CLEISEANO EMANUEL DA SILVA PANIAGUA
(ORGANIZADOR)

Collection:
APPLIED CHEMICAL ENGINEERING

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CIÊNCIAS EXATAS E DA TERRA E ENGENHARIAS

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APRESENTAÇÃO

The e-book: “Collection: Applied chemical engineering” consists of ten book chapters that were organized and divided into four thematic units, namely: *i*) natural products: extraction and purification of active principles; *ii*) development of new materials: study, comparison, different properties and applications; *iii*) use of analytical instruments for food quality control and; *iv*) development and application of bioadsorbents and advanced treatment technologies to remove contaminants from aquatic matrices.

The first theme presents two studies that evaluated the extraction of essential oil from the Baru species plant (*Dipteryxalata Vog.*) with nematicidal activity in combating *Meloidogyne javanica*. The second work evaluated triterpene purification processes from plant bioactives of Amazonian species. The second theme consists of three book chapters aimed at the study and comparison of natural, glass and mixed fibers for future applications; preparation of graphene oxides for production as composites in the form $Cu/TiO_2/rGO$ and estimates of thermodynamic properties of esters used in the production of biodiesel using a Gaussian software associated with the Constantinou and Gani group method.

The third thematic unit consists of two works, one using the UV-Vis spectrophotometry technique to quantify the metallic ions of cadmium, copper, chromium, mercury, nickel and lead in cheeses produced by hand on rural properties; the second work evaluated the Kombucha probiotic and its importance in fermented foods. Finally, the fourth and last theme consists of three works with different approaches. The first deals with the possible environmental impacts that can be caused to water and soil as a result of exposure to Fracking gas present in Mexico. The second presents the study of the adsorption capacity from the biomass generated by the Andiroba species (*Carapaguianensis Aubl.)* in the removal of copper ions present in wastewater from industrial activities. The third chapter presents the study of the influence of the complexity of different aqueous matrices on the degradation of a mixture of drugs using the solar photolysis processes, TiO_2/Solar and its combination with the addition of H_2O_2. This process constitutes one of the advanced treatment technologies to be made feasible on a large scale as a complementary step to conventional water and sewage treatment processes.

In this perspective, Atena Editora has been working with the aim of stimulating and encouraging both Brazilian researchers and those from other countries to publish their work with quality assurance and excellence in the form of books, book chapters and articles that are available in the Editora’s website and other digital platforms with free access.

Cleiseano Emanuel da Silva Paniagua

SUMÁRIO

CAPÍTULO 8

MEXICO'S WATER AND SOIL, THREATENED BY FRACKING GAS?

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ABSTRACT: The answer to the question above is yes, they are in danger, an analysis of environmental and toxicological risks was carried out representing the chemicals used in the extraction of Fracking gas, also known as Shale gas, in addition, the amount of chemical substances used per well was determined, highlighting the fifteen with the highest frequency and their high toxicity, as well as the enormous amount of water that this process requires ranging from 10 to 30 million liters, and that if not receiving treatment, as it would be left to the will of the companies, represents a triple environmental risk, starting with the effect on the availability of water, especially in areas of the deposits of this gas that are located in desert or semi-desert areas for the most part, in addition to the contamination of the water itself with the consequent risk to the health of people and the habitat, and as if that were not enough, the contamination of the soil that it would occupy , a 4 meter deep reservoir would imply half a hectare of land occupied for the average volume of water used in each well. A Gas Shale extraction well was recreated with the most commonly used chemical substances in hydrofracturing, preparing mixtures of one liter of water with the aforementioned substances, subsequently the effectiveness of activated carbon to adsorb said substances was evaluated. Through an ANOVA analysis, the differences in the samples treated with the aforementioned adsorbent were determined, the usefulness of activated carbon was verified to separate the chemical substances that are pollutants from the water in which the mixtures are prepared for the extraction of Shale gas.

KEYWORDS: water, soil, gas, fracking.

