

## Removal of Arsenic From Water Using Some Low Cost Bio-Adsorbents (Single Mixed)



### Chemistry

**KEYWORDS :** GL(Guava Leaf), NL(Neem Leaf), NB(Neem Bark), RH(Rice Husk), BB(Black Berry Seed), Bioadsorbent, Freundlich & Langmuir Isotherm

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### ABSTRACT

*Arsenic is one of the oldest poisons known to men and its applications throughout history are wide and varied. Because arsenic in the bedrock is easily dissolved into surrounding water, inorganic arsenic is frequently present at elevated concentrations in ground water. The catastrophe of arsenic toxicity, caused by arsenic contaminated water, has already been reported in many countries of the world, namely in Bangladesh, India, Nepal, Cambodia, Myanmar, Taiwan, Magnolia, Vietnam, China, Afghanistan, Pakistan, Argentina, Mexico, Chile and the United States. As is a carcinogen which causes many cancers including skin, lung and bladder as well as cardio vascular disease. Various adsorption methods have been used for the removal of arsenic from contaminated water. In present study we tried Neem Leaves (NL), Neem Bark (NB), Black Berry Seed (BB), Guava Leaf (GL) and Rice Husk (RH) carbon as well as their same proportions (1:1) as mixed bio-adsorbents. The efficiency to remove arsenic from water, the application of mixed bio-adsorbents proved to be more useful than the application of single bio-adsorbents. The experiment has followed batch process. The effect of contact time on removal efficiency of arsenic has been studied in detail. The effectiveness of adsorption is justified by adsorption kinetics. The adsorption kinetics has been to follow first order rate mechanism for BB and NL+NB but other adsorbents like NB, RH, NL, GL and NL+BB followed second order kinetics. All adsorbents followed Freundlich and Langmuir isotherm models.*

### Introduction

Some research concludes that even at the lower concentration there is still a risk of arsenic contamination leading to major causes to death. A study was conducted in a contiguous six country study area of Southeastern Michigan to investigate the relationship between moderate arsenic levels and twenty three selected diseases outcomes. Besides as a carcinogen it is also reported to cause several other diseases like the diseases of the circulatory and respiratory system, diabetes mellitus and kidney and liver malfunctioning. Elevated mortality rates were observed for all diseases of the circulatory system. In 1992, the U.S. EPA listed arsenic as a hazardous air pollutant and recommended a permissible exposure limit of  $10\mu\text{gL}^{-1}$ . As per Indian standards if the arsenic level is above  $0.01\text{mgL}^{-1}$ , it is recommended to stop using the water for drinking and cooking. If the arsenic level is below  $0.01\text{mgL}^{-1}$  in the drinking water it is safe to drink. Earlier arsenic has been used as a pesticide and rodent poison, in the production of pigments and chemical weapons (e.g. mustard gas), in semiconductors, in wood preservatives and as a growth promoter for poultry and pigs. Because of wide spread health hazards like cancers, the use of arsenic nowadays is primarily restricted to metallurgical applications and to the manufacture of wood preservatives. Humans can take up arsenic by ingestion, by inhalation and through skin or mucous membranes. Well water in regions of the world that have naturally high levels of arsenic in the ground water will represent a route of exposure through drinking water for humans as well as for livestock. Food and ambient air are other significant vectors of arsenic exposure to humans (9). Arsenic is not only a physical but also a social phenomenon (10). There is a strong link between poverty and arsenicosis diseases. Arsenicosis enhances the economic burden to the poor. Most of the poor arsenicosis patients remain untreated due to financial restraints. For example 20-70% of the patients did not receive treatment in Bangladesh due to financial problems (11). This lack of treatment further deteriorates the overall health and economic conditions of arsenicosis patients to go for treatment, they need to spend a big proportion of their money on this, which finally diminishes the household income and increases the economic burden on the poor victims and their families (12). Moreover, the cost of obtaining arsenic free water also diminishes household income (11). However, the effects of arsenic toxicity on mental health and associated social consequences have not been well reported and hence more scientific attention is needed. Arsenic removal technologies are highly important to irradiate the physical and mental health problems and their social impacts among the ar-

senic affected victims of the society. In this study we have used NL, NB, GL, RH and BB as these are easily available material for the arsenic removal. The objective of this work is to investigate the effectiveness of different biomaterials for adsorption of arsenic from water.

