Batch adsorption studies: To optimize the prepared adsorbent (MOCES) for its efficacy for arsenic removal from water, batch studies of adsorption were carried out for different parameters like adsorbent dose, metal concentration, contact time, pH and temperature. Maximum metal uptake by the adsorbent was determined by taking arsenic concentration (50 mL) in the range of 2-12 mg/L with 1 g MOCES and electromagnetic stirring for 60 min. The mixture is then filtered and filtrate was analyzed for its arsenic concentration through atomic adsorption spectrometry. Similar procedures were adopted to study other sorption parameters by varying the value of the specific parameter and keeping the rest constant.

Percentage removal of arsenic metal from aqueous media was calculated by the formula[26]

$$\text{Removal of arsenic (\%)} = \frac{C_i - C_{eq}}{C_i} \times 100 \quad (1)$$

where, C_i is the initial ion concentration in mg L^{-1}, C_{eq} is equilibrium (or final) ion concentration in solution in mg L^{-1}.

The arsenic adsorption on the adsorbent was calculated[27] by:

$$Q_e = \frac{C_i - C_{eq}}{M} \times V \quad (2)$$

where, Q_e is the mg of arsenic(III) ions adsorbed per gram of adsorbent, C_i is the initial ion concentration in mg L^{-1} , C_{eq} is equilibrium (or final) ion concentration in solution in mg L^{-1}, M is the amount of adsorbent in grams and V is the volume of adsorption medium in liters.

Equilibrium studies: Equilibrium studies were carried out using Langmuir and Freundlich adsorption isotherms equations.

Langmuir equation[28], for dilute solutions is represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} b + \frac{C_e}{Q_0} \quad (3)$$

where 'q_e' is the mg of metal adsorbed per g of adsorbent at equilibrium, C_e is the metal ion concentration at equilibrium. 'Q_0' and 'b' are the constants and can be determined from graph.

A plot of C_e/q_e *vs* C_e resulted a straight line. The slope is Q_0 and intercept is b.

The Freundlich equation was expressed by Freundlich[29] as:

$$x/m = KC_e \times 1/n \quad (4)$$

'x' is the amount of solute adsorbed, m is the weight of adsorbent, C_e is the solute equilibrium concentration. K and 1/n are the constant characteristics of the system.

For linearization of the data, the Freundlich equation was written in logarithmic form[30].

$$\log Q_e = \log K + 1/n \log C_e \quad (5)$$

where, (Q_e = x/m). Plotting log Q_e against log C_e, resulted a straight line graph. Slope of straight line is '1/n' and intercept is equivalent to log K.

RESULTS AND DISCUSSION

Toxic heavy metals in different industries resulted in their higher concentration in waste water and natural water bodies. Specially, the discharge of higher arsenic concentration into the environment is a serious issue. These waste waters have to be treated, before discharging to water bodies. The developed MOCES material showed adsorption characteristics for the removal of arsenic from aqueous media. It has been observed that MOCES showed 91.5 % arsenic removal compared to 86 % removal by unmodified eggshells (Table-1).

TABLE-1
COMPARISON OF UNMODIFIED AND MODIFIED EGG SHELL POWDER

Adsorbent	C_i (mg/L)	C_{eq} (mg/L)	Arsenic removal (%)
Unmodified Egg Shells	2.0	0.28	86.0
MOCES	2.0	0.17	91.5

The adsorption of arsenic(III) on MOCES is affected by different parameters *i.e.* adsorbent dose, arsenic concentration, contact time, pH and temperature.

Effect of MOCES dose on arsenic adsorption: The effect of MOCES dose on the adsorption of arsenic ions was determined by treating 50 mL of arsenic solution (6 ppm) with 0.25-1.5 g of MOCES. The mixture was filtered after a continuous stirring of 1 h at 30 °C and the removal percentage of arsenic was determined. Table-2 showed an increase in percentage removal of arsenic ions with the increase of adsorbent dose upto 1 g and above that no significant change was observed (Fig. 1). This result may be attributed due to the fact that more sorbent surface area provides more pore volume for metal adsorption[31].