ÁGUA E SOLO DO MÉXICO, AMEAÇADOS PELO GÁS DE FRACKING?

RESUMO: A resposta para a pergunta acima é sim, eles estão em perigo, foi realizada uma análise de riscos ambientais e toxicológicos representando os produtos químicos usados na extração do gás de Fracking, também conhecido como gás de xisto, além da quantidade de substâncias químicas utilizadas por poço foi apurado, destacando-se os quinze com maior frequência e sua alta toxidade, bem como a enorme quantidade de água que esse processo requer que varia de 10 a 30 milhões de litros, e que se não recebesse tratamento, seria deixada

para a vontade das empresas, representa um triplo risco ambiental, a começar pelo efeito sobre a disponibilidade de água, principalmente nas áreas das jazidas deste gás que se localizam em grande parte em áreas desérticas ou semidesérticas, além das contaminação da própria água com o consequente risco para a saúde das pessoas e do habitat, e como se não bastasse, a contaminação do solo que iria ocupar, a 4 metros de profundidade res ervoir implicaria meio hectare de terra ocupado para o volume médio de água utilizado em cada poço. Foi recriado um poço de extração de xisto gasoso com as substâncias químicas mais utilizadas na hidrofratura, preparando misturas de um litro de água com as referidas substâncias, posteriormente foi avaliada a eficácia do carvão ativado em adsorver as referidas substâncias. Através de uma análise ANOVA, foram determinadas as diferenças nas amostras tratadas com o referido adsorvente, verificada a utilidade do carvão ativado para separar as substâncias químicas poluentes da água em que as misturas são preparadas para a extração do gás de xisto.
PALAVRAS-CHAVE: água, solo, gás, fracking.

INTRODUCTION

The main objective of this research carried out at the installations of Campus Instituto Tecnologico de Parral of the Tecnologico Nacional de Mexico, was to determine the impact of the extraction of this gas in the hydrosphere and lithosphere since the extraction of this energy is not the usual one for the rest of natural gas, one of the findings is that horizontal drilling is made through which are injected between 4 and 20 million liters of water mixed with sand and additives.

Likewise, the risks to human health and the environment of the chemical substances that are mostly used in the extraction of this gas were sought, which may be useful for future exploitations that will take place especially in the North and East of Mexico, the amount of substances can reach thousands, establishing that 15 of them are the most frequently used, among which are alcohols such as methanol, isopropyl alcohol and ethylene glycol, inorganics such as crystalline silica and soda, as well as BTEX, benzene, toluene, ethylbenzene, xylene and strong acids such as sulfuric and hydrochloric.

Fracking gas or Shale gas is a type of natural gas that, instead of being stored in “bags” underground, is embedded within blocks of sedimentary rocks formed from organic materials.

According to Cartocritica based on information from the National Commission of 2018, Hydrocarbons in Mexico, thanks to the Energy Reform there are companies that began with this practice, hydraulic fracturing began to be used on January 26, 1996, in the Jacinto-5 well, in Tabasco, since then and until the beginning of 2016 (cut of the information received from CNH, 2018), one out of every four oil wells in the country (24.3%) has been hydraulically fractured at some point in its productive life, that is, a total of 7,879 wells of the 32,464 existing have been fractured in the 7,879 fractured wells 36,159 fractures have been carried out. The main oil provinces in which it is estimated that there could be shale hydrocarbons are located in Chihuahua, Coahuila, Nuevo Leon, Tamaulipas, Hidalgo, San Luis Potosi, Veracruz and Puebla. States that, in the north, have important problems of water scarcity and overexploitation of aquifers that would be aggravated by the use of hydraulic fracturing, which requires the use and contamination of large amounts of water that are between 9 and 29 million euros. liters of water. While further south, this technique threatens to contaminate important rivers and aquifers on which thousands of people depend.

