APPLICATION OF DOLOCHAR IN THE REMOVAL OF PHOSPHATE FROM SYNTHETIC WASTE WATER

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Abstract— Since last decade sponge iron has been extensively used in the production of steel. Dolochar i.e sponge iron by-product, has been used as an adsorbent for the removal of phosphorous which is in the form of phosphate in this study. The dose of adsorbent effects, time of contact effects, concentration of phosphate before the experiment effects, etc. on the phosphate removal by the adsorbing material in batch studies were tested. Langmuir isotherm has shown best fit to the experimented data. Phosphate shows a great potential being an adsorbent for removal of phosphate.

Keywords— *Dolochar, Phosphate, Water, Batch studies.*

INTRODUCTION

Lately sponge iron has been extensively used as a raw material in industries for production of steel. The primary unprocessed material required for production of sponge iron are non-coking coal, iron ore & dolomite. With the application of DRI, sponge iron is produced and, the waste generated during this process are de-volatilized dolomite & char; that is termed as Dolochar, which is taken as Sponge Iron industry by-product. It has been reported that a sponge iron industry which has the capacity of producing a 100 tonnes in a single day, can produce 25 tonnes of dolochar in a single day, that would be all in all 9000 tonnes waste in a year and such huge amount of dolochar that is generated can have a vital disposal issue which can therefore be an environmental threat.

To make some use of waste generated in DRI, certain tests has been conducted on it, it was found that it's a carbonaceous material containing invariably 15% to 30% unburnt carbon. That is why it is supposed to have high surface area prerequisite porosity, which makes it suitable for Adsorption. This adsorption potential of dolochar was inspected for the removal of certain nutrients and heavy metals like phosphate, chromium etc. The natural porosity and the existence of aluminium(Al), iron(Fe), magnesium and calcium compounds in the structure of dolochar raises the possibility of the application of the waste in the adsorption of phosphate.

In most of the cases of aqueous environment, the existence of phosphorous is in many forms, such as pyrophosphates, polyphosphates, orthophosphates, organic phosphonates & organic phosphate esters and all of these can be hydrolyzed to orthophosphate. Phosphate being an irreplaceable nutrient is mandatory in most of the ecosystems for activities related to metabolism in living organisms.

In general, most of the aquatic ecosystem have a very low concentration of ambient phosphate, that's why a small change in amount of phosphate can cause radical change in biotic community structure. In this rapid modernization, as phosphate is considered as a vital inorganic element, it is widely used. As a result, discharge of phosphate more than permissible followed by overcharge with so, in ecosystems which are of sensitive nature that are mainly induced through various anthropogenic activities (agricultural, industrial, environmental and household applications). And due to the excessive amount of phosphate in water bodies, eutrophication happens and the occurrence of this process is rapid, which gradually degrades the industrial quality, recreational water resources domestic, agricultural and many more. Therefore, from the perspective of safety of the environmental safety, it is quite unavoidable to eliminate the phosphate pollution in water bodies prior to discharge of wastewater. Different kind of treatment processes has been adopted and documented, such as biological treatment, chemical precipitation, physical processes and processes based on adsorption. But it was observed that physical methods are not efficient, chemical methods are somewhat expensive and biological methods have complex nature. And it was also adjudged as one of the simplest, efficient and cost effective method. Usage of industrial by-products has been explored and is said to be a promising alternative.

LITERATURE REVIEW

L. Panda *et al.* characterized the dolochar samples for the determination of different phases and its distribution. It was analyzed that the sample contains metallic iron as well as fused carbon Calcium-magnesium bearing phases along with pores and voids. The fixed carbon content of so was found to be 13.8% with 81.6 m^2/g Langmuir surface area and 34.1m^2/gmicropore area. Adsorption experiments were done in batches to study howCr(VI) and Cd(II) ions are adsorbed by dolochar particles as a function of temperature, particle size, adsorbent doses, time of contact and pH. It was observed that with the increase in temperature and higher pH theCadmium(II) sorption enhances. In case of Cr(VI) adsorption, removal efficiency was found to be better in low pH.Langmuir isotherm model was found to be a better fitfor this study when it was compared with the Freundlich model, indicating it to be monolayer adsorption. [1]

Ranjan Kumar Dwari *et al*. The thorough study on chemical properties, physical properties and petrography were carried out by SEM, optical microscopy and XRD. The studies done for the Characterization of dolochar revealed that it consists of free form of quartz& locked form of quatrz, Fe particles, CaOand Ca or Mg and/or Ca-Fe-Mg oxide phases. It was seen that the dolochar have high ash fusion temperature and the unburned carbon can be effectively used for power generation. Bythe data of washability ofsample of dolochar of -300mit was indicated that clean coal with ash of 41wt% at yield of 18% can be produced from dolochar having 78wt% ash.[2]

Dr. C. R Mohanty *et al*. investigated the chemical properties and physical properties of dolochar for the reutilization of it as an adsorbant for the removal of chromium from waste water, the physical properties of dolochar such asporosity, specific gravity, density, void ratio, grain size etc. and chemical properties as in chemical compositions. It was obtained that,under optimal condition more than 100% removal was achieved.[3]