### Adsorbents

In the present study some new single or mixed adsorbents are used

1. Black Berry (*Syzygium cumini*) seed powder
2. Guava (*Psidium guajava*) leaf Powder
3. Neem (*Azadirachta indica*) bark and Neem leaf powder
4. Activated Rice husk (*B.N. Oryza sativa*) carbon
5. Mixed adsorbents (1:1) (NL+BB) (NL+NB)

### Material Development

Black Berry Seed (BB), Guava Leaf (GL), Neem Leaf (NL) and Neem Bark (NB) were collected and were washed with tap water to remove dirt and other particulate matter. They were dried in sunlight. The collected materials were grounded and sieved to get the particle size of 60-250 $\mu\text{m}$ . Acid treated biomasses were washed with distilled water until maximum colour was removed. Rice Husk (RH) was obtained from a grocery store in M.P. Rice husk was partially carbonized in laboratory Oven at  $250^\circ\text{C}$  to  $300^\circ\text{C}$  for 4 to 5 hours. The partially carbonized material was then completely carbonized in muffle furnace at temperature  $500^\circ\text{C}$  to  $600^\circ\text{C}$ . The material from muffle furnace was cooled to room temp. Material was then repeatedly washed with hot boiling water. Acid Treated biomass was washed with distilled water.

### Preparation of Arsenic Standard Solution

Dissolved 1.320gm Arsenic Trioxide ( $\text{As}_2\text{O}_3$ ) in 10ml distilled water containing 4gm Sodium Hydroxide (NaOH) and dilute to 1000ml with distilled water.

1ml = 1.0mg As

Now diluted 10ml arsenic stock solution to 1000ml with distilled water to prepare arsenic intermediate solution. For making arsenic standard solution diluted 10ml arsenic intermediate solution to 100ml distilled water.

### Batch Adsorption Studies

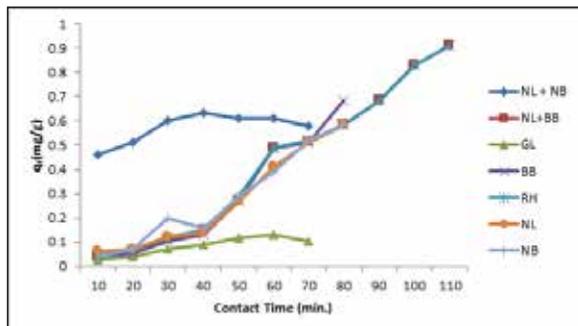
Batch adsorption studies were carried out by using different single adsorbents and their combinations in different proportions using amount of all single and mixed adsorbents is 2g/L. The measurements as pH, conductivity and TDS were taken by

Systronics-MV-VI, Systronics-113 and Toshniwal TCM-15 respectively. Effect of pH, effect of contact time, effect of temperature, effect of adsorbent dose were studied. Variation in contact time was studied in detail.

**Result and Discussion**

**Effect of Contact Time**

Effect of contact time (10 to 100 minutes) on adsorption of arsenic from an optimum initial arsenic concentration by different adsorbents is presented in Fig.1. The mixture was agitated at 25°C with 225rpm. The sample was taken at regular intervals, filtered and then analyzed. Observations are represented in Fig.1. It was found that the arsenic removal increases with increase in contact time to some extent. The removal of arsenic by the adsorbents increases, reaches a maximum value and then decreases with the increase in contact time (It may be due to desorption process).



**Fig. 1 : Effect of contact time on adsorption of arsenic**

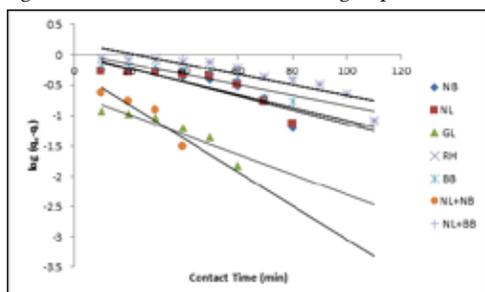
**Kinetics of Arsenic Adsorption**

In order to investigate the mechanism of this adsorption process the pseudo first order kinetic model, the pseudo second order kinetic model, the intraparticle diffusion model and Elovich model were all used to test the experimental data.

