Preparation of adsorbent from eco-friendly material for treatment of Petroleum industry effluent

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Abstract

The produced water obtained along with crude oil upon extraction is reinjected into the reservoir to maintain its water pressure and improve its oil producing characteristics. Treatment and handling of produced water before reinjection has been a major concern for the upstream industries. A commonly used method for treatment of produced water is adsorption. In this paper we have also done a comparative study of existing material used for preparing activated carbon and their industrial application. We are using eco friendly materials for preparing activated carbon which was not used earlier for treating petroleum industry produced water at polishing stage. Our objective is to use this technique by preparing activated carbon prepared from bamboo and coconut shells in order to minimize the cost and improve efficiency. We shall assess the removal efficiency of contaminants using the selected carbon and analyze the effect of various parameters like initial concentration, temperature, etc on the removal of contaminants from the produced water. We shall also study the kinetics of the process, and analyze the adsorption models, and breakthrough curves.

Keywords: adsorption, bamboo, coconut shells, efficiency, kinetics, produced water

Introduction

1.0 Produced water and its environmental impacts

Extraction of oil and gas from reservoirs is accompanied by flow of water or brine, which is referred to as produced water. As the extraction of oil continues and the reservoir matures, the quantity of production water exceeds the volume of hydrocarbons before the reservoir is exhausted. The cost of handling this water is too high and contributes to a major chunk of economical expense of the industry. Hence it is vital to understand the behavior of and problems involved in dealing with produced water. [1]

In early years, production waster was treated as waste, instead of treating the water it was disposed off. However, with advancement in technologies and water conservation being the need of the hour in growing years, production water has been used for reinjection into the reservoir well which serves two purposes: it produces additional petroleum through secondary recovery, and controls land subsidence in some areas.

Production water consists primarily of oil, grease, and dissolved organic compounds like benzene, naphthalene, and toluene. Salts in produced water are generally chlorides and sulfides of elements such as Calcium (Ca), Magnesium (Mg), and Sodium (Na). Lead, chromium, and nickel being the major constituent, barium, manganese, iron, strontium, zinc, silver, cadmium, lithium, copper, mercury, arsenic, selenium, boron, and antimony may also be present in trace amounts.

Before disposing produced water, or injecting it into the reservoir, it is important to treat it. Primary stage of produced water treatment involves three phase separators, knock out drums, and heater treaters and the secondary stage of treatment consists of Induced Gas Floatation, Induced Static Floatation, Micro Bubble Floatation. The final stage of treatment involves activated carbon media filtration.

Table 1 Characteristics of typical oil field PW [1]

Parameter	Unit	Value
Density	kg/m^3	1014-1140
Surface tension	dynes/cm	43-78
TOC	mg/l	0-1500
COD	mg/l	1220
TSS	mg/l	1.2-1000
pH	-	4..3-10
Total oil	mg/l	2-565
Volatile (BTX)	mg/l	0.39-35
Chloride	mg/l	80-200000
Bicarbonate	mg/l	77-3990
Sulphate	mg/l	2-1650
Sulphide	mg/l	10
Total polar compounds	mg/l	9.7-600
Higher acids	mg/l	1-63
Phenols	mg/l	0.009-23

Table: 1 source: Masoud Nasiri1 , Iman Jafari1* Periodica Polytechnica Chemical Engineering 61(2), pp. 73-81, 2017

If untreated, production water is harmful for the environment, as well as the reservoir conditions and operational equipments. The chloride content in production water is ten times higher than that of sea water. Untreated production water can adversely affect the groundwater, wildlife, and also alter the reservoir conditions and hamper oil recovery.