TABLE-2
RESULTS OF MOCES DOSE ON ARSENIC ADSORPTION

Sr No.	MOCES (g)	C_i (mg/L)	C_e (mg/L)	Arsenic removal (%)
1	0.25	6.0	3.86	35.66
2	0.5	6.0	3.61	39.83
3	0.75	6.0	3.19	46.83
4	1.0	6.0	2.64	56.00
5	1.25	6.0	2.71	54.83
6	1.5	6.0	2.73	54.50

Effect of arsenic concentration on adsorption: The metal adsorption is dependent, on the initial arsenic concentration present in the aqueous media. For this study MOCES (1 g) was added in 50 mL of arsenic (III) ion solutions in the range of 2-12 ppm at contact time of 1 h. The filtrate is checked for its arsenic concentration. The percentage adsorption was calculated and results are incorporated in Table-3. Percentage

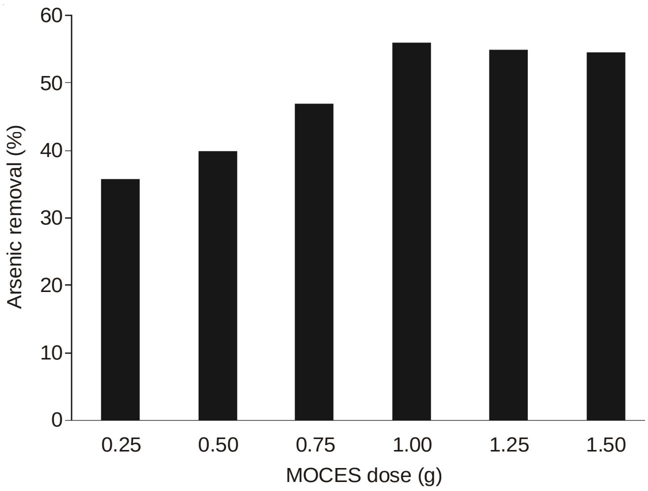

Fig. 1. Effect of MOCES dose on adsorption of arsenic

arsenic removal has been observed in the range of 91.5-36.1 %. Arsenic ions are absorbed by specific sites on adsorbent, which are friendlier for adsorption but as concentration increases adsorbent gets saturated and exchange sites are reduced. The effect of arsenic initial concentration, on adsorption is shown in Fig. 2. Similar pattern has been reported by Yeddou and Bensmaili[32].

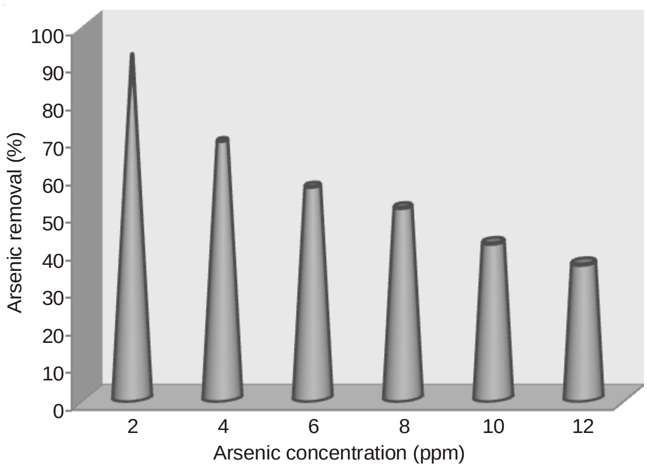

Fig. 2. Effect of initial concentration of arsenic

Effect of contact time on adsorption: The efficiency of MOCES at different time intervals was studied by varying time intervals between 30-80 min. For this, 50 mL of arsenic solutions (6 ppm) and MOCES (1 g) were agitated electromagnetically at 30 °C and arsenic concentration in the filtrates was examined through atomic absorption spectroscopy. The percentage adsorptions are shown in Table-4. The removal of arsenic ions increases with contact time to some extent (Fig. 3). Results showed a fast rate of sorption during the first 60 min of the sorbate-sorbent contact with maximum arsenic uptake of 0.168 mg/g of MOCES. Percent removal becomes almost insignificant towards the end as shown in Fig. 4. This may be due to the exhaustion of binding sites which are available on large surface area of the adsorbent and which are gradually filled up, therefore shows insignificant change.

