B−38 EVALUATION OF BIOSORBENT EFFICIENCY FOR PRB TECHNOLOGY AT DIFFERENT TEMPERATURE

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1. INTRODUCTION

Nowadays, heavy metals have become the cause of water pollution and an environmetal priority in order to achieve strict regulations and protect human health[1]. For this reason, many passive treatment had been studied in separate or in combination to remove toxic heavy metals from groundwater. Recently, studies have shown that passive treatment such as Permeable Reactive Barrier has higher potential advantage than conventional remediation methods, because of its long-term operation and low cost[2]. Although this technique started by using zero valent ion, they had experienced problems, therefore it is required a new material alternative. Furthermore, the application of biosorbents on heavy metal removal has gained attention, since there are plenty studies of different biosorbent that could be used for PRB technology[3]. However, even though there are abundant biosorbents, the use of high efficient materials on Permeable Reactive Barriers in cold regions remains little explored[4]. Thus, this investigation evaluate *Undaria pinnatifida* and *Phragmites australis* to state whether these biomasses can be applied at different temperatures on PRB technology.

2. MATERIALS AND METHODS

Undaria pinnatifida and *Phragmites australis* were chosen from different efficient biosorbents previously studied because of its availability and high performance respectively.[5,6] As for the case of *Undaria pinnatifida,* batch experiments were perfomed for raw material (RSW), and waste from a food factory in Miyagi Prefecture. (CSW) in the case of Reed, it was harvested near Hirose river, Japan. Biomaterials were washed to remove impurities and reduced to particle size of 0.125-0.250 mm and 1-2 mm for storage into a desiccator. Solutions of lead were prepared by using lead (II) acetate trihydrate.

0.1 g of biomaterial was added to 50 ml of lead solution and shaken for 24 hours and Langmuir model was used to describe heavy metal sorption from the equation:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{1a}$$

Whereas:

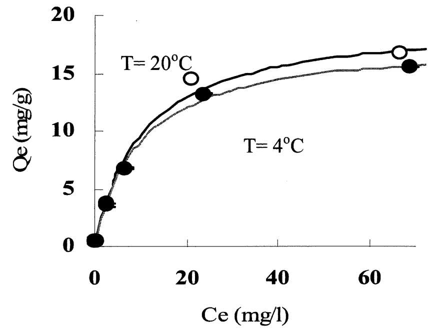
$\boldsymbol{Q_{max}}$ is the maximum amount of metal ions adsorbed per unit weight of adsorbent
$\boldsymbol{Q_e}$ is the equilibrium metal concentration in solid
$\boldsymbol{C_e}$ is the equilibrium metal concentration in liquid phase
$\boldsymbol{b}$ is the coefficient of affinity between the metal ion and the adsorbent

This widespread model was plotted at concentrations of 1.1, 10, 50, 100 and 400 mg/L. Batch experiments were held under same conditions at two different temperatures (4°C and 20°C), factors such as pH, particle size, concentration and contact time were analyzed in combination with temperature. Finally, the efficiency of mixed material was quantified.

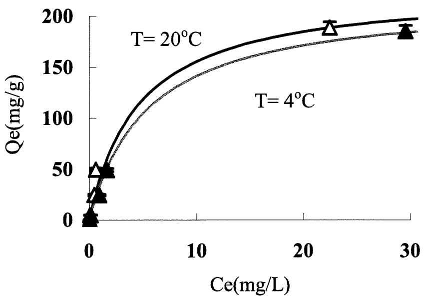
3. RESULTS AND DISCUSSION

(1) Langmuir isotherm of biomaterials

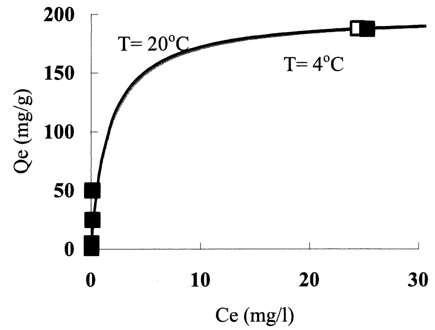
Two equilibrium isotherms plotted for each biomass using Langmuir model are shown in Fig. 1



(a) Reed (R)



(b) Commercial Seaweed (CSW)



(c) Raw Seaweed (RSW)

Fig.1 Effect of temperature on adsorption capacity of biomasses. (a) R, (b) CSW and (c) RSW .

It can be observed that R and CSW biomasses increase the metal concentration in the equilibrium when exposed to 4°C. These results indicate endothermic sorption process. However, in the case of RSW, it did not show significant change at a low temperature. Higher adsorption capacity was observed from RSW and CSW. This result could be attributed to the alginic acid of the seaweed.

(2) Analysis of temperature effect and particle size

From the results, when using big particle size (1-2 mm) the adsorption capacity of R did not change significantly when exposed to low temperatures. However, for smaller particle size (0.125-0.250 mm) affinity was reduced at 4°C. In the case of CSW, Qmax increased with temperature at 20°C, and decreased at low temperatures. The same trend occured to the affinity constant for both particle sizes. RSW did not change its adsorption capacity when exposed to low temperature at big particle size (1-2 mm), while small particle size (0.125-0.250 mm) differs from this result. Thus, this results showed that the influence of temperature is higher on affinity to the biomass surface than Qmax. For all tested biomasses, results indicate a tendency of lead affinity reduction due to low temperature at smaller particle size.