MATERIALS AND METHODS

This study is of type:

a) Experimental - Sand samples are handled, water is added and 5 of the chemical substances most used in this activity are evaluated, the effectiveness of activated carbon to remove contaminants from the water is evaluated.

b) Descriptive. - The extraction process is studied by the hydro fracture method of the so-called Shale Gas, the chemical substances involved in said process as well as their toxicological and environmental risks are detailed, the above through documentary research.

c) Transversal, because it is a photograph of the situation at the end of 2018, when the current Federal administration began.

Population or Sample

The population is made up of Shale oil and gas wells that in Mexico can reach several thousand, as a sample 7 mixtures with sands from the region are used, the population of chemical substances reaches about 2000 and the sample described is the 15 most frequently used.

Instrument

Observation guides physicochemical and organoleptic data of the mixtures, color and odor for the 7 prepared mixtures, preparation of comparison tables and tables for data analysis.

RESULTS

Water and chemicals per well.

A well from which this gas is being extracted uses an average of 20,000 m3 of water, according to reports from the United States Environmental Agency, 70% of the companies report that the origin of this water is fresh or new, it would involve 1,105.7 kg of sand, 35,000 liters of chemical substances, which would represent 42,424 kg of them.

Fracturing fluids are handled both water-based and diesel-based, the former occurs in 93% of cases, it reports that in the operations of 420 companies in 38,000 wells, 14 chemicals are the most frequent for fracking, at an average maximum concentration of 0.43% by mass, the most frequent are methanol, hydrochloric acid and hydrogenated light petroleum distillates, the general composition of fracture mixtures includes 88% water, 10% quartz and less From 1% chemical additives, there are 698 unique ingredients.

The chemical substances that in the aforementioned mixtures range from sodium chloride, gelatin and citric acid, to others with a high degree of toxicity, the most used is methanol in almost 80% of the 650 fracturing products, followed by isopropyl alcohol in 42% of the products, ethylene glycol in 18.3% and crystalline silica in 32%., hydrated light petroleum distillates, and caustic soda are used as foaming agents as well, being the substances most used with this purpose is 2-butoxyethanol, in 67 products BTEX appear that involve benzene, toluene, xylene and ethylbenzene, in addition to 1-butanol and propylene oxide, hydrofluoric acid, lead and sulfuric acid, in addition to silica and formaldehyde.

Toxicology of fracking chemicals.

A. Methanol:

Inhalation and dermal absorption are the most common routes of entry for occupational exposure. It is metabolized to formic acid which mediates the toxic effects. Weakness, anorexia, headache, nausea. It causes retinal lesions that can progress to permanent blindness as well as pancreatitis, metabolic acidosis. Sedation at high doses can cause seizures and even coma as well as hemorrhagic or ischemic brain damage. Long-term neurological sequelae such as parkinsonism.

B. Isopropyl alcohol:

It is metabolized in the liver to acetone. Prolonged skin contact can cause: After ingestion: nausea, vomiting, abdominal pain, hemorrhagic gastritis, hematemesis. Acute kidney failure, rhabdomyolysis, hemolysis. Depressant effect on the central nervous system ranging from mild sedation to coma.

C. Ethylene glycol:

After its oral intake, it is metabolized by the liver, giving rise to three compounds that mediate its toxic effects. Sedation, metabolic acidosis. It causes acute kidney injury that may require emergency dialysis with variable medium and long-term sequelae on kidney function. Hypertension, tachycardia, cardiac arrhythmias, seizures. Acute pulmonary edema. There are reports of neurological sequelae that manifest weeks after exposure with cranial nerve dysfunction.

D. Silicon dioxide / crystalline silica:

Acute silicosis: after inhalation of high concentrations, it manifests in weeks or a few years with dyspnea, cough, weight loss, fatigue, fever, permanent changes in lung imaging studies, progression to respiratory failure and heart failure of pulmonary origin. Chronic silicosis: manifests 10 to 30 years after initial exposure. It causes chronic cough with or without sputum production, dyspnea on exertion, pathological findings in lung imaging studies, alteration in respiratory function tests. Risk factor for developing bronchogenic carcinoma.