Effect of pH on adsorption: The pH of the solution has a significant impact, on the uptake of heavy metals. It relates with the charge on the surface of adsorbent, speciation of the adsorbate and the degree of ionization. Arsenic pH solution in the range of 2-12 were adjusted by adding 0.1 M HCl and 0.1 M NaOH. The removal of arsenic ions was studied by keeping the quantity of MOCES (1 g), arsenic concentration (6 ppm) and temperature (30 °C) constant. Results are incorporated in Table-5. The adsorption of arsenic increased with increase in

TABLE-3
RESULTS OF ARSENIC(III) CONCENTRATION

Sr No.	C_i (mg/L)	C_e (mg/L)	M (g)	V (lit.)	Q_e (mg/g)	Arsenic removal (%)
1	2.0	0.17	1.0	0.05	0.091	91.50
2	4.0	1.25	1.0	0.05	0.137	68.75
3	6.0	2.64	1.0	0.05	0.170	56.66
4	8.0	3.91	1.0	0.05	0.204	51.11
5	10.0	5.83	1.0	0.05	0.208	41.70
6	12.0	7.66	1.0	0.05	0.217	36.16

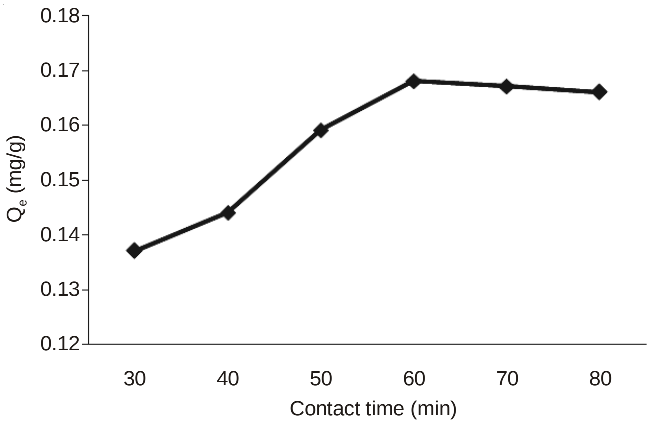

Fig. 3. Effect of contact time *versus* Q_e

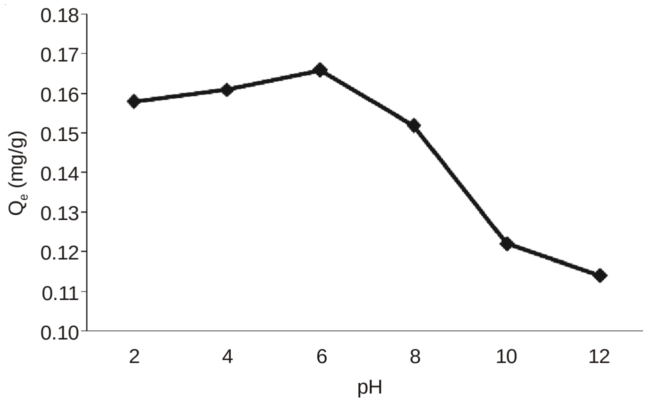

Fig. 5. Comparison of pH and Q_e

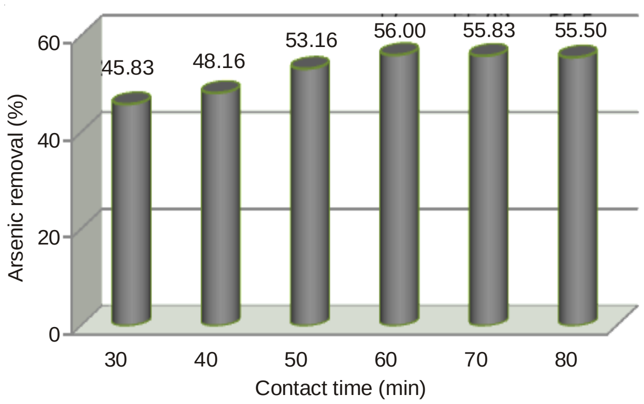

Fig. 4. Effect of contact time *versus* removal of arsenic (%)

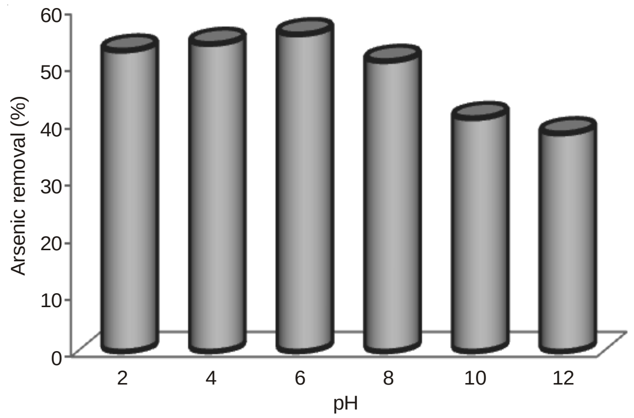

Fig. 6. Comparison of pH and adsorption of arsenic

pH from 2-6 as represented in Fig. 5 and 6 and further no significant change of percentage removal was observed. Less sorption at higher pH could be associated with the hydroxyl ions competing with metal ions for the sorption sites on adsorbent and to the reversal of the surface charges present on the sorbents[33].