Parameter	**Drinking water criteria**	**CBM produced water**	**Natural gas produced water**
pH	6.5 – 8	7 - 8	6.5 – 8
TDS (mg/L)	500 (taste)	4,000 – 20,000	20,000 – 100,000
Benzene (ppb)	5	<100	1000-4000
Na+ (mg/L)	200	500-2000	6000-35000
Barium (mg/L)	-	0.001-0.1	0.1-40
Cl- (mg/L)	-	1000-2000	13000-65000
HCO3	-	150-2000	2000-10000

Table 2 source: Hayes, T. and Arthur, D. 2004. Overview of Emerging Produced Water Treatment Technologies.

Adsorption treatment process

Adsorption process involves the physical adhesion of the polluting chemicals onto to the surface of a solid. It can be accomplished by using a variety of materials like activated carbon, bentonite, sand, coal, etc. Activated carbon is commonly used in removal of wide variety of salts and oil, and has proved to be technically feasible. Upon experimental research on petroleum hydrocarbon contaminated produced water, it was found that PAC (powdered activated carbon) is more effective than GAC (granular activated carbon), and hence its use is recommended. Activated carbon adsorption has been recommended by United States Environment Protection Agency (USEPA) as one of the best available technologies for removing organic impurities.

Powdered activated carbon can be used in cases of industrial oil spills and algae blooms that contaminate municipal waters. On the other hand, granular activated carbon can remove impurities present in amounts lesser than the detection limits. However, a plant requires a well-equipped set up to use GAC, and also to thermally regenerate it. Thermal regeneration of GAC in a furnace is classified as 'green technology'.

Performance of adsorbents is affected by many factors like pH, temperature, concentration of contaminants, and amount of suspended solids and oils. The medium is backwashed regularly to remove large particulates which block its active sites. Adsorbents are capable of removing iron, total organic carbon, heavy metals, and oil content of produced water.

The rate of adsorption medium usage is important for cost of adsorption process. When all the active sites have been occupied, or the adsorbent is exhausted, it is necessary to regenerate or dispose it. Easy regeneration of adsorbent is necessary to make the process cost effective.

Adsorption by activated carbon is used in the oil and gas industry for many purposes. It is used in midstream gas processing for condensate decolorization. Decolorization helps to prepare the condensate to be transported further in pipelines for fractionation. It also helps in removal of sulfur. Activated carbon is also used as a catalyst carrier in mercaptan sweetening of heavy fraction hydrocarbons. This is done by catalytic extraction of mercaptans from heavy hydrocarbons,

1.1. Adsorption isotherms

The adsorption of a substance from a liquid medium onto the surface of a solid adsorbent leads to the development of thermodynamically stable environment, based on the properties of the solute and the adsorbent. When the system reaches equilibrium, the rate of adsorption of the liquid medium onto the adsorbent is equal to the rate of desorption of the solute back into its parent medium. At this stage, the net adsorption is said to be zero.[2]

Many mathematical expressions have been developed to describe the equilibrium distribution of the solute in both phases at constant temperature. This helps interpreting the adsorption process. However, the most commonly used relations are Langmuir and Freundlich isotherms.

1.1.1. Langmuir isotherm

The Langmuir equation for a solid-liquid system is written as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$$

Where, K_L is empirical constant related to the affinity of the binding sites, L/mg; and q_{max} is the maximum amount of the adsorbed impurity per unit mass of adsorbent, mg/g. q_e is the amount of adsorbed impurity per unit mass of adsorbent, mg/g; and C_e is the amount of unadsorbed impurity per unit mass of adsorbent, mg/g.

The equation can be written in linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L}$$

Therefore, a plot of C_e / q_e vs C_e gives a straight line with slope $1/q_{max}$ and intercepts $1/q_{max}K_L$.

The essential characteristics of the isotherm can be defined using a dimensionless parameter R_L which is given as:

$$R_L = \frac{1}{1 + K_L C_0}$$

Where, equilibrium parameter is R_L, and C_0 = initial impurity concentration, mg/L.