The Langergen pseudo first order rate expression is given as

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t$$

Where  $q_e$  and  $q_t$  are amounts of fluoride ions adsorbed (mg/g) on adsorbent at equilibrium and at time  $t$ , respectively and  $K_1$  is rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). The slope and intercept of plot  $\log (q_e - q_t)$  against  $t$  give values of  $K_1$  and  $q_e$  respectively. Pseudo first order plot  $\log(q_e - q_t)$  against  $t$  is shown in Fig.2. Pseudo first order rate constant ( $k_1$ ),  $q_e(\text{exp})$ ,  $q_e(\text{the})$  and linear correlation factor ( $R^2$ ) values are given in Table 1.  $q_e(\text{the})$  values for BB and NL+NB obtained from pseudo first order plot were found to be in good agreement with  $q_e(\text{exp})$  values than those obtained from pseudo second order plot. This indicates that BB and NL+NB followed first order kinetics and weak Vander Waal forces (physisorptions) are playing major role in adsorption. But for other adsorbents like NB, RH, NL, GL and NL+BB there may be a possibility for chemisorptions playing a significant role in the rate determining step.



**Fig. 2 : Pseudo first order plot of effect of contact time on**

**adsorption of arsenic.**

**Table-1 : Pseudo First Order Model**

Adsorbent	$q_e$ (exp)	$K_1$	$q_e$ (the)	$R^2$
NB	0.583	0.02	1.020	0.870
NL	0.583	0.02	0.993	0.860
GL	0.131	0.02	0.030	0.683
RH	0.911	0.01	0.362	0.900
BB	0.683	0.01	0.704	0.891
NL+NB	0.611	0.02	0.650	0.686
NL+BB	0.911	0.01	1.570	0.900

exp (experimental), the (theoretical)

The Langergen pseudo second order kinetic model is given as  $t/q_t = 1/(K_2 q_e^2) + t/q_e$

Where  $K_2$  is rate constant of second order adsorption ( $\text{mg/g/min}$ ) (2). Slope and intercept of plot of  $t/q_t$  against  $t$  gives values of  $q_e(\text{the})$  and  $k_2$  respectively. Pseudo second order plot  $t/q_t$  against  $t$  is shown in Fig.3. Pseudo second order rate constant ( $K_2$ ),  $q_e(\text{exp})$ ,  $q_e(\text{the})$  and  $R^2$  values are given in Table 2.  $q_e$  (the) values for NL, NB, GL, RH and NL+BB obtained from pseudo second order plot were found to be in good agreement with  $q_e(\text{exp})$  values than those obtained from pseudo first order plot. This indicates that NL, NB, GL, RH and NL+BB followed second order kinetics.

**Fig.3 : Pseudo second order plot of effect of contact time on adsorption of arsenic**

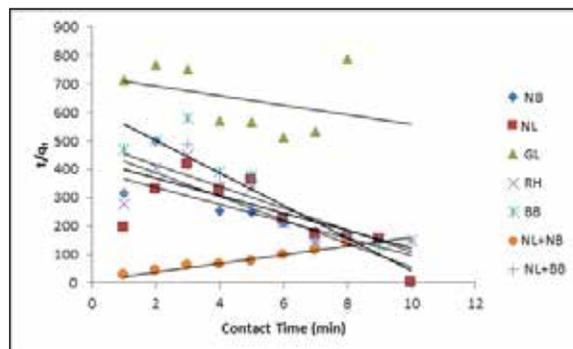
**Table – 2 : Pseudo Second Order Model**

Adsorbent	$q_e$ (exp)	$K_2$	$q_e$ (the)	$R^2$
NB	0.583	0.03	0.270	0.980
NL	0.583	0.01	0.471	0.880
GL	0.131	0.06	0.130	0.730
RH	0.911	0.01	0.800	0.910
BB	0.683	0.05	0.171	0.680
NL+NB	0.611	0.62	2.001	0.610
NL+BB	0.911	0.01	0.740	0.910

According to Weber and Morris , the intraparticle diffusion rate-constant ( $K_i$ ) is given by the following equation

$$q_t = K_i t^{1/2} + A$$

$K_i$  ( $\text{mg/g/min}^{1/2}$ ) intraparticle diffusion constant and A gives an idea about the thickness of the boundary layer. Table 3 are determined from the slope and intercept of the plot  $q_t$  against  $t^{1/2}$ . Fig.4 showed a linear relationship after certain time but they do not pass through origin due to boundary layer effect. The larger the intercept, the greater the contribution of surface sorption in rate determining step. Initial portion is attributed to the liquid film mass transfer and linear portion to the intraparticle diffusion.