Effect of temperature on adsorption: Effect of medium temperature on arsenic ions uptake by the MOCES was determined using 50 mL of arsenic ion (6 ppm) solutions. MOCES (1 g) at contact time of 1 h was added and the temperature was varied between 30-80 °C on a water bath. Results of temperature variation are shown in Table-6. Adsorption, is an exothermic process, therefore, the adsorptivity is decreased with increase in temperature. Figs. 7 and 8 show similar pattern of arsenic uptake, which decreased by increasing the temperature. Maximum removal of metal ion was observed at 30 °C.

Adsorption isotherms: The resulted data is analyzed for its isothermal fits. The Langmuir and Freundlich constants, along with correlation regression has been calculated by corresponding plots (Figs. 9 and 10) and results are given in

TABLE-4
RESULTS OF EFFECT OF CONTACT TIME ON ADSORPTION

Sr No.	Time (min)	C_i (mg/L)	C_e (mg/L)	M (g)	V (lit.)	Q_e (mg/g)	Arsenic removal (%)
1	30	6.0	3.25	1.0	0.05	0.137	45.83
2	40	6.0	3.11	1.0	0.05	0.144	48.16
3	50	6.0	2.81	1.0	0.05	0.159	53.16
4	60	6.0	2.64	1.0	0.05	0.168	56.00
5	70	6.0	2.65	1.0	0.05	0.167	55.83
6	80	6.0	2.67	1.0	0.05	0.166	55.50

TABLE-5
RESULTS OF pH VARIATION

Sr No.	pH	C_i (mg/L)	C_e (mg/L)	M (g)	V (lit.)	Q_e (mg/g)	Arsenic removal (%)
1	2.0	6.0	2.84	1.0	0.05	0.158	52.66
2	4.0	6.0	2.77	1.0	0.05	0.161	53.83
3	6.0	6.0	2.67	1.0	0.05	0.166	55.50
4	8.0	6.0	2.96	1.0	0.05	0.152	50.83
5	10.0	6.0	3.55	1.0	0.05	0.122	40.83
6	12.0	6.0	3.71	1.0	0.05	0.114	38.16

TABLE-6
RESULTS OF TEMPERATURE VARIATION

Sr No.	Temp. (°C)	C_i (mg/L)	C_e (mg/L)	M (g)	V (lit.)	Q_e (mg/g)	Arsenic removal (%)
1	20	6.0	2.97	1.0	0.05	0.151	50.50
2	30	6.0	2.64	1.0	0.05	0.168	56.00
3	40	6.0	2.66	1.0	0.05	0.167	55.66
4	50	6.0	2.76	1.0	0.05	0.162	54.00
5	60	6.0	2.88	1.0	0.05	0.152	52.00
6	70	6.0	3.06	1.0	0.05	0.147	49.00

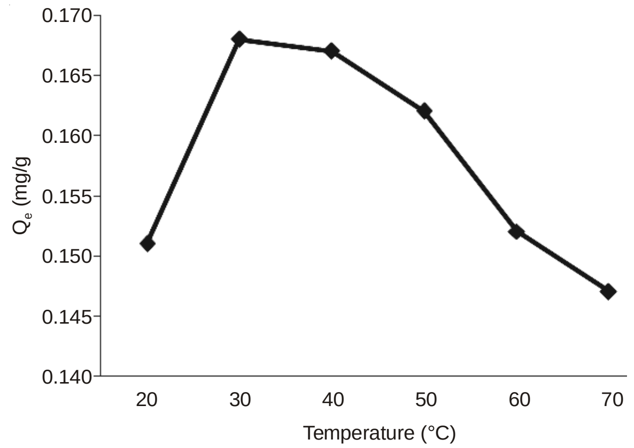

Fig. 7. Comparison of temperature and adsorption of arsenic (Q_e)