Value of R_L	Type of isotherm
>1	Unfavourable
1	Linear
0-1	Favourable
0	Irreversible

Table 3: Equilibrium parameter for Langmuir model (Vargas *et al.*, 2009)

1.1.2. Freundlich isotherm

Freundlich isotherm can applied to non ideal adsorption on heterogeneous surfaces. It can be mathematically expressed as:

$$q_e = K_F C_e^{\frac{1}{n}}$$

Where, q_e is the amount of adsorbed impurity per unit mass of adsorbent, mg/g; and C_e is the amount of unadsorbed impurity per unit mass of adsorbent, mg/g. K_F is the Freundlich constant, mg/g; and n is empirical constant.

Freundlich adsorption model is used when multiple layer coverage of the surfaces is expected and the site is heterogeneous with different binding energy. K is a constant for given adsorbate and n is a constant for given adsorbent at a particular temperature. The exponent $1/n$ is usually less than 1.0 because sites with the highest binding energy are utilized first, followed by weaker sites, and so on.

2.0 Experimental Study

2.1 Preparation of adsorbents

For the study, two types of activated carbon samples were prepared. First, dry bamboo was procured from the nearby vendor. It was then separated into two types, powdered bamboo and granular bamboo. Granular bamboo was prepared by cutting up the bamboo into small pieces, approximately 3mm x 3mm in size. At the same time, coconut shells were procured and dried in an air dryer for one hour, at a temperature of 60°C. Coconut shells and bamboo were chosen due to their easy availability, and low cost. Our objective is to device a cheap method for the industrial application of adsorption technique. More importantly, bamboo and coconut shells have high lignin content. High lignin content imparts better adsorption characteristics (especially of metal ions).

The dried bamboo was then divided into four parts and placed in four crucibles. These crucibles were then placed in the Muffle furnace at 400°C for two hours, in order to carbonize the sample and get rid of the ash content.

The samples of bamboo placed weighed as follows:

A – 4.5 gm
B – 6.6 gm
C– 11.4 gm
D – 12 gm

The charred sample was then grinded and weighed accurately. To this sample, accurately weighed Barium Chloride was added in order to activate the sample. In order to allow the chemical to impregnate and react with the sample, it was placed in the oven at 400°C for 4 hours. Once the impregnation was done, the sample was washed with water and then allowed to dry. With the completion of this step, the sample of desired activated carbon was ready. The same procedure is repeated for coconut shells.

Various types of samples of activated carbon were considered and their properties and efficacy were studied. Different types of available water samples were considered for the study. The results are summarized as follows.

Nomenclature:

GAC – Granular Activated Carbon
PAC – Powdered Activated Carbon
PW – Produced Water
ACTF – Amorphous Carbon Thin Film
ACNFN – Activated Carbon Nanofiber Nonwoven

Activated carbon type	**Water source**	**Temperature**	**Chemical**	**Technology**	**Efficacy**	**Adsorption isotherm**
PAC Bentonite	Petroleum Comp, Egypt	-	-	-	98.3% oil recovery	Freundlich is more efficient
ACTF from plant leaves	Raw PW	308K	1% (wt/wt) sulfuric acid	FTIR, BET, EDX, SEM, TEM	66.36%	Thomas model is most efficient
Organoclay, zeolite	PW	-	-	Hydrocyclone, AOP	-	-
GAC Nigerian bamboo	PW from FCC unit	400-500 ºC	0.1M HCl	Refractometer, spectrophotometer	62.4%	Freundlich is most efficient
GAC non fiber, non-woven ACNFN	Emulsified oil	-	Polymeric solution	Electrospinning	95%	Various adsorption models
GAC charcoal Nigeria bamboo	Refinery waste from Warri petrochemical	300-400 ºC	0.1M zinc chloride	Atomic spectrophotometer for Pb and Cu	Effective removal of Pb and Cu	-

Table 4: Comparative Study of Various parameters based on different papers

Figure 1: Dry bamboo samples subjected to muffle furnace at temperature of 380-400 C.