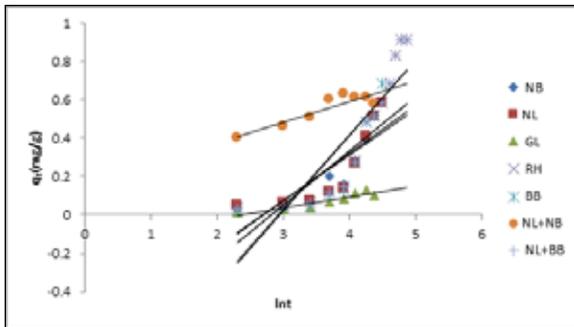
**Fig. 4 : Intraparticle diffusion plot of effect of contact time on adsorption of arsenic**

**Table – 3 : Intraparticle Diffusion Model**

Adsorbent	$K_i$	A	$R^2$
NB	0.09	0.36	0.930
NL	0.08	0.34	0.900
GL	0.004	0.07	0.720
BB	0.10	0.45	0.900
RH	0.12	0.55	0.950
NL+NB	0.07	0.92	0.954
NL+BB	0.12	0.56	0.951

The linearized form of Elovich kinetic equation is presented as  $q_t = 1/\beta\{\ln(\alpha\beta)\} + \ln t/\beta$

found to be  $\leq 0$  indicates that there is no any contribution of surface sorption in rate determining step. Elovich kinetic model constants  $\alpha$  and  $\beta$  are calculated from the intercept and slope of plot Fig.5  $q_t$  against  $\ln t$ . Constant  $\alpha$  depends upon initial rate of adsorption which is found to be high but constant  $\beta$  which is desorption constant has the low value for the same adsorption. Table 4 are determined from the intercept and slope of plot  $q_t$  against  $\ln t$ .



**Fig. 5 : Elovich plot of effect of contact time on adsorption of arsenic**

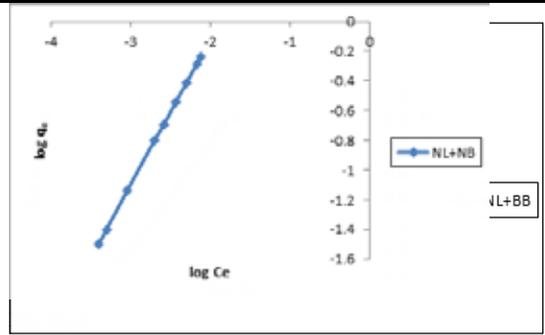
**Table – 4 : Elovich Model**

Adsorbent	$\alpha$	$\beta$	$R^2$
NB	0.54	20.0	0.220
NL	0.11	7.14	0.530
GL	0.01	16.60	0.091
BB	0.39	16.66	0.206
RH	3.63	2.60	0.880
NL+NB	4.19	5.00	0.542
NL+BB	3.59	2.56	0.885

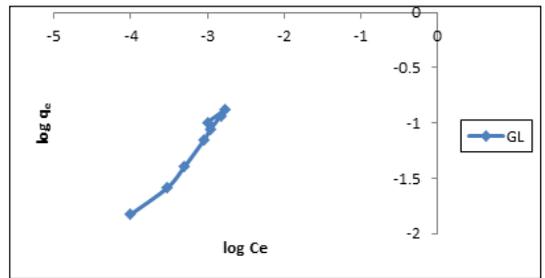
Freundlich and Langmuir adsorption isotherms were used to study the adsorption behavior of arsenic ions on adsorbents. The linear form of Freundlich isotherm equation is employed for the adsorption of arsenic onto the adsorbents and is represented by

$$\log q_e = \log k_f + 1/n \log C_e$$

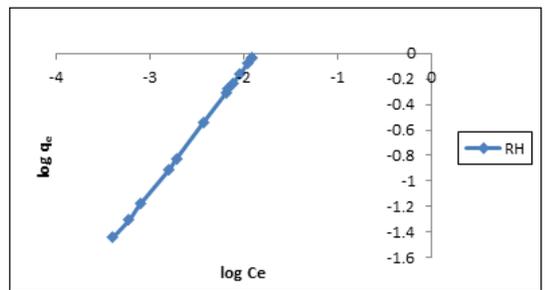
Where  $q_e$  is the amount of arsenic adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of arsenic in solution (mg/L). A plot (Fig. 6(a-g)) of  $\log q_e$  against  $\log C_e$  gives a straight line,  $K_f$  and  $n$  are constant incorporating factors affecting the adsorption capacity and intensity of adsorption calculated from the intercept and slope of the plot respectively. The values of  $K_f$ ,  $n$  and  $R^2$  are given in Table 5.  $K_f$  values were found to be high for good adsorbents and low for poor adsorbents and follow the same order as the order of adsorption capacities of adsorbents. Values of constant  $n$  lie between 1 and 10 indicating the adsorption of arsenic which obeys the Freundlich adsorption isotherm.