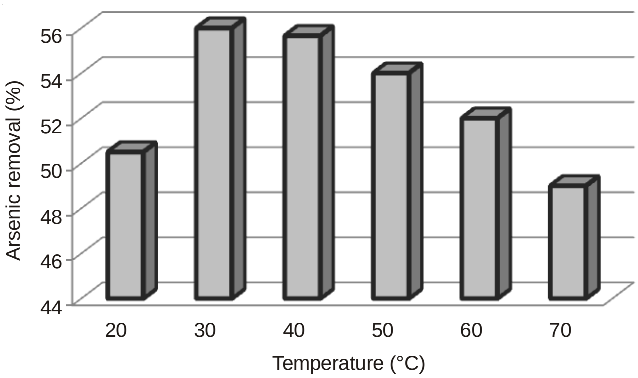

Fig. 8. Comparison of temperature and adsorption of arsenic

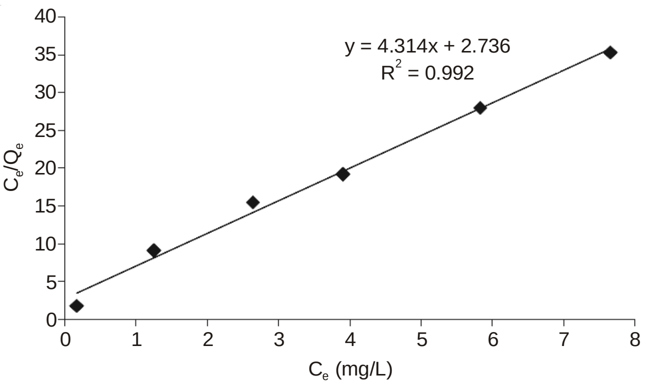

Fig. 9. Langmuir isotherm (linear)

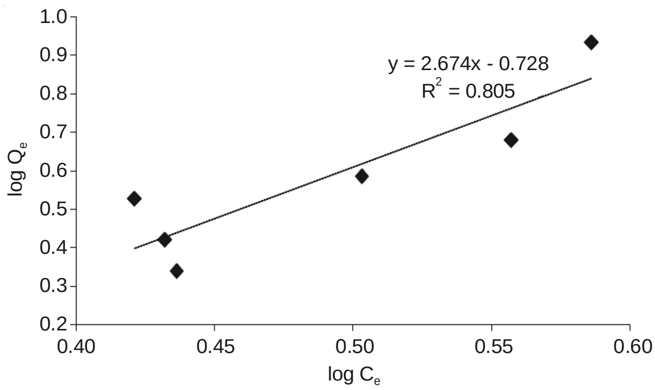

Fig. 10. Freundlich isotherm (linear)

Table-7. Freundlich isotherm model showed that the calculated 'n' and 'K' values are qualitative and related to the distribution of site-bonding energies and the removal efficiency of adsorbent. The Langmuir fit is considered to be evidence, that sorption stops at one monolayer and is consistent with specific and strong sorption on specific sites. Regression coefficient, less than 1 shows that data fits well in both isotherms models.

The results of the above experiments prove that the adsorbent prepared by modification of egg shells is very effective in removal of arsenic(III). The developed modified adsorbent is cost effective as it uses solid waste as a raw material. This treatment technique is environmentally friendly because it not only converts waste into a resource but also provides an efficient and economic way of waste disposal.

Conclusion

The present study shows that the manganese oxide coated egg shells (MOCES) obtained from waste poultry egg shells is a cost effective and efficient adsorbent for removal of arsenic ions from aqueous solutions. Adsorption process is a function of adsorbent and adsorbate concentrations, pH, temperature and time of agitation. The effective pH for arsenic adsorption was found to be 6. Maximum adsorption occurred at 1 h of contact time at 30 °C. The percentage removal of arsenic increased with increasing the sorbent dose and the amount of arsenic adsorbed (mg/L) per gram of adsorbent increased with increase in initial arsenic concentration. Since the studies in the literature focusing specifically on arsenic removal are rare, results of this study may contribute significantly for further

TABLE-7
ISOTHERM MODEL CONSTANTS AND CORRELATION REGRESSION COEFFICIENTS
FOR ARSENIC ADSORPTION FROM AQUEOUS SOLUTIONS

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	Q_0	b	R^2	K	1/n	R^2
MOCES	4.317	0.365	0.992	0.183	2.67	0.805

research on arsenic sorption and may prove useful in design of wastewater treatment plants for the removal of arsenic. This study provides a cost effective adsorbent that uses waste as a resource and may help to get rid of waste disposal expenses.

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