(3) Analysis of temperature effect on lead adsorption in function of time

R biomass gradually removed lead from the first 30 minutes better at 20°C than 4°C. Therefore, low temperature slows the removal process for R. As for CSW, after 60 minutes it reaches the equilibrium at 4°C; and at 20°C when the solution reaches 240 minutes higher adsorption can be observed. It is possible that when the removal process started, physical adsorbance occurred at 4°C, whereas after a period of time because of endothermic condition the amount of contaminant adsorbed at 20°C increased. At low temperature RSW results did not differ significantly from both temperatures until it reaches the equilibrium after 1440 minutes. Table 1

Table 1 Lead removal in function of time at 20 °C and 4 °C

Time	4 °C Qe (mg/g)			20 °C Qe (mg/g)		
Min	RSW	CSW	R	RSW	CSW	R
30	4.28	3.99	1.95	4.16	3.47	2.13
60	3.76	4.35	2.27	4.1	3.69	2.22
240	4.32	4.38	2.71	4.36	4.62	2.8
1440	4.97	4.86	3.1	4.97	4.99	3.26

(4) Analysis of temperature effect and variation of pH on biomasses

The influence of pH was tested at 10 mg/L in batch adsorption experiments (Fig.2). Firstly, for R a raise of pH can be observed at temperature of 20°C, nevertheless it does not change significantly from the initial pH. On contrary, at lower temperature pH raises and then reduces in time. Secondly, CSW pH varies at both temperatures, and adjusts after achieving the equilibrium. RSW shows a constant trend from the first 30 min can be observed at both temperatures since there is not significant change of pH. In summary, it can be seen that for both seaweed types there is an increase of pH from the initial value at different temperatures whereas reed biomass has different behaviour. The increment of pH could be close related to the adsorption of heavy metal[7].

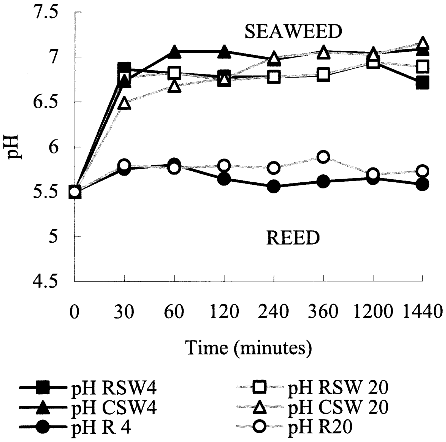


Fig.2 Variation of pH at different temperature

(5) Comparison of seaweed and reed.

Quantity of adsorbed contaminant in the first 30 minutes is 3.9 mg/g for CSW, 4.5 mg/g for RSW, on contrary of common reed 0.5 mg/l. Although after 6 hours an increasing uptake trend starts for reed biomass, it barely achieves values between 1.8-1.7 mg/l of contaminant uptake mass in 24 hours. It is evident that seaweed surface area is more suitable for this contaminant. This could be attributed to difference of microstructure surface of the biomasses which make more suitable for lead uptake, and its carboxylic groups. However, higher uptake was observed at low concentrations for R in comparison of both types of SW.

(6) Removal efficiency for mixed material at different concentrations.

Table 1 shows the comparison of adsorption at different temperatures for low concentrations by using mixed materials. Fig. 3 describes the behavior of mixed material (1:1 in dry weight) at 20°C and 4°C. The process at low temperatures seems to slightly increase the performance of the removal process, which cannot be understood as both biomasses showed endothermic removal process. Consequently, statistical analysis was made, showing significance in low concentrations. It can be estipulate the differences on adsorption at low temperature, as lower percentage removal is adsorbed at high temperatures; however from the significant values obtained the difference varies between concentrations.

Table 1 Lead removal by mixed materials

Co (mg/L)	20 °C *Ce (mg/L)*	*(%)*	4°C *Ce (mg/ L)*	*(%)*	P-val.
0.1	0.100	0.03	0.098	2.35	0.06
0.5	0.133	73.47	0.094	81.15	0.01*
1	0.101	89.87	0.098	90.15	0.39
5	0.314	93.71	0.234	95.33	0.01*
10	0.546	94.54	0.556	94.44	0.27

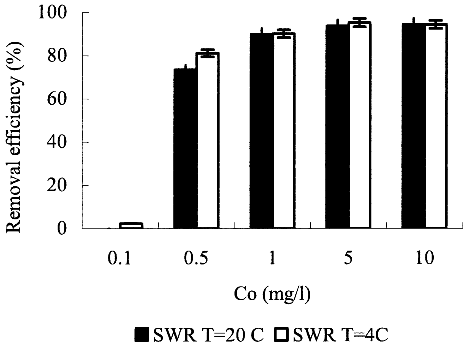


Fig.3 Removal efficiency by mixed materials

3. CONCLUSIONS

Temperature seems to affect specially affinity of lead to the biomasses. However, as mixed material further study is needed to asseverate the results obtained and to understand the mechanism at these extreme temperatures.

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