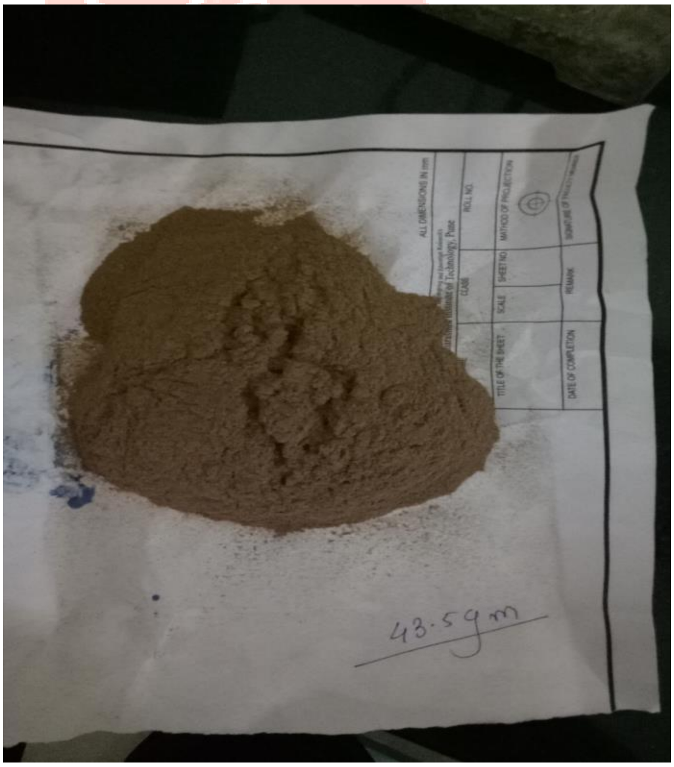

Figure 2: Powdered form of local bamboo.

Figure 3: Dry bamboo samples placed in crucibles to carbonize in muffle furnace.

The activated carbon samples of coconut shells and bamboo are then used to analyze their properties of adsorption at various temperatures and pH. The efficacy of the sample is determined, and the adsorption curve is studied.

Results

By using activated carbon prepared by Bamboo and coconut shell for petroleum produced water treatment at polishing stage, there will be increase in the removal efficiency of impurity (by adsorption process). Comparing it with prepared activated carbon with commercially activated carbon, reduces the treatment cost. This work examines the adsorption and treatment of pollutants in produced wastewater from petroleum field using granular activated carbon and powdered activated carbon. Tthis work provides an alternative to currently available commercial activated carbon. Proper utilization of waste material in terms of value added product.

Discussion

Problem exists for petroleum field crude production during winters as the temperature drops there is formation of scum/ jelly. API gravity of crude is low and Water cut is high. Scum is formed because of impurities like organic compounds, n-HEM (n-hexane extractable material) (O & G). Operator Company doesn't want to change the existing setup and also don't want to invest more money. Scum increases injection pressure and reduced injectivity. So the problem was identified at the polishing stage where adsorption beds are used for removal of residual hydrocarbon, the ppm concentration of residual oil during winter's increases. Pressure maintenance is not achieved & production declines. Operator Company wants modification where setup design is not changed and small or reduced operating cost is incurred. If choking/ clogging of adsorption bed exist then operator has to discard the existing adsorbent in use, increases cost. After studying the problem we have concluded to replace the existing adsorbent material with easily available, economical, biodegradable and reusable material as adsorbent.

Conclusion

Not much variety of cheap and bio degradable adsorbents are available in market for commercial use for treating produced water**.** we will be able to make better use of this cost effective, abundant available and biodegradable adsorbent, it is easy to convert it into activated carbon that becomes more useful and value-added adsorbent. The mode of operation selected in this study is batch type. which will prove helpful in the selection of various parameters useful in the design and fabrication of a continuous treatment process having low input and high output policy. This work can provide practical solution to the operator company as an ecofriendly substitute of adsorbent material.

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