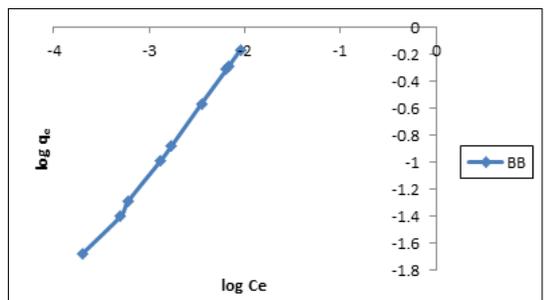
**Fig. 6(b)**



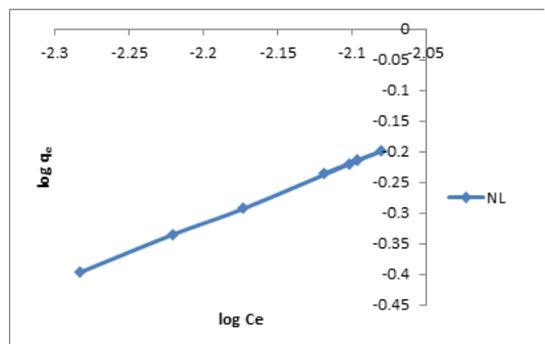
**Fig. .6(c)**



**Fig. 6(d)**



**Fig. 6(e)**



**Fig. 6(f)**

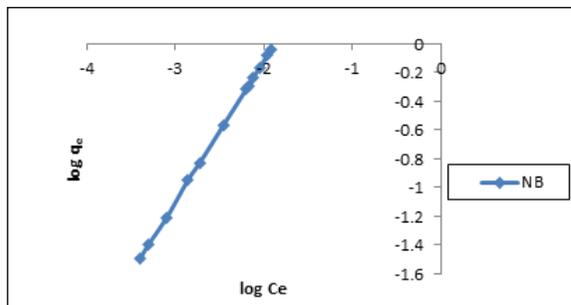


Fig.6(f)

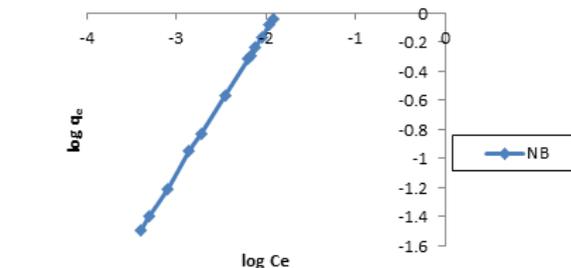


Fig. 6(g)

Fig. 6(a-g) : Freundlich Isotherm Plots

Table - 5 : Freundlich Isotherm Parameters

Adsorbent	$K_f$	$n$	$R^2$
NL	1.009	8.3	0.920
NB	70.79	1.0	0.990
GL	1.12	2.5	0.970
BB	1.77	2.4	0.860
RH	63.09	1.0	0.990
NL+NB	70.79	1.0	0.999
NL+BB	66.06	1.0	0.990

The linear form of Langmuir isotherm is represented by the following equation

$$1/q_e = 1/a + 1/abC_e$$

When  $1/q_e$  is plotted against  $1/C_e$ , a straight line with slope  $1/ab$  is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Fig. 7(a-g). The Langmuir constants  $a$  (adsorption capacity, mg/g) and  $b$  (energy of adsorption, L/mg) are calculated from the intercept and slope of the linear plot. Equilibrium parameter  $R_L$  is represented as follow

$R_L = 1/(1+bC_0)$  where  $C_0$  is initial concentration of arsenic (mg/L). The values of  $a$ ,  $b$  and  $R^2$  are given in Table 6. A linear plot of  $1/q_e$  against  $1/C_e$  suggests the applicability of the Langmuir isotherms.