- ### E. Sodium Hydroxide / Caustic Soda:

After its ingestion, it causes inflammation of the tongue and mouth, drooling, vomiting, inflammation of the airway causing stridor and voice changes, there may be esophageal perforation that causes mediastinitis, and possible peritonitis due to stomach or intestinal perforation. Chronic complications: esophageal strictures that cause chronic pain and malnutrition. There is a relationship between esophageal stricture and esophageal carcinoma.

F. Benzene:

Acute effects: dizziness, headache, vertigo, bone marrow damage. Mutagen and carcinogen associated with aplastic anemia, acute and chronic leukemias, multiple myeloma, and lymphoma.

G. Lead:

Children under 6 years of age, and particularly under 36 months, are more susceptible to toxic effects causing behavioral and cognitive alterations that persist into adolescence and adulthood. It has also been associated with hearing loss, especially at high frequencies. Abdominal pain, vomiting, constipation, anemia. Permanent kidney damage decreases vitamin D levels, which affects bone and dental development. Exposure in pregnant women increases the risk of miscarriage, preterm delivery, and small-for-gestational age delivery. In adults, acute symptoms after exposure to high concentrations: abdominal pain, constipation, anorexia, muscle and joint pain, fatigue, headache, memory disturbances, irritability, anemia. Due to chronic exposure, psychiatric symptoms, tremor, neuropathy, brain damage, high blood pressure, kidney damage, fertility disorders are added. Possible carcinogen.

H. Diesel:

Chronic rhinitis, asthma, myopia, cardiovascular events, Increases the risk of lung cancer, bladder and leukemia.

I. Hydrofluoric acid:

By contact: severe burns, electrolyte disorders and cardiac arrhythmias, ophthalmic injuries. Inhalation: damage to the airway that can cause respiratory failure.

J. Copper:

Acute poisoning: nausea, vomiting, diarrhea, gastrointestinal bleeding, anemia, kidney and liver failure, death. Chronic overload has been associated with neurodegenerative diseases. In animal models it is associated with the development of atherosclerosis and diabetes mellitus.

K. Naphthalene:

After ingestion: vomiting, cough, pneumonitis, respiratory failure.

L. Xylene:

Dizziness, headache, blurred vision and other visual disturbances, muscle weakness, speech disturbance, lethargy, and coma.

M. Acetaldehyde:

Oral intake: vomiting, tachycardia, hypertension, hyperventilation. Inhalation: irritation of the nose and rest of the respiratory tract, cough; with longer exposures: pulmonary edema and loss of consciousness.

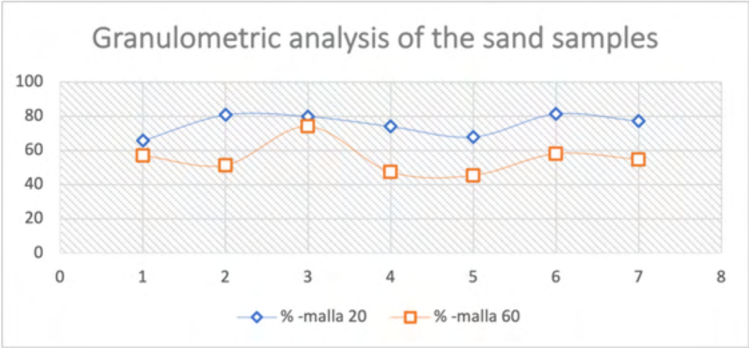
N. Sulfuric acid:

In individuals chronically exposed to acid breezes: dental erosion. After ingestion: pain and burning in the esophagus, asphyxia, stomach injury that can cause bleeding, perforation and peritonitis. Long-term complications: esophageal stricture, fistulas. Association with esophageal cancer.