Rajesh Roshan Dash *et al*. investigated how the phosphorous peak would appear in EDS spectra of dolochar that is spent and it confirmed adsorption of phosphate. RSM and ANOVA analysis were applied for modelling as well as optimization of phosphate removal and it was analyzed by batch test, and it resulted in 98.13% phosphate removal.[4]

Prangya Ranjan Rout *et al*. examined the effect of initial concentration of the phosphate solution, agitation, contact time, adsorbent dose etc. on the adsorption of phosphate on the adsorbent material in batch test were examined.
Pseudo second order kinetic model and Langmuir isotherm model were observedto be the best fit to the datas gained by the experiment with $R\ 2$=0.98 and R2= 0.99, respectively. Spent dolochar showed a nature of slow phosphate release in the results of thin layer funnel analytical test. The results advised that the dolochar can be effectively used as an adsorbing medium for the removal of phosphate from wastewater and the spent dolochar also has scope for being utilized as slow release phosphate fertilizer.[5]

R. R. Dash *et al*. made an attempt to investigate different properties so that it can be re-utilized as absorbent for discarding the impurities present in water. Batch studies were done with dolochar as adsorbent to study its behavior on the removal of chromium(VI) from synthetic waste water. The physical properties of dolochar such as porosity, specific gravity,density, void ratioand chemical composition that are classified under chemical properties have been analyzed. Batch experiments have been conducted for adsorption, by varying pH, adsorbent dose, particle size, adsorbate concentration, contact time on the removal of chromium. It was found that under optimal conditionsapproximately more than 94% of the removal was achieved.[6]

A.M.Baraka *et al.* Investigated the removal potential of acid activated red mud on phosphate. The removal efficiency was observed to be higher when the pH values is in between 8 and 12. The maximum removal efficiency was achieved innext one hour.The highestuptake percentage was achieved at an adsorbent loading weight of 0.5gm per 100ml. The equilibrium adsorption capacity of adsorbent was measured and extrapolated by the use of linear Freundlich and Langmuir isotherms, and the experimental datas were found to have a better fit with the Freundlich isotherm model. The morphological characteristics of the red mud was evaluated by the use of scanning electron microscope. SEM image of RM after adsorption of phosphate showedthat phosphate ions were covered on the surface of RM.[7]

Prangya Ranjan Rout *et al*. Investigatedthe nature of adsorption of Grounded Burnt Patties; the waste generated from the fuel used in earthen stoves in kitchen, as an adsorbent for the removal of nutrient like phosphate from aqueous solution.The adsorbent categorization was done by SEM analysis, PIGE analysis and PIXEanalysis,X-Ray Diffraction (XRD) and the mechanisms of adsorption by Fourier Transferred Infra-Red spectroscopy (FTIR). The effects of initial solution concentration, adsorbent dose, agitation, contact time etc. on the phosphate adsorptionin the batch test were examined. The equilibrium data was used in different kinetic models as well as adsorption isotherms.[8]

METHODOLOGY

a. Collection and preparation of the adsorbent.

The samples of dolochar were collected from several industries sponge iron located in Odisha, India. The samples that were collected were grounded, then they were sieved and were then washed with distilled water more than once to remove any foreign particles that are present on the surface (if any present), soluble materials and then they were dehydrated in hot-air oven at 100°C for overnight. For the adsorption study dolochar sample of particle size less than 0.6 mm were used.

b. Preparation of Adsorbate

Stock solution of Phosphate of 50ppm was prepared synthetically by the addition of monobasic potassium phosphate (KH_2PO_4) anhydrous to distilled water. Then different concentrations that were needed were prepared by dilution. For the optimization of different sorption parameters this phosphate solution that was prepared synthetically was used in the batch study.

c. Analytical methods

The determination of Phosphate concentration in aqueous solutions was done by the Stannous Chloride method which is a standard method. Ammonium Molybdate reagent, Stannous Chloride Reagent and filtered sample were added to be a single solution and it was analyzed after few minutes with a UV spectrophotometer.

d. Adsorption experiments

- Batch study

The batch experiments were donefor the parameter's optimization. Parameters such as pH, adsorbent dose, initial concentration andtime of contact,that are involved in the adsorption process. The removal efficiency in percentage of phosphate and equilibrium capacity of uptake were determined by using the following equation:

$$Efficiency\ of\ uptake\ (\%) = \frac{(C_0 - C_e)}{C_0} * 100$$

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e are the initial concentration of and equilibrium concentration of phosphate (mg/L), V; volume of phosphate solution (mL), and m ; mass of adsorbent (g).

- Adsorption isotherm studies

For the isotherm studies, certain amount of adsorbent (2.5 g/ L) was individually mixed with each of the variably concentrated phosphate (1-50 mg/L) solution of 50 ml and agitated at 150 rpm for 1h. The experimentally obtained equilibrium values were fixedin the Langmuir isotherm &Freundlich isotherm models according to the following equations, respectively.

$$q_e = (q_m KLC_e)/(1+KLC_e)$$

$$q_e = K_f\ C_e^{1/n}$$

where, K_L; adsorption constant (L/g), q_m; the maximum adsorption capacity (mg/g), K_f (mg/g); Freundlich constant and 'n'; Freundlich exponent.