Table - 6 : Langmuir Isotherm Parameters

Adsorbent	$a$	$b$	$R^2$
NL	12.5	0.80	0.995
NB	20.0	5.00	0.999
GL	0.22	10.0	0.966
BB	0.56	20.0	0.991
RH	2.63	50.0	0.998
NL+NB	16.66	6.25	0.999
NL+BB	3.03	33.33	0.991

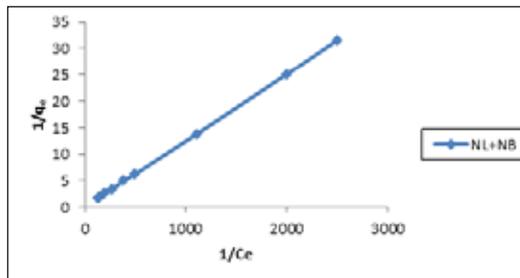


Fig. 7(a)

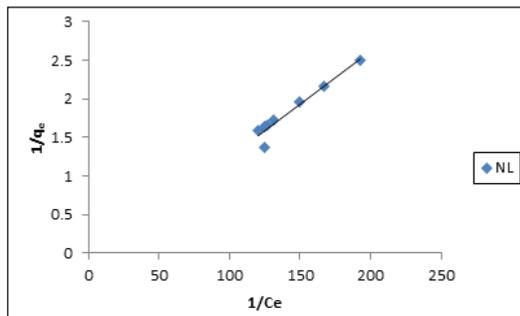


Fig. 7(b)

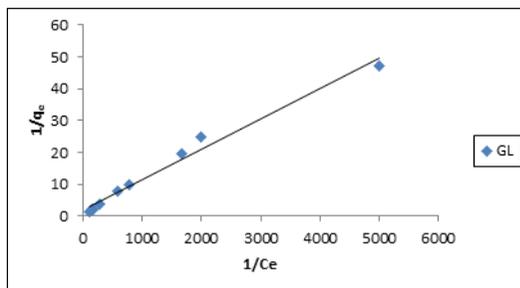


Fig. 7(c)

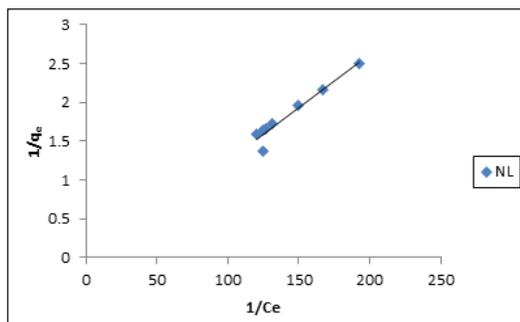


Fig. 7(d)

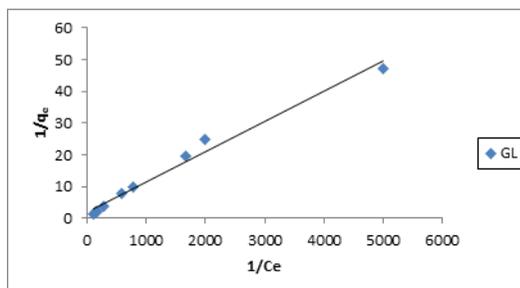


Fig. 7(e)

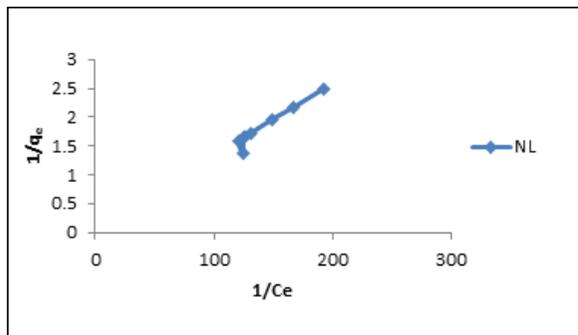


Fig. 7(f)

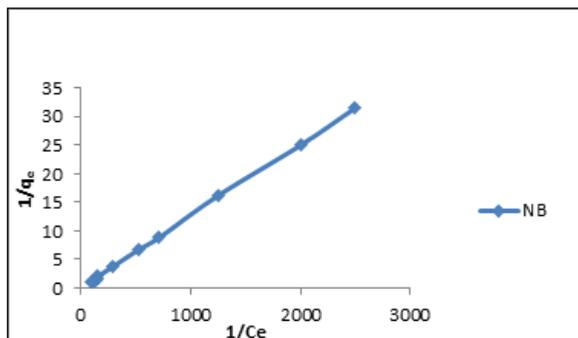


Fig. 7(g)

Fig. 7(a-g) : Langmuir isotherm plots of different adsorbents

### Conclusion

The adsorbents used in the present study have proved to be very efficient and economical for removing arsenic from water. The substrate raw materials employed are widely available and inexpensive. The arsenic removal capacity of these adsorbents is appreciably high. Thus it can be concluded that these alternative adsorbents seem to offer a very cheap and useful products for effective removal of arsenic from water. It is also clear from the above data that mixed adsorbents give more effective and satisfactory results as compared to the single one.

### Acknowledgement -

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