RESULTS OF THE EXPERIMENTS: MIXTURES OF HYDRO FRACTURE AND ACTIVATED CARBON

A. Granulometric analysis

After collecting 7 sand samples from different sites in the region, it was necessary to perform the appropriate granulometric analysis, since the most commonly used sieves for the implementation of Fracking are 20/40 (0.42 mm - 0.84 mm), followed by 30 / 50 (0.6 mm - 0.3 mm) and 40/70 (0.425 mm - 0.212 mm); using the Ro-tap accommodating the sieves from largest to smallest aperture size (10, 20, 30, 50, 60, 200) were separated the 7 samples, to then homogenize those that could pass through the 20 to 60 mesh, to obtain a granulometric average of the sands commonly used in hydraulic fracturing.



Graphic 1: Granulometric analysis of the 7 sand samples between 20 and 60 mesh.

B. Fracking mixtures

In this case, for the micro-scale recreation of a shale gas extraction well, everything was done based on a total volume of 1 liter, having as measurements 94.6% water, 5.23% sand and 0.17% chemical additives. Applying these measures as a basis, 946ml of water, 52.3g of sand and 1.7g of chemical additives were added divided equally: hydrochloric acid, xylene, toluene, naphthalene and sulfuric acid, which were the only ones implemented in the recreation of the well.

C. Physical-chemical tests

The pH of the 7 samples, density, viscosity and organoleptic characters were taken, in order to know more about the medium that had just been generated, it was found that the 5 chemical substances that were mixed with sand and water (these substances were acids hydrochloric and sulfuric, naphthalene) average a relative density of 1.1804, applying

$$\rho_T = 0.2\rho_1 + .2\rho_2 + .2\rho_3 + .2\rho_4 + .2\rho_5$$
$$\rho_T = 0.2(1190) + 0.2(1840) + 0.2(865) + 0.2(867) + 0.2(1140) = 1{,}180.4 \text{ Kg/m3}$$

E. Activated carbon treatment

The mixture has a very acidic pH close to 2 and when treated with Activated Carbon it becomes basic with 7.3, this is ratified by the ANOVA test showing a very good significance in the difference of the means of the pH values. Regarding the organoleptic tests, the water has a penetrating naphthalene odor upon treatment with fracking, after treatment with activated carbon this color disappears completely, which indicates that this substance was mainly adsorbed on the activated carbon.

F. Settling and analysis of the sands by x-ray fluorescence

The sand is separated is mixed with water and chemicals by a rapid decantation, the measurements show that the silica decreases when treated with the fracking substances from 5000 to almost 3000 ppm, the chlorine from the hydrochloric acid rises in the sand, the aluminum rises notably, which indicates that it is released from the sands being relatively dangerous, which is intensified by arsenic, which rises in a high percentage, the above is reflected when analyzing activated carbon and is due to its great capacity to adsorption, since the concentration of both silica and aluminum in it increases a lot, but sulfur and chlorine decrease in it.

PH	M-1	M-2	M-3	M-4	M-5	M-6	M-7
Start	6.96	1.87	2.29	2.04	1.92	5.95	3.07
24 hours later	7.89	1.97	2.47	2.39	2.05	6.71	6.40
After the carbon	8.02	5.03	7.38	7.73	6.94	8.01	8.20

Table 1. PH taken along the treatment

DISCUSSION

The hydrofracturing process for the extraction of Shale gas represents an enormous environmental risk starting with the availability of water, requiring an average of 20,000 m3 per well and contaminating it with up to hundreds of chemical substances, most of them with serious health risks short-term highlighting the respiratory system, various digestive organs, kidney and central nervous system and carcinogens, thus demonstrating that it is essential that the water used in this process be treated after use and with great caution during the process itself.

The efficiency of activated carbon to adsorb a good part of the pollutants from the water was experimentally and statistically verified, since a large part of them are organic substances, although it was made sensory, the naphthalene was adsorbed almost entirely as well as the 2 acids hydrochloric and sulfuric, which are extremely strong, although our results can be taken as preliminary, they indicate how promising activated carbon is as a purification treatment of these enormous volumes of contaminated water, of course it is recommended to extend the experimentation with mixtures of chemical substances, with activated carbon as an adsorbent and other methods of restoring the sanitation of the water.

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