- Adsorption kinetics studies

For this study,determinedquantities of adsorbents were taken and added to 100ml solution of adsorbate, thenthe solutions wereagitated at 150 rpm. The samples were withdrawn from agitation afterdifferent specifictime period (5-90 min) & the residual phosphate was analyzed in the solution. The values obtained from the adsorption batch test were used in the pseudo-first order & pseudo-second order kinetic models in order to find the best model to which the values of the experiment fits as per the equations given below.

$$q_t = q_e\ (1 - \exp\ (- k_1 t))$$

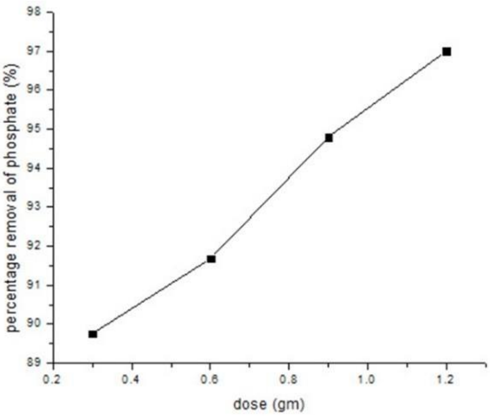
$$q_t = k_2 q_e^2 t/1 + k_2 q_e t$$

Where, q_t(mg per g) is the quantity of phosphate removed at time *t* (min), q_e(mg per g) is the quantity of phosphate uptake at equilibrium, *k1* is the first-order reaction rate constant (min 1) and *K2*represents the second-order reaction rate constant (g per mg per min).

RESULT AND DISCUSSION

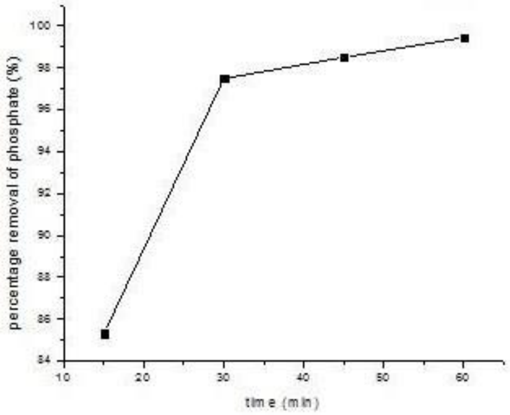
- Effect of Adsorbent Dose

The investigation of the adsorbent dose effects on phosphate adsorption was done by varying dolochar amount in synthetic wastewater containing 50 mg/L phosphate and other factors are kept constant. It was observed that the efficiency of the removal of phosphate was increased from 89.76 % to 97% by increasing the adsorbent dose from 0.3 to 1.2gm. With the increase in adsorbent's concentration, the phosphate adsorption rate increases as more surface area for adsorption is available. Beyond a certain extent, there is nosignificantlyphosphateuptakewhen doses were increased. It is the result of reaching the saturation limit after the addition of certain amount of adsorbent dose during the process.



- Effect of Contact Period

The effect of contact period on the phosphate adsorption by the adsorbent was experimentally investigated by varying the contact period and keeping other parameters as desired. The contact period of 60 min can be considered as themost conducive contact period to reach the equilibrium stage, resulting almost 99.5 % of removal of phosphate. It was observed that at the point of initial of adsorption, graph shows the curve slope was observed to be very steep which indicates very fast adsorption rate (97.5 % removal took place). This implies that, at the beginning of the test procedures of the batch experiment almost the entire adsorbent'ssurface area was free from any ions that are to be adsorbed, thus, exposing highamount of pores &surface area that are available for sorption process. As time passes, more of the available area of thesurface and pore of the dolochar get saturated with ions of phosphate. Thus, the availability of thesurface of dolochar for phosphate adsorption reduces, so does the adsorption rate. Evidently very less amount of phosphate gets removed during the last phase of equilibrium.



- Effect of pH

For measuring the effect of pH of the solution on the adsorption capacity of dolochar, it was varied from certain acidic level to certain alkaline level. There is not much difference made by changing the pH, there is negligible difference, but from the experiment data it was seen that at Acidic pH it shows slightly better result.

- Effect of Initial Concentration

Initial concentration of phosphate was variedbetween 5 mg/l to 50mg/l so that the effect of initial concentration of phosphate on the capacity of being adsorbed of dolochar can be examined. It was found that initially when the concentration was low the removal efficiency is higher.

CONCLUSION

Overall it was observed from the batch studies that, at lower initial concentration, higher adsorbent dose, slightly acidic to neutral pH it shows better adsorptionresults and it was alsoobserved that with optimal conditions it can have potential of removing 99% of pollutants and Langmuir isotherm and pseudo second order kinetic model shows to be a better fit for this study.

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